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The WORKING GROUP is comprised of representatives of the U.S. Departments of Agriculture; Commerce; Defense; the Interior; Health, Education, and Welfare; State; Transportation; and Labor; and the U.S. Environmental Protection Agency.

The pesticide MONITORING PANEL consists of representatives of the Agricultural Research Service, Animal and Plant Health Inspection Service, Extension Service, Forest Service, Department of Defense, Fish and Wildlife Service, Geological Survey, Food and Drug Administration, Environmental Protection Agency, National Marine Fisheries Service, National Science Foundation, and Tennessee Valley Authority.

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Pesticide monitoring activities of the Federal Government, particularly in those agencies represented on the pesticide MONITORING PANEL which participate in operation of the national pesticides monitoring network, are expected to be the principal sources of data and interpretive articles. However, pertinent data *in summarized form*, together with interpretive discussions, are invited from both Federal and non-Federal sources, including those associated with State and community monitoring programs, universities, hospitals, and nongovernmental research institutions, both domestic and foreign. Results of studies in which monitoring data play a major or minor role or serve as support for research investigation also are welcome; however, the *Journal* is not intended as a primary medium for the publication of basic research. Manuscripts received for publication are reviewed by an Editorial Advisory Board established by the MONITORING PANEL. Authors are given the benefit of review comments prior to publication.

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PESTICIDES IN PEOPLE

*Epidemiology of Organochlorine Insecticides in the Adipose Tissue of Israelis*¹

M. Wassermann,² L. Tomatis,³ Dora Wassermann,² N. E. Day,³ Y. Groner,² S. Lazarovici,² Deborah Rosenfeld²

ABSTRACT

This paper reports the findings obtained in 1967-71 during an investigation of organochlorine insecticides (OCI) storage in the adipose tissue of Israelis.

Specimens of adipose tissue (307) collected during autopsy from Israelis who had no known occupational exposure to organochlorine insecticides were analyzed by the gas chromatographic method for organochlorine insecticides (DDT-derived material; alpha, beta, and gamma isomers of BHC, dieldrin, and heptachlor epoxide).

*Findings indicate a positive age association for DDT-derived material stored in the adipose tissue of Israelis of both sexes. Males generally were found to store higher amounts of *p,p'*-DDT and total DDT than females.*

Comparison of adipose tissue from stillborns with tissue from infants showed that DDT increased in the first months of postnatal life, but storage levels of BHC, dieldrin, and heptachlor epoxide remained approximately the same. DDT levels continued to rise with age levels, except for a slight decrease in the 24-through-44-year-olds. The highest levels of DDT were found in the age group of 70 and over; second highest were among 45-to-69-year-olds. These findings in Israel differ from the authors' earlier findings in South Africa, Thailand, Nigeria, and Brazil, which revealed the highest concentrations of OCI in the 24-through-44-year-olds.

This research study was supported by the U.S. Department of Health, Education and Welfare, Public Health Service, National Communicable Disease Center, Atlanta, Ga., Research Grant No. BSS-CDC-IS-9, and by an agreement of the World Health Organization—International Agency for Research on Cancer.

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World Health Organization—International Agency for Research on Cancer, Lyon, France.

A positive age association with DDT storage in all ages was observed in 1965 and 1967 surveys by the authors in people from Kenya and Israel, and by Davies and Milby in the nonwhite population of the USA.

In the countries studied, the storage level of DDT and derived material increases with age in the general population up to the age of 45, and either rises or falls after 45 years, depending on the country. This leads the authors to the opinion that the age group of 25 through 44 years may be the most suitable indicator of DDT storage levels in a community.

*A positive relationship between *p,p'*-DDT and dieldrin storage was also noted.*

Introduction

The presence of DDT and its metabolite DDE in the adipose tissue of the population of Israel was first demonstrated in a study carried out by Wassermann et al. (1) in 1963-64. They revealed that these chemicals were stored in the adipose tissue of people who had no known occupational exposure to the chemicals and suggested that the DDT storage process is influenced by individual factors such as sex and age.

A further study carried out by the same investigators in 1965-66 (2) ascertained that Israelis over 10 years of age stored higher amounts of DDT-derived material than did those under 10 years of age. Males over 10 stored higher amounts of DDT-derived materials than did females.

A study by Polishuk, Wassermann, et al. (3) on pregnant Israeli women indicated less storage of DDT-derived

material, BHC isomers, and dieldrin than in nonpregnant women of the same age. The organochlorine insecticides (OCI) found in the fat tissue of pregnant women were present also in the maternal and fetal blood in all cases studied. These findings suggested that, in pregnancy, the metabolism of organochlorine insecticides is enhanced and that they pass the placental barrier.

Data published up to the mid-sixties on the storage of DDT-derived material in the adipose tissue of people from various countries affirmed the concept of organochlorine insecticides as "current constituents of the human body" (4). Other studies revealed the impact exerted on OCI storage in man by individual factors such as age, sex, and race (1, 2, 5-11), by particular physiological states (3, 12), as well as by living and working conditions (7, 13).

Concern for the potential hazard to human health by organochlorine insecticide accumulation in the body increased following reports that OCI are potent hepatic microsomal inducers which may quantitatively alter the response to various drugs and toxic compounds as well as to naturally occurring substances in the animal body. This may lead to alteration of homeostasis of biochemical (endocrine, immunologic, etc.) processes (3, 14-16). Experimental evidence of the capacity of OCI to increase tumor incidence in laboratory animals was also reported (17-19).

Thus it became necessary to assess the size and trends of OCI storage in populations in general and to find which age group would be most useful for studying this storage phenomenon in various areas of the world.

This paper reports the findings of a study of OCI storage in Israelis and compares the data to those obtained by the same investigators in various populations in Africa, Asia, and South America in the framework of a program launched by the World Health Organization International Agency for Research on Cancer, Lyon, France.

Methods and Materials

A total of 307 samples of adipose tissue were collected from 1967 to 1969 during autopsy from the subcutaneous fat of the abdominal wall of persons who had no known occupational exposure to pesticides. The distribution of samples according to age and sex is shown in Table 1. Samples of 1-2 g of adipose tissue were collected in jars containing 10% formalin. Specimens of 500-mg adipose tissue were extracted three times with a total of 20 ml of petrol ether and cleaned by means of a Kontes Co-Distiller. The extract was reduced to 0.5 cc, from which 5-20 μ l were injected into a Microtek MT-220 gas chromatograph equipped with dual electron-capture detector and strip chart recorder. A

6-ft U-shaped glass column packed with 5% QF-1 on 60-80 mesh chromoport xxx and a 4-ft U-shaped glass column packed with 10% SE-30 on 60-80 mesh chromoport xxx were used. A mixture of pure organochlorine insecticides was used as standard; the concentration of each compound was 0.1 ppm. Recovery was about 85% for the compounds identified in this study. The sensitivity of detection was 0.1 to 0.3 μ g/kg wet weight for the compounds.

TABLE 1.—Distribution of human adipose tissue samples by age and sex of subject

AGE	MALES	FEMALES	TOTAL
Stillborns	26	18	44
0-11 months	22	18	40
5-24 years	38	23	61
25-44 years	29	24	53
45-69 years	32	31	63
70 and over	27	19	46
Total	174	133	307

Results and Discussion

In 307 samples of adipose tissue collected from Israelis who had no known occupational exposure to organochlorine insecticides, gas-chromatographic analysis revealed the presence of DDT-derived material; alpha, beta, and gamma isomers of BHC; dieldrin; and heptachlor epoxide.

It must be stressed that, as noted in previous studies (20-23), marked individual variations in storage levels were observed among individuals of the same sex and age group who were not occupationally exposed to OCI's. Similar individual variations were observed in experimental animals kept in experimental conditions which all were exposed to the same level of DDT (24).

The broad spectrum of age groups and the relatively large number of cases investigated in this study enabled us to follow up the dynamics of OCI storage in the population by age and sex.

Concentration of OCI in the adipose tissue of the stillborn group averaged: total DDT 0.7 ppm; total BHC 0.04 ppm; dieldrin 0.02 ppm; and traces of heptachlor epoxide below 0.01 ppm, thus indicating the accumulation of these compounds during fetal life (Tables 2-4).

The first months of life in the external environment led to an increased DDT storage. In the age group up to 11 months, total DDT averaged 5.8 ppm; the storage level of BHC, dieldrin, and heptachlor epoxide remained about the same as in stillborn. DDE averaged 51% of total DDT-derived material. The mean total *p,p'*-DDE was 5.7 ppm and the mean total *o,p'*-DDT was 0.5 ppm. There was a significant difference in the storage of *p,p'*-DDT and total DDT between the stillborn and the 0-through-11-month age group ($p < 0.01$).

COMPOUND	AGE GROUP AND NUMBER OF CASES					
	STILLBORNS 26	0-11 MOS. 22	5-24 YR. 38	25-44 YR. 23	45-63 YR. 32	70+ YR. 27
<i>p,p'</i> -DDT	Range Mean ± SD	0.0940 — 5.0000 2.6566 ± 1.7438	0.4444 — 23.3330 4.1500 ± 4.5308	0.0550 — 11.1200 3.2841 ± 3.0574	0.2190 — 24.0000 5.8968 ± 5.4581	0.3570 — 34.2850 7.1626 ± 8.3018
<i>p,p'</i> -DDD	Range Mean ± SD	<0.0001 — 0.0428 0.0134 ± 0.0141	0.0028 — 0.7140 0.1913 ± 0.5935	0.0555 — 3.0440 0.8606 ± 0.6006	0.0920 — 14.1025 1.5722 ± 2.4413	0.1085 — 7.0450 1.8190 ± 1.6826
<i>p,p'</i> -DDE	Range Mean ± SD	0.0175 — 1.7410 0.5329 ± 0.1975	0.0860 — 8.7655 2.2101 ± 2.5431	0.3194 — 17.9440 9.8255 ± 8.8706	1.4100 — 20.6920 10.2741 ± 4.6160	2.1110 — 31.2810 10.4486 ± 6.8228
<i>o,p'</i> -DDT DDD	Range Mean ± SD	<0.0001 — 0.0260 0.0100 ± 0.0100	<0.0001 — 0.1100 0.0130 ± 0.0283	0.0040 — 1.1250 0.1472 ± 0.1794	0.0263 — 4.4740 0.3673 ± 0.7583	0.0180 — 0.9800 0.2381 ± 0.1889
<i>o,p'</i> -DDE	Range Mean ± SD	<0.0001 — 0.0250 0.0090 ± 0.0584	<0.0001 — 0.0940 0.0164 ± 0.0173	0.0120 — 0.0910 0.0594 ± 0.0663	0.0120 — 0.8850 0.0949 ± 0.5874	0.0070 — 0.2080 0.0532 ± 0.0424
Total <i>p,p'</i> -DDT	Range Mean ± SD	0.0525 — 3.1209 0.7963 ± 0.8261	1.1288 — 18.6333 5.3101 ± 4.3301	0.8557 — 36.6056 15.8348 ± 13.3770	1.8817 — 43.9410 18.9144 ± 9.8861	3.2243 — 70.4700 20.6214 ± 15.8210
Total <i>o,p'</i> -DDT	Range Mean ± SD	0.0043 — 0.0449 0.0201 ± 0.0100	0.0027 — 0.2147 0.0341 ± 0.0480	0.0853 — 1.1384 0.2137 ± 0.1838	0.0129 — 2.3061 0.3312 ± 0.5184	0.0369 — 1.0335 0.2974 ± 0.2100
Total DDT	Range Mean ± SD	0.0671 — 3.1359 0.8164 ± 0.8240	1.1484 — 18.8480 5.3435 ± 4.0977	0.9471 — 38.7134 16.0482 ± 13.4530	2.0797 — 48.5702 19.3874 ± 10.3620	3.3065 — 71.1441 20.9188 ± 15.9130
α -BHC	Range Mean ± SD	<0.0001 — 0.0458 0.0091 ± 0.0099	0.0027 — 0.0580 0.0091 ± 0.0349	0.0100 — 0.1240 0.0298 ± 0.0245	0.0053 — 0.6200 0.0445 ± 0.1136	0.0045 — 0.0886 0.0191 ± 0.0141
β -BHC	Range Mean ± SD	<0.0001 — 0.1150 0.0140 ± 0.2236	0.0021 — 1.0580 0.0721 ± 0.2168	0.0259 — 2.0010 0.2818 ± 0.4689	0.0054 — 2.9350 0.4468 ± 0.7866	0.0500 — 2.9470 0.5408 ± 0.8004
γ -BHC	Range Mean ± SD	<0.001 — 0.0777 0.0130 ± 0.1732	0.0016 — 0.1090 0.0198 ± 0.0224	0.0010 — 3.9170 0.1343 ± 0.6263	0.0010 — 12.1430 0.4365 ± 2.2124	0.0010 — 1.2876 0.0735 ± 0.2417
Total BHC	Range Mean ± SD	0.0054 — 0.1201 0.0361 ± 0.0283	0.0123 — 1.0810 0.1009 ± 0.2191	0.0492 — 4.3530 0.3987 ± 0.4498	0.0232 — 12.7010 0.5074 ± 0.8031	0.0600 — 3.0230 0.6334 ± 0.8101
Dieldrin	Range Mean ± SD	0.0003 — 0.1180 0.0305 ± 0.0283	<0.0001 — 0.0940 0.0183 ± 0.0224	0.0116 — 0.2100 0.1070 ± 0.1311	0.0066 — 0.4660 0.1364 ± 0.1229	0.0140 — 0.8020 0.1630 ± 0.7182
H. Epoxide	Range Mean ± SD	<0.0001 — 0.0102 0.0030 ± 0.0028	<0.0001 — 0.0120 0.0007 ± 0.0025	0.0001 — 0.0480 0.0211 ± 0.0412	<0.0001 — 0.1320 0.0205 ± 0.0316	<0.0001 — 0.0770 0.0102 ± 0.0027

TABLE 3.—Concentration (ppm) of organochlorine insecticides in adipose tissue of Israeli females

COMPOUND	AGE GROUP AND NUMBER OF CASES						70+ YR 13
	STILLBORN 18	0-11 MOS. 18	5-24 YR. 23	25-44 YR. 24	45-63 YR. 31	70+ YR. 13	
<i>p,p'</i> -DDT	Range	0.0028 — 0.3480	<0.0001 — 1.7850	0.2940 — 7.2910	0.0042 — 7.5100	0.0333 — 11.3540	0.5140 — 12.7010
	Mean ± SD	0.1040 ± 0.0806	2.1533 ± 2.6008	3.4744 ± 3.0769	2.6009 ± 2.2226	4.4725 ± 2.7399	3.6708 ± 3.0170
<i>p,p'</i> -DDD	Range	<0.0001 — 0.1125	<0.0001 — 0.1666	0.1142 — 1.5278	0.0091 — 2.1210	0.0709 — 4.3478	0.1270 — 2.9166
	Mean ± SD	0.0146 ± 0.0245	0.0192 ± 0.0400	1.0508 ± 1.8711	0.6896 ± 0.5036	1.0529 ± 0.9342	0.9769 ± 0.6058
<i>p,p'</i> -DDE	Range	0.0242 — 1.3131	0.1750 — 15.4900	0.5367 — 21.2698	0.0952 — 20.6348	0.7031 — 24.4690	3.0110 — 22.0310
	Mean ± SD	0.3599 ± 0.3464	3.2578 ± 3.5688	8.2292 ± 6.6352	8.2756 ± 5.4223	8.3721 ± 5.1870	3.5812 ± 4.6689
<i>o,p'</i> -DDT DDD	Range	<0.0001 — 0.0820	<0.0001 — 1.4750	0.0364 — 0.1710	0.0001 — 0.2440	0.0020 — 2.4200	0.0455 — 10.4010
	Mean ± SD	0.0125 ± 0.0173	0.1320 ± 0.3382	0.1517 ± 0.1459	0.0824 ± 0.0592	0.2229 ± 0.4151	0.1535 ± 0.0819
<i>o,p'</i> -DDE	Range	<0.0001 — 0.0350	<0.0001 — 0.0795	0.0100 — 0.0840	<0.0001 — 0.3120	0.0090 — 0.1350	0.0150 — 0.1818
	Mean ± SD	0.0126 ± 0.0100	0.0211 ± 0.0245	0.0457 ± 0.0265	0.0591 ± 0.0748	0.0424 ± 0.0316	0.0533 ± 0.0436
Total <i>p,p'</i> -DDT	Range	0.0460 — 1.8108	1.2939 — 21.3623	1.2103 — 26.3727	0.1194 — 25.4047	0.8874 — 36.3285	5.5692 — 31.1115
	Mean ± SD	0.5198 ± 0.4234	6.2476 ± 5.4799	13.6579 ± 3.9867	12.4778 ± 7.2702	14.8069 ± 9.0557	15.3846 ± 7.1211
Total <i>o,p'</i> -DDT	Range	0.0083 — 0.0820	<0.0001 — 1.5636	0.0508 — 0.1888	0.0036 — 0.5916	0.0574 — 2.5704	0.0678 — 0.5480
	Mean ± SD	0.0265 ± 0.0200	0.1556 ± 0.3561	0.2087 ± 0.1473	0.1483 ± 0.1183	0.2701 ± 0.4363	0.2143 ± 0.1149
Total DDT	Range	0.0845 — 1.8928	1.3399 — 21.4610	1.2611 — 26.4717	0.1230 — 25.5416	0.9822 — 38.8989	5.7099 — 31.3674
	Mean ± SD	0.5464 ± 0.4329	6.4032 ± 5.6787	13.9141 ± 10.0004	12.6261 ± 7.2928	15.0770 ± 9.3343	15.5989 ± 1.1267
α -BHC	Range	<0.0001 — 0.0227	<0.0001 — 0.0891	0.0028 — 0.0350	0.0032 — 0.1050	0.0070 — 0.0680	0.0068 — 0.6310
	Mean ± SD	0.0103 ± 0.0100	0.0147 ± 0.0245	0.0217 ± 0.0173	0.0232 ± 0.0200	0.0207 ± 0.0141	0.0497 ± 0.1371
β -BHC	Range	<0.0001 — 0.1031	<0.0001 — 0.1284	0.0202 — 0.1480	0.0007 — 2.1050	0.0157 — 2.1420	0.0294 — 1.3300
	Mean ± SD	0.0248 ± 0.0245	0.0178 ± 0.0300	0.1880 ± 0.3150	0.2059 ± 0.4178	0.4580 ± 0.6385	0.2854 ± 0.3781
γ -BHC	Range	<0.0001 — 0.0400	<0.0001 — 0.0616	0.0010 — 0.0691	0.0010 — 1.8683	0.0010 — 0.4630	0.0010 — 0.5799
	Mean ± SD	0.0168 ± 0.0141	0.0145 ± 0.0173	0.0270 ± 0.0316	0.1947 ± 0.4017	0.0402 ± 0.0872	0.0884 ± 0.1386
Total BHC	Range	0.0146 — 0.1154	0.0019 — 0.1460	0.0414 — 0.1680	0.0473 — 2.1330	0.0671 — 2.1630	0.0888 — 1.3950
	Mean ± SD	0.0519 ± 0.0265	0.0471 ± 0.0400	0.2366 ± 0.3151	0.4238 ± 0.5620	0.5189 ± 0.6245	0.4234 ± 0.4299
Dieldrin	Range	<0.0001 — 0.0143	<0.0001 — 0.1250	0.0072 — 0.3150	0.0028 — 0.3150	0.0150 — 3.9600	0.0131 — 0.2330
	Mean ± SD	0.0033 ± 0.0040	0.0240 ± 0.0316	0.0909 ± 0.0768	0.0913 ± 0.0964	0.1242 ± 0.1162	0.0960 ± 0.0678
H. Epoxide	Range	<0.0001 — 0.0037	<0.0001 — 0.0374	<0.0001 — 0.0510	<0.0001 — 0.0520	<0.0001 — 0.0730	<0.0001 — 0.1320
	Mean ± SD	0.0005 ± 0.0011	0.0025 ± 0.0085	0.0115 ± 0.0200	0.0081 ± 0.0141	0.0147 ± 0.0179	0.0104 ± 0.0300

AGE GROUP AND NUMBER OF CASES

COMPOUND	STILLBORN	AGE GROUP AND NUMBER OF CASES					70+ YR.
		0-11 MOS.	5-24 YR.	25-44 YR.	45-69 YR.	46	
<i>p,p'</i> -DDT	0.0028 ± 1.2500 0.1824 ± 0.2490	<0.0001 — 5.0000 2.4301 ± 2.1870	0.2940 — 23.3330 3.8953 ± 4.0577	0.0042 — 11.1200 2.9742 ± 2.7327	0.0333 — 24.0000 5.1738 ± 4.1645	0.3570 — 34.2850 5.7204 ± 6.8687	
<i>p,p'</i> -DDD	<0.0001 — 0.1125 0.0139 ± 0.0200	<0.0001 — 1.7140 0.1139 ± 0.4602	0.0555 — 3.0440 0.9323 ± 1.2463	0.0091 — 2.1210 0.7545 ± 0.6045	0.0709 — 14.1025 1.3167 ± 1.8773	0.1085 — 7.0450 1.4712 ± 1.4030	
<i>p,p'</i> -DDE	0.0175 ± 1.7410 0.4621 ± 0.4759	0.0860 — 15.4900 2.6815 ± 3.0920	0.3194 — 21.2698 9.2236 ± 8.1383	0.0952 — 55.0310 9.3997 ± 8.5836	0.7031 — 24.4690 9.3382 ± 4.9996	2.1110 — 31.2810 10.0003 ± 6.0423	
<i>o,p'</i> -DDT DDD	<0.0001 — 0.0820 0.0111 ± 0.0141	<0.0001 — 1.4750 0.0665 ± 0.2354	0.0040 — 1.1250 0.1489 ± 0.1676	0.0001 — 2.7170 0.1654 ± 0.3704	0.0020 — 4.4740 0.2962 ± 0.6262	0.0180 — 0.9800 0.2032 ± 0.1597	
<i>o,p'</i> -DDE	<0.0001 — 0.0350 0.0105 ± 0.0100	<0.0001 — 0.0940 0.0185 ± 0.0224	0.0100 — 0.0840 0.0542 ± 0.0557	<0.0001 — 0.6110 0.0745 ± 0.1122	0.0090 — 0.8850 0.0691 ± 0.1212	0.0070 — 0.2080 0.0532 ± 0.0424	
Total <i>p,p'</i> -DDT	0.0460 — 3.1209 0.6832 ± 0.7036	1.1288 — 21.3623 5.7319 ± 4.9038	0.8557 — 36.6056 15.0140 ± 12.2540	0.1194 — 67.9005 14.1864 ± 11.5060	0.8874 — 43.9410 16.8932 ± 9.7083	3.2243 — 70.4700 18.4584 ± 13.2120	
Total <i>o,p'</i> -DDT	0.0043 — 0.0820 0.0228 ± 0.0141	<0.0001 — 1.5636 0.0888 ± 0.2486	0.0508 — 1.1384 0.2118 ± 0.1709	0.0036 — 2.3061 0.2484 ± 0.4020	0.0486 — 4.6292 0.3732 ± 0.6515	0.0369 — 1.0335 0.2631 ± 0.1769	
Total DDT	0.0671 — 3.1359 0.7060 ± 0.7038	1.1184 — 21.4610 5.8204 ± 4.9017	0.9471 — 38.7134 15.2436 ± 12.3080	0.1230 — 68.1350 14.4347 ± 11.5310	0.9822 — 48.5702 17.2664 ± 10.1020	3.3065 — 71.1441 18.7214 ± 13.2840	
α -BHC	<0.0001 — 0.0458 0.0096 ± 0.0100	<0.0001 — 0.0891 0.0116 ± 0.0173	0.0028 — 0.1240 0.0267 ± 0.0224	0.0032 — 0.6200 0.0349 ± 0.0854	0.0050 — 0.1800 0.0247 ± 0.0265	0.0045 — 0.6310 0.0317 ± 0.0900	
β -BHC	0.0001 — 0.1150 0.0184 ± 0.0245	<0.0001 — 1.0580 0.0477 ± 0.1640	0.0202 — 2.0010 0.2464 ± 0.4201	0.0007 — 2.9350 0.3377 ± 0.6573	0.0157 — 4.7760 0.4799 ± 0.7710	0.0294 — 2.9470 0.4353 ± 0.6715	
γ -BHC	<0.0001 — 0.0777 0.0146 ± 0.0141	<0.0001 — 0.1090 0.0174 ± 0.0224	0.0010 — 3.9170 0.0938 ± 0.4974	6.0010 — 12.1430 0.3270 ± 1.6631	0.0010 — 0.0630 0.0302 ± 0.0686	0.0010 — 1.2876 0.0796 ± 0.2126	
Total BHC	0.0054 — 0.1207 0.0426 ± 0.0283	0.0019 — 1.0810 0.0767 ± 0.1667	0.0414 — 4.3530 0.3366 ± 0.4120	0.0232 — 12.7010 0.4688 ± 0.7034	0.0541 — 4.7980 0.5347 ± 0.7616	0.0600 — 3.0230 0.5467 ± 0.6872	
Dieldrin	<0.0001 — 0.1180 0.0193 ± 0.0412	<0.0001 — 0.1250 0.0209 ± 0.0283	0.0072 — 0.3150 0.1011 ± 0.1149	0.0038 — 0.4660 0.1160 ± 0.1136	0.0150 — 3.9600 0.1581 ± 0.1526	0.0131 — 0.8020 0.1353 ± 0.1360	
H. Epoxide	<0.0001 — 0.0102 0.0020 ± 0.0026	<0.0001 — 0.0374 0.0015 ± 0.0059	<0.0001 — 0.0510 0.0175 ± 0.0346	<0.0001 — 0.1320 0.0148 ± 0.0265	<0.0001 — 0.1180 0.0202 ± 0.0283	<0.0001 — 0.1320 0.0103 ± 0.0173	

In the 5-through-24-year age group, the mean total DDT was 15.2 ppm. DDE averaged 67.8% of total DDT-derived material. The mean total *p,p'*-DDT was 15.01 ppm and the mean total *o,p'*-DDT was 0.2 ppm. There was a significant difference in the storage of *p,p'*-DDT and total DDT between the age group under 11 months and the group 5 through 24 years ($p < 0.01$). Total BHC averaged 0.34 ppm, dieldrin 0.1 ppm, and heptachlor epoxide 0.02 ppm.

In the 25-through-44-year age group, total DDT averaged 14.4 ppm. DDE constituted 65.6% of total DDT. The mean total *p,p'*-DDT was 14.2 ppm, and *o,p'*-DDT was 0.25 ppm. Total BHC was 0.47 ppm, dieldrin was 0.12 ppm, and heptachlor epoxide was 0.01 ppm.

In the 45-through-69-year age group, the mean total DDT was 17.3 ppm. DDE constituted 60.7% of total DDT. The mean total *p,p'*-DDT was 16.9 ppm, and that of *o,p'*-DDT was 0.37 ppm. Total BHC was 0.53 ppm, dieldrin was 0.16 ppm, and heptachlor epoxide was 0.02 ppm.

In the group aged 70 years and over, the mean total DDT-derived material was 18.7 ppm. DDE constituted 59.8% of total DDT. The mean total *p,p'*-DDT was 18.5 ppm and total *o,p'*-DDT was 0.26 ppm. Total BHC was 0.5 ppm, dieldrin was 0.14 ppm, and heptachlor epoxide was 0.01 ppm.

From these data it was concluded that the storage level of DDT and derived material increased with age, the highest values being found in the 70-year-and-over age group.

Tables 3 and 4 also showed that males stored higher amounts of *p,p'*-DDT and total DDT in all the age groups, except the 0-through-11-month age group in which the DDT storage levels were of about the same order: 5.34 ppm total DDT in males and 5.82 ppm total DDT in females.

The authors found the trend for a positive age association of DDT storage in populations living in various areas of the world. In the general populations of South Africa (25), Thailand (23), Nigeria (22), and Brazil (20), the 25-through-44-year age group stored the highest amount of OCI in both sexes, after which there was a decrease in the storage level. In the general population of Uganda, the storage level of DDT was comparable in the 5-through-24- and 25-through-44-year age groups (26).

In the general populations of Kenya (21), Israel (2), and *this paper*, and nonwhite populations of the USA (8), it appears that a positive age association with DDT storage occurs in all ages.

These data suggest that the level of the OCI storage process tends to vary after the age of 45 years; in some

populations it is higher and in others it is lower than in the 25-through-44-year age group. It appears reasonable therefore, to consider the 25-through-44-year age group the best indicator of OCI storage in a community for purposes of comparison (Table 5).

TABLE 5.—Storage of DDT-derived material in adipose tissue of 25-through-44-years-olds in several countries

COUNTRY	TOTAL DDT, PPM			REFERENCES
	M & F	MALES	FEMALES	
Uganda	2.9	3.6	1.2	Wassermann et al. (2)
Kenya	4.5	4.6	4.2	Wassermann et al. (2)
Nigeria	6.5	7.4	5.9	Wassermann et al. (2)
Brazil	7.8	9.6	6.3	Wassermann et al. (2)
South Africa				Wassermann et al. (2)
White	8.5	10.5	6.6	
Bantu	6.5	8.6	4.4	
Thailand	13.0	15.5	10.2	Wassermann et al. (2)
Israel	14.4	15.9	12.2	This paper.

In the study carried out on OCI storage in the adipose tissue of people from Nigeria (22), a positive age association up to the age of 45 years was found both for DDT and dieldrin. These findings confirmed experimental data the authors had obtained in rats submitted to a high dosage of *p,p'*-DDT: namely, a parallel increase in the storage of dieldrin, although these animals had not received additional dieldrin apart from that naturally in food and water (27). In the present study the authors compared the concentration of dieldrin in the adipose tissue of people having: (1) high concentration of *p,p'*-DDT, and (2) low concentration of *p,p'*-DDT.

The statistical analysis revealed increased storage of dieldrin ($p < 0.01$) in the group with a higher concentration of *p,p'*-DDT.

These findings may be explained by a biochemical interrelationship of the two compounds in the animal body: the presence of a large amount of DDT interfering with the detoxication of dieldrin resulting in its accumulation in adipose tissue.

LITERATURE CITED

- (1) Wassermann, M., M. Gon, D. Wassermann, and L. Zellermyer. 1965. DDT and DDE in the body fat of people in Israel. *Arch. Environ. Health* 11:9, 375-380.
- (2) Wassermann, M., D. Wassermann, L. Zellermyer, and M. Gon. 1967. Storage of DDT in the people of Israel. *Pestic. Monit. J.* 1:2, 15-20.
- (3) Polishuk, Z. W., M. Wassermann, D. Wassermann, Groner, S. Lazarovici, and L. Tomatis. 1970. Effect of pregnancy on storage of organochlorine insecticides. *Arch. Environ. Health* 20:2, 215-217.
- (4) Wassermann, M. and D. Wassermann. 1966. Recognition of a new group of toxic substances as curative constituents in the human body: the organochlorine insecticides. *Proc. XV Int. Cong. Occup. Health, Vienna, Austria*, 6:2, 954.
- (5) Brown J. R. 1967. Organochlorine pesticide residues in human depot fat. *Can. Med. Ass. J.* 97:367-372.

- 6) Davies, J. E., W. F. Edmundson, N. J. Schneider, and J. C. Cassady. 1968. Problems of prevalence of pesticide residues in humans. *Pestic. Monit. J.* 2:80-85.
- 7) Davies, J. E., and J. H. Milby. 1969. Epidemiology of pesticides. In: Mrak, E. M. Report of the secretary's commission on pesticides and their relationship to environmental health, Parts I and II. U.S. Department of Health, Education and Welfare.
- 8) Fiserova-Bergerova, V., J. L. Radomski, J. E. Davies, and J. H. Davis. 1967. Levels of chlorinated hydrocarbon pesticides in human tissue. *Ind. Med. Surg.* 36: 65-70.
- 9) Hunter, C. G., J. Robinson, and A. Richardson. 1963. Chlorinated insecticide content of human body fat in southern England. *Brit. J. Med.* 1:221-224.
- 10) Robinson, J., A. Richardson, C. G. Hunter, A. N. Crabtree, and H. J. Rees. 1965. Organochlorine insecticide content of human adipose tissue. *Brit. J. Ind. Med.* 22:220-229.
- 1) Zavon, M. R., R. Tyre, and L. Laforre. 1969. Chlorinated hydrocarbon insecticide content of the neonate. *Ann. N.Y. Acad. Sci.* 160:196-200.
- 2) Curley, A. and R. Kimbrough. 1969. Chlorinated hydrocarbon insecticides in plasma and milk of pregnant and lactating women. *Arch. Environ. Health* 18:156-164.
- 3) Hayes, W. J., Jr., G. E. Quinby, K. C. Walter, J. W. Elliott, and W. M. Upholt. 1958. Storage of DDT and DDE in people with different degrees of exposure to DDT. *Arch. Industr. Hlth.* 18: 398-406.
- 4) Conney, A. H., R. Welch, R. Kuntzman, R. Chang, M. Jacobson, A. D. Munro-Faure, A. W. Peck, A. Bye, A. Poland, P. J. Poppers, M. Finster, and J. A. Wolff. 1971. Effects of environmental chemicals on the metabolism of drugs, carcinogens and normal body constituents in man. *Ann. N.Y. Acad. Sci.* 179:155-172.
- 5) McLean, A. E. M., and E. K. McLean. 1969. Diet and toxicity. *Brit. Med. Bull.* 25:278-281.
- 6) Wassermann, M., D. Wassermann, E. Kedar, and M. Djavaherian. 1971. Immunological and detoxication interaction in *p,p'*-DDT fed rabbits. *Bull. Environ. Contam. Toxicol.* 26:426-435.
- 7) Nagasaki, H., S. Tomis, T. Mega, M. Marugami, and N. Ito. 1971. Development of hepatomas in mice treated with benzene hexachloride. *Gann* 62:431.
- (18) Tomatis, L., V. Turusov, N. Day, and R. T. Charles. 1972. The effect of long-term exposure to DDT on CF-1 mice. *Int. J. Cancer* 10:489-506.
- (19) Turusov, V. S., N. E. Day, L. Tomatis, E. Gati, and R. T. Charles. 1973. Tumors in CF-1 mice exposed for six consecutive generations to DDT. *J. Nat. Cancer Inst.* 51:983.
- (20) Wassermann, M., D. P. Nogueira, L. Tomatis, N. E. Day, E. Athie, D. Wassermann, M. Djavaherian, and C. Guttel. 1972. Storage of organochlorine insecticides in people of Sao Paulo, Brazil. *Ind. Med. Surg.* 41:3, 22.
- (21) Wassermann, M., M. G. Rogoff, L. Tomatis, N. E. Day, D. Wassermann, M. Djavaherian, and C. Guttel. 1972. Storage of organochlorine insecticides in the adipose tissue of people of Kenya. *Ann. Soc. Belge Med. Trop.* 52:6, 509-514.
- (22) Wassermann, M., G. O. Sofoluwe, L. Tomatis, N. E. Day, D. Wassermann, and S. Lazarovici. 1972. Storage of organochlorine insecticides in people of Nigeria. *Environ. Physiol. Biochem.* 2:59-67.
- (23) Wassermann, M., M. Trishnananda, L. Tomatis, N. E. Day, D. Wassermann, V. Rungpitarangsi, V. Chiamsakol, M. Djavaherian, and S. Cucos. 1972. Storage of organochlorine insecticides in the adipose tissue of people in Thailand. *The Southeast Asian J. of Trop. Med. and Public Health* 3:2, 280-285.
- (24) Tomatis, L., V. Turusov, B. Terracini, N. Day, W. Barthel, R. T. Charles, G. B. Collins, and M. Boiocchi. 1971. Storage levels of DDT metabolites in mouse tissues following long term exposure to technical DDT. *Tumori* 57:377-396.
- (25) Wassermann, M., D. Wassermann, S. Lazarovici, A. M. Coetzee, and L. Tomatis. 1970. Present state of the storage of the organochlorine insecticides in the general population of South Africa. *S. Afr. Med. J.* 44:646-648.
- (26) Wassermann, M., L. Tomatis, D. Wassermann, N. E. Day, and M. Djavaherian. Storage of OCI in the adipose tissue of Ugandans. *Bull. Environ. Contam. Toxicol.* (In press).
- (27) Wassermann, M., D. Wassermann, and S. Lazarovici. 1969. Effects of thyroidectomy on the storage of organochlorine insecticides. *Bull. Environ. Contam. Toxicol.* 4:6, 327-336.

RESIDUES IN FOOD AND FEED

Polychlorinated Biphenyl and Organochlorine Pesticide Residues in Canadian Chicken Eggs¹

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ABSTRACT

A nationwide survey in Canada of polychlorinated biphenyl (PCB) and organochlorine pesticide residues in eggs revealed an average of less than 10 ppb for both groups of compounds. PCB's and p,p'-DDE were found in all samples; at least 95 percent also contained dieldrin and p,p'-DDT. Lindane and cis- and trans-chlordane were present in 75 percent of all eggs. No significant differences were observed among the different regions of the country.

Introduction

The presence of polychlorinated biphenyls in the environment in general and the food supply in particular has been a growing concern for several years (1,2). A recent incident of PCB contamination (0.6-1.9 ppm) of thousands of eggs in the United States, due to contaminated poultry feed, is evidence of this environmental problem (3). A nationwide survey of PCB's in domestic chicken eggs in Canada was therefore undertaken; initial samples were collected in 1971.

The analytical data presented in this paper were obtained from the liquid portion of the egg only. This paper presents data on PCB's and several organochlorine pesticides.

Sampling Procedure

Twenty dozen grade A eggs were collected from each of the following five regions of the country: Eastern (Newfoundland, Prince Edward Island, Nova Scotia, and New

Brunswick); Quebec; Ontario; Central (Manitoba and Saskatchewan); and Western (Alberta and British Columbia).

The stipulation was that all eggs from a specific region be produced locally. The eggs were stored at 8°C until analyzed.

Analytical Methods

All solvents were of a glass-distilled, residue-free grade and were checked for purity. Pesticides and decachlorobiphenyl standards were 99 percent pure as verified by gas chromatography (GC). Aroclor 1260 was used as supplied by the manufacturer, Monsanto Chemical Company.

EXTRACTION

The liquid content of 12 eggs was pooled and stirred with a glass rod until thoroughly mixed. A 50-g sample was extracted for 3 min in a soil dispersion mixer (St. Manufacturing Co., St. Louis, Mo.) with a 300-ml mixture of hexane and acetone (2:1 v/v), previously warmed to 40°C. The extract was filtered through prewashed anhydrous Na₂SO₄ to remove the water, concentrated on an all-glass rotary evaporator (<25°C), and diluted up to 50 ml. A 1-ml aliquot was evaporated in a preweighed aluminum dish to determine lipid content.

CLEANUP AND SEPARATION OF PCB'S AND PESTICIDES

An aliquot equivalent to approximately 2 g of lipid was subjected to the low-temperature micro precipitation technique (4) and further cleaned on a 5 percent Flori-

¹ Health Protection Branch of the Department of National Health and Welfare, Tunney's Pasture, Ottawa, Canada.

column (deactivated with 5 percent distilled water after heating overnight at 140°C) (5). PCB's and pesticides were partly separated on a silicic acid column according to Armour and Burke (6), except that the silicic acid was prewashed with the eluent used for the pesticides, heated overnight at 130°C, and deactivated with 5 percent distilled water. A final cleanup for the pesticide fraction was carried out as before on a 5 percent Florisil column.

IDENTIFICATION AND QUANTIFICATION

The PCB fraction was concentrated to 1 ml; the pesticide fraction was carefully evaporated to dryness under a gentle stream of N₂ and redissolved in 1 ml of hexane. A 5- μ l aliquot was injected into a Varian Aerograph Series 1400 gas chromatograph with an electron-capture detector (tritium foil) under the following conditions:

Column: ¼-in.-by-6-ft glass, packed with 6 percent OV-210 + 4 percent SE-30 on Chromosorb W(AW) 60/80 (0.6 g OV-210 + 0.4 g SE-30 + 10 g solid support)

Temperatures: Injector 220°C
Column 212°C
Detector 225°C

To give a retention time of 13 min for *p,p'*-DDT an approximate flow rate of 50 ml N₂/min was used. Standard solutions were made up to contain 50x10⁻⁵ μ g/ μ l of Aroclor 1260 (5 μ l were equivalent to a 2 (full-scale deflection) (FSD) for the highest peak on a 1-mV recorder) or 0.5-5.0x10⁻⁵ μ g/ μ l of pesticide, depending upon the individual response of the pesticide (e.g., 5x10⁻⁵ μ g/ μ l of *p,p'*-DDT). A 10- μ l aliquot of the standard pesticide solution had a ½ FSD for *p,p'*-DDT.

A 5- μ l injection of standard solution was made before and after every two sample injections.

PCB's and pesticides were quantitated by using peak heights. Peaks 8, 10, and 11-15 in Aroclor 1260, according to the numbering system of Reynolds (7) and the Organization for Economic Cooperation and Development (O.E.C.D.) (8), were used for quantification.

CONFIRMATION OF PCB'S

The PCB fractions of 64 samples were pooled to give a total of approximately 13 μ g of PCB.

Thin-layer chromatography (TLC) was carried out on precoated aluminum oxide (type E) F₂₅₄ 20-by-20-cm plates (Brinkman Instruments, Ltd., Canada), activated at 110°C for 1 hr. A total of 2.5 μ g of PCB from the pooled sample was spotted at a concentration of 0.25 μ g/spot; two reference spots of Aroclor 1260 at 2.5 μ g/spot were applied at each end of the line of origin. The TLC plate was developed in 1 percent acetone in

hexane and the reference spots were made visible with AgNO₃ (9). The standard Aroclor 1260 showed two spots and the corresponding areas of the sample, as well as a blank, were scraped, eluted with hexane, and gas-chromatographed as above.

A portion of the pooled sample of PCB equivalent to 1 μ g of PCB was perchlorinated and the resultant derivative was identified by GC according to Berg et al. (10), except that a Griffin-Worden pressure vessel (Kontes Glass Co. k-767100) was used for perchlorination.

CONFIRMATION OF PESTICIDES

All pesticide fractions, besides having been gas-chromatographed as before, were also run on a different column under the following conditions:

Column: ¼-in.-by-6-ft glass, packed with 5 percent QF-1 on Chromosorb W(AW) 60/80 (0.5 g QF-1 + 10 g solid support)

Temperatures: Injector 208°C
Column 175°C
Detector 229°C

To give a retention time of 26 min for *p,p'*-DDT, a flow rate of approximately 40 ml N₂/min was used.

The pesticide fractions of every other 10 samples were pooled and chromatographed on TLC plates as above. The five pooled samples were spotted at a concentration of 1.2-1.6 μ g/spot of estimated pesticide; two reference spots of an appropriate standard pesticide mixture (2.5 μ g/spot for an individual pesticide) were applied at each end of the line of origin. After development and visualization of the standards, the TLC plate was divided into five areas corresponding to the following pesticides, in order of increasing R_f value:

1. dieldrin, heptachlor epoxide, and lindane
2. cis- and trans-chlordane and *p,p'*-TDE
3. *p,p'*-DDT
4. DDMU, *o,p'*-DDT, *o,p'*-DDE, and heptachlor
5. *p,p'*-DDE, aldrin

Each area was then subdivided into six equal portions corresponding to the five pooled samples and a blank. Adsorbent from these portions was removed, and the pesticides were eluted with hexane and rechromatographed on both GC columns.

CONTROLS

Samples were spiked by adding 1 ppm and 1-10 ppb levels of Aroclor 1260 and pesticides to 50 g of whole liquid egg before extraction.

At different times during the survey three blanks were run through the complete analytical procedure, starting with a simulated extraction using the same solvent mixture used for the egg samples.

Results and Discussion

Results in Table 1 indicate that the mean level of all residues was below 10 ppb. A PCB and pesticide problem in eggs on the Canadian market apparently does not exist.

TABLE 1.—PCB and pesticide residues in whole liquid Canadian chicken eggs

COMPOUND	AVERAGE PPB ¹	MAXIMUM PPB OBSERVED	PERCENTAGE OF SAMPLES CONTAINING RESIDUES
PCB's as Aroclor 1260	8	27	100
Lindane	3	10	75
Heptachlor	2	10	67
Heptachlor epoxide	1	3	70
<i>p,p'</i> -DDE	7	110	100
Dieldrin	1	6	96
<i>p,p'</i> -DDT	5	192	98
trans-Chlordane	2	8	78
cis-Chlordane	1	4	81

¹ Average derived from a total of 100 samples, each sample representing one dozen eggs.

The maximum PCB residue was close to 0.03 ppm and the maximum total DDT level (sum of *p,p'*-DDT and *p,p'*-DDE levels) was close to 0.3 ppm, although the latter represents a single instance of high *p,p'*-DDT and *p,p'*-DDE levels in the same sample. The second-highest total DDT value was 0.07 ppm.

The low levels found in this investigation ought not to be taken as absolute, since recovery studies for eight different egg samples ranged from 25 to 115 percent at the 1-10 ppb level. PCB's, *p,p'*-DDT and *p,p'*-DDE, however, had better than 50 percent recovery at all times. Egg samples spiked at the 1 ppm level had >80 percent recovery, except for lindane which had 60 percent recovery. The blanks gave no significant findings.

The low level of *p,p'*-DDT and *p,p'*-DDE in chicken eggs may reflect low pesticide intake by the chickens, since eggs are an important elimination route for these pesticides (11).

Table 2 shows a rather even distribution of PCB's and pesticides. The mean levels of *p,p'*-DDT in the Western and Eastern regions were relatively higher than in the rest of the country only because of one or two individual high values.

The GC patterns of PCB's in individual egg samples were similar to those of Aroclor 1260. During confirmation of PCB's on TLC plates two distinct areas were observed which, when scraped and eluted, had two GC patterns consisting of the following Aroclor 1260 peaks numbered according to the system of Reynolds (7) and O.E.C.D. (8):

	Fraction 1 ($R_{p,p'-DDE}$ 1.15)	Fraction 2 ($R_{p,p'-DDE}$ 1.00)
most of:	8,9,11,13,15,17,18	10,12,14,16
some of:	10,16	9

TABLE 2.—Regional distribution of PCB and pesticide residues in Canadian chicken eggs

COMPOUND	AVERAGE PPB ^{1,2}				
	WESTERN REGION	CENTRAL REGION	ONTARIO	QUEBEC	EASTERN REGION
PCB's as Aroclor 1260	7	9	10	7	8
Lindane	trace	4	5	3	1
Heptachlor	trace	3	4	3	1
Heptachlor epoxide	1	1	1	1	trace
<i>p,p'</i> -DDE	9	8	7	5	8
Dieldrin	2	1	1	1	1
<i>p,p'</i> -DDT	12	4	2	1	8
trans-Chlordane	trace	3	3	3	1
cis-Chlordane	trace	2	2	1	1

¹ Average derived from a total of 20 samples from each region; each sample represents one dozen eggs.

² Trace = <1 ppb.

The combination of both fractions gave a GC pattern quite similar to Aroclor 1260, except for peak 10 which was considerably higher. The latter may be an indication of the presence of Aroclor 1254, but no attempt was made to correct for it.

All pesticides reported in the tables were confirmed by TLC as described, including chlordanes whose presence in eggs has been reported earlier (12). Although *o,p'*-DDT was suspected in several samples and has been previously reported in eggs (12), this pesticide could not be confirmed by the TLC procedure. Trace (<1 ppb) of *p,p'*-TDE were also observed but not confirmed. Peaks similar in retention time to aldrin were occasionally found, but could not be confirmed on QF-

The average lipid content for whole liquid egg obtained with the hexane/acetone extraction was 10.93 percent \pm 1.05. Data in Tables 1 and 2 may be converted to ppb on a lipid basis by using a factor of approximately 9.

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LITERATURE CITED

- (1) Zitko, V., and P.M.K. Choi. 1971. PCB and other industrial halogenated hydrocarbons in the environment. Technical Report no. 272 of the Fisheries Research Board of Canada.
- (2) Hammond, A. L. 1972. Chemical Pollution: Polychlorinated biphenyls. Science 175:155-156.
- (3) PCB in eggs. 1971. Chem. Eng. News. 49:(34) 30.
- (4) McLeod, H. A., and P. J. Wales. 1972. A low temperature cleanup procedure for pesticides and their metabolites in biological samples. J. Agr. Food Chem. 20: 624-627.
- (5) Langlois, B. E., A. R. Stemp, and B. J. Liska. 1971. Rapid cleanup of dairy products for analysis of ch

minated insecticide residue by electron capture gas chromatography. *J. Agr. Food Chem.* 12:243-245.

- (6) *Armour, J. A., and J. A. Burke. 1970. Method for separating polychlorinated biphenyls from DDT and its analogs. J. AOAC. 53:761-768.*
- (7) *Reynolds, L. M. 1969. Polychlorobiphenyls (PCB's) and their interference with pesticide residue analysis. Bull. Environ. Contam. Toxicol. 4:128-143.*
- (8) *Jensen, S., and G. Widmark. O.E.C.D. Report 1966-1967.*
- (9) *McLeod, H. A., P. J. Wales, R. A. Graham, M. Osadchuk, and N. Bluman. 1969. Analytical methods for pesticide residues in foods. Manual of the Health Protection Branch. Dept. Natl. Health and Welfare, Ottawa, Canada.*
- (10) *Berg, O. W., P. L. Diosady, and G. A. V. Rees. 1972.*

Column chromatographic separation of polychlorinated biphenyls from chlorinated hydrocarbon pesticides and their subsequent gas chromatographic quantitation in terms of derivatives. *Bull. Environ. Contam. Toxicol.* 7:(6), 338-375.

- (11) *Cecil, H. C., G. F. Fries, J. Bitman, S. J. Harris, R. J. Lillie, and C. A. Denton. 1972. Dietary *p,p'*-DDT, *o,p'*-DDT or *p,p'*-DDE and changes in egg shell characteristics and pesticide accumulation in egg contents and body fat of caged white leghorns. Poultry Sci. LI:(1)130-139.*
- (12) *Foster, T. S., H. V. Morley, R. Purkayastha, R. Greenhalgh, and J. R. Hunt. 1972. Residues in eggs and tissues of hens fed a ration containing low levels of pesticides with or without charcoal. J. Econ. Entomol. 65:(4), 982-988.*

RESIDUES IN FISH, WILDLIFE, AND ESTUARIES

DDT Plus PCB's in Blubber of Harbor Seals

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ABSTRACT

Samples of blubber from 13 harbor seals (*Phoca vitulina richardii*) were collected in 1971 from San Miguel Island, Calif.; the Columbia River, Oreg.; Puget Sound, Wash.; and the Pribilof Islands, Alaska. Total amounts of DDT plus PCB's ranged from 380.7 to 2,350.0 ppm in five San Miguel Island seals; 459.4 to 1,620.0 ppm in two Puget Sound seals; 27.7 to 109.9 ppm in three Columbia River seals; and 6.8 to 27.8 ppm in three Pribilof Islands seals. There was no indication of loss of total DDT plus PCB's in three samples reanalyzed after 2 years in frozen storage.

Introduction

Organochlorine pesticides have been found in seals in widespread parts of the world (1,2), but few data have been published on pesticides in harbor seals (*Phoca vitulina richardii*) from the eastern North Pacific Ocean. Up to 142 ppm DDE, 7.1 ppm DDD, and 2.6 ppm DDT were found in blubber from two harbor seals taken off central California (3). Up to 1,039 ppm total DDT and 145 ppm PCB's (polychlorinated biphenyls) were found in California sea lions (*Zalophus californianus californianus*) from San Miguel Island, Calif. (4), one of the areas sampled in this study. This report documents the amounts of DDT and its metabolites plus PCB's in the blubber of 13 harbor seals (*Phoca vitulina richardii*) collected in 1971 from four areas of the eastern North

Pacific Ocean: San Miguel Island, Calif.; Columbia River, Oreg.; Puget Sound, Wash.; and the Pribilof Islands, Alaska.

Harbor seals of the subspecies *richardii* are nonmigratory and occur in the eastern North Pacific Ocean from Mexico to the Bering Sea. If food species preyed on by the seals do not migrate far, these seals might be used to locate geographical areas where organochlorine hydrocarbon levels are high. Harbor seals living off British Columbia feed near shore on demersal fish and octopus, although some migratory Pacific salmon (*Oncorhynchus* sp.) are eaten seasonally (5). Harbor seals feeding off Amchitka Island, Alaska, eat Atka mackerel (*Pleurogrammus monopterygius*) and octopus (*Octopus* sp) (6). A study of harbor seals in Washington showed that cods, flounders, Pacific herring, and sculpins made up 93 percent of the total diet. Squid and octopus make up another 6 percent (7). Harbor seals apparently feed on both migratory and nonmigratory species.

Sampling Procedures

All seals appeared to be in good health at the time of collection, except one seal from Washington which had apparently died from a deep laceration from a previous injury. Samples were collected by taking about 100 g of blubber from the belly area of each seal, near the midline and anterior to the mammarys. Blubber wa

¹ Northwest Fisheries Center, National Marine Fisheries Service, National Oceanic and Atmospheric Administration, 2725 Montlake Boulevard East, Seattle, Wash. 98112.

ected for this study because organochlorine compounds are lipophilic (*I*). Samples were placed in new glass bottles and shipped frozen to the testing laboratory, ARF Institute, Inc., Madison, Wis.

ages were estimated by counting layers of dentine in upper canine teeth (8,9). The error in assigning ages to harbor seals is not known. Body length was measured from the tip of the snout to the end of the tail, with the seal placed on its back.

Analytical Procedures

Samples of blubber were analyzed by gas-liquid chromatography for the following organochlorine compounds: aldrin, chlordane, endrin, heptachlor, heptachlor epoxide, methoxychlor, toxaphene, dieldrin, heptachlor hexachloride (BHC), PCB's, and the *o,p'* and *p,p'* isomers of DDE, DDD, and DDT. Only BHC, PCB's, and the *p,p'* isomers of DDE, DDD, and DDT were detected in 13 samples analyzed in 1971 and in 3 samples analyzed in 1973. Confirmatory tests by use of thin-layer chromatography (10) on the rerun samples confirmed DDE, DDD, DDT, and PCB's, but not BHC. Levels of BHC will not be reported because of the negative confirmatory test.

To determine concentrations of the various organochlorine compounds, the entire 100-g sample of blubber was cut up while frozen, run through a hand food chopper, and transferred to ether-rinsed 4-oz glass jars. A random 5-g portion was placed in a tared 100-ml beaker and the weight was recorded. The sample was oven-dried at 40°C for 3 to 5 days, weighed for moisture content, and transferred to a 100-ml volumetric flask containing petroleum ether. The blubber consisted almost entirely of fat and dissolved entirely in the petroleum ether. No weighable amounts of insolubles were found. Cleanup was carried out on a Florisil column following standard procedures (11). Next, the resulting solutions were concentrated to 10-15 ml and made to 25 ml with hexane. Sample solutions of 10 μ l or less were injected into a Barber-Coleman Model 5360 gas chromatograph with an Sr90 electron-capture detector and following instrument conditions:

Columns: 4-ft-by-4-mm glass packed with 5 percent DC-200 on gas chrom Q 80/100 (packed with 3 percent OV-17 on gas chrom Q 100/120 for BHC). An OV-17 + QF-1 column was added in 1973.
Temperature: Detector 250°C; injector 230°C; column 210°C (180°C for BHC).
Carrier gas: Nitrogen at a flow rate that gave *p,p'*-DDT a retention time of 6-8 minutes (12-14 minutes for BHC).

Injection heights were measured to quantitate organochlorine pesticide residues. Recovery rates ranged from 80 to 90 percent for all organochlorine compounds. Recoveries were run through the entire procedure.

including the drying step. No corrections were made for recovery rates. The lower limits of detection were 0.02 ppm for DDE, DDD, and DDT, and 0.05 ppm for PCB's. Pesticide levels were only slightly higher on a fat basis than on a wet-weight basis, so results are reported here on a wet-weight basis only.

Aroclor 1254 was used as the standard for PCB's. Only the peak between DDT and DDD was used for estimation of PCB's, so the values for PCB's are not precise. Values for total DDT undoubtedly include some PCB's. To avoid possible errors, total DDT and PCB's were summed.

Because of high laboratory costs, only one sample was analyzed by the silicic acid method to separate DDT from PCB's (12). The blubber from this seal, a 176-cm male from San Miguel Island, had 2,110.0 ppm DDE, 3.98 ppm DDD, 96.1 ppm DDT, and 572.0 ppm PCB's. Total DDT plus PCB residues were 18 percent higher from the silicic acid method than were results from regular analyses. This difference is within the limits of analytical variability.

Glass bottles used to store the samples had paper lid-liners. The amounts of organochlorine compounds found in a sample of unused lid-liners would have had a maximum effect of 0.086 ppm total DDT plus PCB's. Because the additions, if they occurred, would have had little effect on the observed values, data were not adjusted.

Results

Levels of total DDT plus PCB's ranged from 380.7 to 2,350.0 ppm (geometric mean 610.7) in San Miguel Island seals, 459.4 to 1,620.0 ppm (geometric mean 862.7) in Puget Sound seals, 27.7 to 109.9 ppm (geometric mean 62.5) in Columbia River seals, and 6.8 to 27.8 ppm (geometric mean 11.3) in Pribilof Islands seals (Table 1). Geometric means were computed because of the skewed distributions of the organochlorine compound residues. The organochlorine levels overlapped in San Miguel Island and Puget Sound seals, and in Columbia River and Pribilof Islands seals. Levels in the Columbia River and Pribilof Islands seals did not overlap the levels in San Miguel Island and Puget Sound seals. A one-way analysis-of-variance test shows that the mean total DDT plus PCB levels differed significantly between areas ($P < 0.01$).

The Pribilof Islands are isolated from areas of high population and industrialization; the Columbia River drains large agricultural areas in Oregon, Washington, and Idaho; and San Miguel Island and Puget Sound are close to highly industrialized areas. Harbor seals taken near heavily populated and industrialized areas had the highest total DDT plus PCB levels, and seals

TABLE 1.—Total DDT¹ plus PCB's in blubber of harbor seals collected in 1971

LOCATION	NO. OF SEALS	MONTH COLLECTED	AGE, YR	LENGTH, CM	MOISTURE, %	FAT, %	TOTAL DDT + PCB'S (MG/KG; WET WT)	
							GEOMETRIC MEAN	INDIVIDUAL VALUES
California: San Miguel Island	5	June	9-30 +	153-176	0.9-1.4	96.6-99.2	610.7	380.7; 418.5; 435.5 518.3; 2,350.0
Oregon: Columbia River	3	May	2-4	112-126	1.8-3.6	96.2-100.0	62.5	27.7; 80.4; 109.9
Washington: Puget Sound	2	June-August	1	95-119	2.4-5.0	90.5-95.1	862.7	459.4; 1,620.0
Alaska: Pribilof Islands	3	August	(²)	135-175	2.6-6.2	92.8-100.0	11.3	6.8; 7.1; 27.8

¹ DDE + DDD + DDT.² Canine teeth lost.

taken from the most isolated area, the Pribilof Islands, had the lowest levels. However, larger samples are needed to verify these results. Variability due to sex and age could not be evaluated for these data because of the small sample sizes. Maximum residue levels occurred in male seals in each area, but the oldest seals did not have the highest total DDT plus PCB levels within an area.

After 2 years of frozen storage, two samples from San Miguel Island and one from the Pribilof Islands were reanalyzed. Total DDT plus PCB values were +18 percent, -16 percent, and -3 percent, respectively, of the original values. Results from the original and rerun samples are within the limits of analytical variability and indicate no significant changes in residue levels.

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LITERATURE CITED

- (1) Holden, A. V., and K. Marsden. 1967. Organochlorine pesticides in seals and porpoises. *Nature* 216(512):1274-1276.
- (2) Sladen, W. J. L., C. M. Menzie, and W. L. Reich. 1966. DDT residues in Adelie penguins and a crested eater seal from Antarctica. *Nature* 210(5037):670-671.
- (3) Shaw, S. B. 1971. Chlorinated hydrocarbon pesticide in California sea otters and harbor seals. *Calif. F. Game* 57(4):290-294.
- (4) DeLong, R. L., W. G. Gilmartin, and J. G. Simps. 1973. Premature births in California sea lions: association with high organochlorine pollutant residue levels. *Science* 181(4105):1168-1170.
- (5) Spalding, D. J. 1964. Comparative feeding habits of fur seal, sea lion, and harbor seal on the British Columbia coast. *Bull., Fish. Res. Bd. Can.* 46: 52 pp.
- (6) Kenyon, K. W. 1965. Food of harbor seals at Amchik Island, Alaska. *J. Mammal.* 46(1):103-104.
- (7) Scheffer, T. H., and C. C. Sperry. 1931. Food habits of the Pacific harbor seal, *Phoca richardi*. *J. Mammal.* 12(3): 214-226.
- (8) Fiscus, C. H., G. A. Baines, and F. Wilke. 1964. Pelagic fur seal investigations, Alaska waters, 1962. U.S. Fish. Wildl. Serv. Spec. Sci. Rep. Fish. 475. 59 pp.
- (9) Laws, R. M. 1952. A new method of age determination for mammals. *Nature* 169(4310):972-973.
- (10) Mulhern, B. M., E. Cromartie, W. L. Reichel, and A. A. Belisle. 1971. Semiquantitative determination of polychlorinated biphenyls in tissue samples by thin layer chromatography. *J. Ass. Offic. Anal. Chem.* 54: 548-550.
- (11) U.S. Food and Drug Administration. 1968. Pesticide analytical manual. Vol. 1. Sec. 211.15. Washington, D.C.
- (12) Armour, J. A., and J. A. Burke. 1970. Method for separating polychlorinated biphenyls from DDT and its analogs. *J. Ass. Offic. Anal. Chem.* 53(4):761-768.

Chlorinated Hydrocarbon and Mercury Residues in Woodcock in the United States, 1970-71¹

Donald R. Clark, Jr., and M. Anne Ross McLane

ABSTRACT

During late 1970 and early 1971, 229 woodcock (*Philohela minor*) were collected from 23 Eastern and Midwestern States. Analyses for chlorinated hydrocarbons and mercury in these migratory birds showed generally low levels which are not considered dangerous to human consumers. In this survey, Louisiana woodcock had lower residues of heptachlor epoxide and DDE than those tested in a 1965 survey. PCB levels, however, may have increased. Mirex levels were greatest in Mississippi and Louisiana woodcock.

Pooling of birds and averaging of individually analyzed birds did not provide equivalent estimates of equivalent residues; pool values tended to be larger and more variable. Levels of six chlorinated hydrocarbons and mercury were negatively correlated with the latitude of the collection site. However, this relationship seemed weakest for PCB's. Among eight chemical residues, PCB levels were most often unrelated with levels of the other seven. Levels of chlorinated hydrocarbons in wings were correlated with levels in breast muscle and in carcass; however, mean levels of certain residues differed significantly among wing, muscle, and carcass even when compared on a lipid basis.

Introduction

From October 1970 to February 1971, 229 woodcock (*Philohela minor*) were collected for chemical analysis from 23 Eastern and Midwestern States. Survey objectives were to establish base residue levels of organochlorine insecticides, PCB's, and mercury, and to determine geographic distribution of mirex. Providing impetus for this survey was an earlier Canadian study (1) which

effected the closing of the 1970 woodcock hunting season in New Brunswick, Ontario, Canada. At that time a series of 46 woodcock showed a range of 3 to 771 ppm (lipid weight) DDT plus metabolites, with a weighted mean of 60 ppm. In a more comprehensive study in 1973, woodcock averaged 25.8 ppm (lipid weight) DDT and metabolites from 164 analyses of 527 woodcock from New Brunswick (2).

In the 1970-71 study of U.S. woodcock, data from analyses were summarized by contaminant and compared to residue levels reported elsewhere and to U.S. Government guideline levels for meat destined for human consumption. Analytical findings were put to several other uses: pinpointing of the geographic distribution of woodcock containing mirex; comparison of data from pooled samples versus averages of individually analyzed birds; measurement of north-south geographic variation in residue levels; determination of correlations of residues of various toxicants with one another; and quantification of the relationships of residue levels in wing versus breast muscle, and wing versus carcass.

Analytical Methods

Among the 23 States represented in this survey were localities as far north as Maine and as far south as Florida. Several Midwestern States were sampled, including Minnesota and Missouri. Table 1 lists specific States represented and the number of woodcock collected in given counties of each State. Sampling began in October in the Northern States and ended in February in the Southern States.

¹U.S. Dept. of Interior—Fish and Wildlife Service, Patuxent Wildlife Research Center, Laurel, Md. 20811.

TABLE 1.—States and counties sampled for chlorinated hydrocarbon and mercury residues in woodcock, 1970-71

STATE	COUNTY	BIRDS COLLECTED
Alabama	Mobile	10
Arkansas	Chicot	2
	Faulkner	2
	Grant	2
	Hempstead	4
Florida	Alachua	9
	Marion	1
Georgia	Cherokee	5
Kentucky	McCracken	1
	Ohio	4
Louisiana	Iberville	16
	Pointe Coupee	4
Maine	Hancock	3
	Penobscot	5
	Washington	2
Maryland	Calvert	2
	Dorchester	1
	Montgomery	1
	Worcester	6
Michigan	Mackinac	3
	Schoolcraft	7
Minnesota	Pine	10
Mississippi	Clay	5
	Leake	5
	Oktibbeha	5
Missouri	Callaway	4
New Hampshire	Merrimack	1
	Rockingham	1
	Strafford	3
	Unrecorded locality	5
New Jersey	Atlantic	2
	Burlington	3
	Cape May	8
	Monmouth	1
	Morris	4
	Salem	2
New York	Jefferson	8
	St. Lawrence	2
North Carolina	Johnston	6
	Pender	4
Pennsylvania	Berks	1
	Bradford	5
	Centre	1
	Eric	2
	Tioga	1
Rhode Island	Unrecorded locality	5
South Carolina	Georgetown	8
	Lancaster	2
Tennessee	Coffee	1
	Hardeman Chester ¹	2
	Haywood	2
	Lauderdale	5
Vermont	Essex Caledonia ¹	4
	Orleans	1
West Virginia	Mason	10
Wisconsin	Portage	6
	Sauk	4

¹ Bordering counties; collection sites overlapped.

Mercury analyses were performed on 222 of the 229 birds and all 229 were analyzed for chlorinated hydrocarbons. One hundred of these birds were analyzed in five bird pools. Two pools from both Louisiana and New Jersey were analyzed; one pool from each State having a total sample of ten or fifteen birds was an-

alyzed. Pool birds were selected randomly from 1 sample from each State. Pools of livers were analyzed for mercury and pools of breast muscle were analyzed for both mercury and chlorinated hydrocarbons.

To determine organochlorine residue levels for wing breast muscle, and carcass subsamples, 40 comparison birds were chosen randomly from the 129 woodcock remaining after pooling.

Samples of muscle from birds analyzed individually for chlorinated hydrocarbons consisted of approximately one-half (20 to 30 g) the breast muscle and excluded skin. A 5-g sample was taken from each pooled bird. Pooled samples of breast muscle for mercury analysis consisted of 1 g of muscle from each bird. Entire livers were used for both individual and pooled samples which were analyzed for mercury.

Each wing sample included both wings, with distal segments and feathers removed. Carcass samples consisted of the remainder of the bird after samples of breast muscle, the liver, wings, skin, gastrointestinal tract, head, feet, and scaled portions of the legs had been removed. All samples were homogenized prior to analysis. Analyses were performed by WARF Institute, Inc., Madison, Wis.

Samples analyzed for chlorinated hydrocarbons were weighed, air dried with sodium sulfate for 48 hours, extracted with petroleum ether : ethyl ether (17:7) Soxhlet apparatus for 8 hours, cleaned, and separated into two fractions by passage through a florisil column of petroleum ether : ethyl ether, 95:5, 85:15. An aliquot of the first elution was passed through a standard silicic acid—celite column with petroleum ether, hexane, acetonitrile, and methylene chloride (3). Analysis was performed by electron-capture gas chromatography on a Barber-Coleman Pesticide Analyzer model 5300. The column was glass, 1208 mm by 4 mm, packed with 5 percent DC-200 80/100 mesh Gas Chrom Q. Injection temperature was 240°C; column was 200°C; detector was 245°C. The carrier gas was nitrogen at a flow rate of 80 ml/min. Lipid weight was determined from an aliquot of the extract which was reduced to dryness on a steam bath and placed in a 40°C oven for 2-4 hours before weighing.

Total mercury content was determined by cold vapor atomic absorption. Samples were digested by reflux with sulfuric—nitric acid mixture (4). A mixture of hydroxylamine, stannous chloride, and sulfuric acid was added to the digest to reduce the mercury II ions to mercury metal. Samples were aerated at 3 liters/minute and passed through the absorption cell.

Limits of sensitivity (wet weight, ppm) were 0.05 for mercury, 0.01 for PCB's, and 0.005 for DDE, DDT, mirex, heptachlor epoxide, and dieldrin.

recoveries of mercury from spiked samples ranged from 85 to 98.5 percent. Percentage recoveries for chlorinated hydrocarbons were: DDE and PCB's, 75-85; DDD and mirex, 80-90; DDT, 75-80; dieldrin, 82-94; and heptachlor epoxide, 85-90. Analytical readings were not corrected for recovery. Confirmation consisted of running duplicate analyses. For mercury, five pooled liver samples and three individual livers were duplicated; for chlorinated hydrocarbons, one pooled muscle sample, three individual muscle samples, and four carcasses were duplicated.

In addition to arithmetic means, median values are given throughout this paper because all residue data were skewed with most values toward the low end of the distribution. Statistical tests were completed after $\log_{10}(x + 1)$ transformation of the data. Trace residues were entered in the computations at the stated "less than" value, and "not detected" values were entered as zeros.

Results and Discussion

WOODCOCK AS HUMAN FOOD

Data for U.S. woodcock (Table 2) show that residue levels are generally low; average levels of DDT plus metabolites are approximately one-half those of the mean New Brunswick sample reported by Dilworth et al. (2) in 1973.

Data are presented by States (Table 3) because concern for residues in game species is centered at the State level. However, sample sizes were small and samples were not selected randomly within States. Therefore, data are statistically representative only of the area(s) actually sampled and not of the State as a whole. Because woodcock were collected during the hunting season to determine those residue levels to which hunters might be exposed, annual variation by seasons is not measured by these data.

Action Guidelines of the United States Department of Agriculture (USDA) for chlorinated hydrocarbons in meat (lipid weight) of domestic animals intended for human consumption are: DDT and metabolites, 7 ppm; PCB's, 5 ppm; dieldrin, 0.3 ppm; heptachlor epoxide, 0.3 ppm; and mirex, 0.1 ppm (John Spaulding, Ph.D., Residue Evaluation and Planning Group, USDA, *personal communication*).

Tables 2 and 3 reveal that numerous organochlorine means are apparently in excess of the USDA official limits. Because of skewed distributions, medians are both lower than and more representative of the dosage likely to be encountered in any given specimen. Nevertheless, many median values also appear to be in excess. In actuality, breast muscle of woodcock contains only 1.9 ± 0.1 percent fat (mean and 1 standard error for the 40 comparison birds), whereas hamburger, for example, may contain 28 percent fat, or 15 times the

mean fat in woodcock. Therefore, in considering the safety of chlorinated hydrocarbon residues in woodcock (Tables 2, 3), it is appropriate to multiply guideline levels by approximately 15. There are no median values, including those for mirex which are discussed below, which exceed these adjusted guidelines.

The maximum level of mercury in fish muscle allowed by the Food and Drug Administration (FDA), United States Department of Health, Education, and Welfare, is 0.5 ppm (wet weight) (Spaulding, *personal communication*).

Among the State pools of breast muscle analyzed for mercury, the highest residue values, 0.31 ppm for Florida and 0.30 ppm for Alabama, were below the 0.5 ppm level. Mercury levels in breast muscle of woodcock apparently present no hazards to humans according to established tolerance levels.

LOUISIANA WOODCOCK

McLane et al. (5) report residues (lipid weight) of heptachlor epoxide, dieldrin, DDE, DDD, and DDT in 33 woodcock collected January 1965 in West Baton Rouge, Pointe Coupee, and Iberville Parishes of Louisiana. Analyses of 10 birds in the present sample afford a comparison for the same area 6 years later. To make this comparison, the authors' 1970-71 data were re-analyzed according to McLane et al. (5); trace readings were used at one-half the stated "less than" values. This results in data slightly different from Louisiana values in Table 3. The mean (1.87 ppm) and median (0.88 ppm) residues for heptachlor epoxide in 1965 were higher than the mean (0.04 ppm) and median ("not detected") levels found in 1971. The mean (1.65 ppm) and median (0.48 ppm) residues for dieldrin in 1965 do not differ greatly from the mean (0.80 ppm) and median (0.56 ppm) values found in 1971. DDE was present in 1965 at mean (17.90 ppm) and median (16.15 ppm) levels which exceed the mean (6.88 ppm) and median (3.32 ppm) residues of 1971. The 1965 measurements of DDD and DDT included trace amounts of PCB's; therefore, it is not possible to judge whether DDD and DDT have increased or decreased. It would seem that mean (3.65 ppm) and median (3.92 ppm) levels of PCB's in 1971 have increased over the trace amounts present in 1965.

GEOGRAPHIC DISTRIBUTION OF MIREX

Mirex was found in breast muscle of ten individually analyzed woodcock from five States. Only one of five birds from Maryland had a residue of 0.658 ppm (lipid weight), resulting in a State average of 0.132 ppm. Two of five woodcock from Alabama had residues of 2.18 ppm and 2.20 ppm; State average was 0.876 ppm. Two of five birds from Tennessee had residues of 0.783 ppm and 5.64 ppm; State average was 1.28 ppm. One of ten birds from Louisiana contained 26.7 ppm; State average was 2.67 ppm. Mississippi showed the highest

TABLE 2.—Residues of chlorinated hydrocarbons and mercury in U.S. woodcock, 1970-71

CHEMICAL ¹	BIRDS SAMPLED	BIRDS WITH NO DETECTABLE RESIDUE	BIRDS WITH TRACE RESIDUE	RESIDUE LEVEL, PPM	
				WET WEIGHT	LIPID WEIGHT
DDE	129	0	5		
Mean				0.217	11.2
Median				0.036	2.47
Range				0.004-8.67	0.196-432
DDT	129	46	56		
Mean				0.010	0.573
Median				0.005	0.364
Range				0-0.220	0-14.0
DDD	129	23	38		
Mean				0.030	1.64
Median				0.009	0.647
Range				0-0.870	0-55.7
Dieldrin	129	12	63		
Mean				0.018	1.07
Median				0.005	0.381
Range				0-0.550	0-30.7
Heptachlor epoxide	129	89	22		
Mean				0.003	0.188
Median				0	0
Range				0-0.082	0-8.67
Mirex	129	119	0		
Mean				0.010	0.762
Median				0	0
Range				0-0.440	0-33.6
PCB's	129	4	23		
Mean				0.075	4.65
Median				0.060	3.65
Range				0-0.43	0-25.7
Mercury	122	0	12		
Mean				0.197	—
Median				0.145	—
Range				0.05-1.1	—

¹ Mercury analyses are of liver; other analyses are of breast muscle.

levels, with four of ten woodcock containing 4.54 ppm, 10.5 ppm, 11.5 ppm, and 33.6 ppm. State average was 6.01 ppm.

State pools showed small amounts of mirex in birds killed in Minnesota, 0.714 ppm; Wisconsin, 0.620 ppm; and South Carolina, 0.545 ppm. The only other State pool with mirex was Mississippi, which had 17.7 ppm.

Mirex levels up to 0.192 ppm appeared in one carcass sample from each of the following States: North Carolina, Kentucky, Tennessee, Florida, Georgia, West Virginia, and Vermont. A woodcock from New York showed 0.141 ppm mirex in the carcass and 1.23 in the wing.

In summary, woodcock showed heaviest mirex residues in Mississippi and Louisiana, States where mirex has been used in attempts to control the imported fire ant (*Solenopsis saevissima*).

POOLS VERSUS AVERAGES

It is important to determine how well pooled samples reflect averages of individual birds because pooling is

often used to reduce the number and therefore the cost of analyses in surveys of residue levels. The present data allow statistical comparison of one series of residue readings, each reading based on five birds pooled prior to homogenization and analysis, with another series of values, each value derived by averaging residue reading from five birds analyzed individually. Pool values and averages of individuals are paired: one of each is available from several States. However, geographic variation within States has not been completely accounted for in the experimental design because the collecting localities are not completely the same for each pool-average pair. Results in Table 4 show a general similarity between pools and averages. However, the similarities are not consistent as shown by the lack of significant correlation coefficients for DDT and dieldrin. Although t-tests for paired data revealed no significant differences between pairs of logarithmic means for pools and averages, means of pools were larger in five of seven cases. More extensive experimentation reveals that pooling increases the levels of residues which are detected, and explanation and quantification will be required.

TABLE 3.—Geographic summary of chlorinated hydrocarbon and mercury residues in individually analyzed U.S. woodcock, 1970-71

STATE	N ²	RESIDUE LEVELS, PPM ¹														
		DDE + DDT + DDD			DIELDRIN			HEPTACHLOR EPOXIDE			PCB'S			MERCURY		
		MEAN	ME-DIAN	RANGE	MEAN	ME-DIAN	RANGE	MEAN	ME-DIAN	RANGE	MEAN	ME-DIAN	RANGE	MEAN	ME-DIAN	RANGE
Fla.	5	10.6	9.50	3.03-22.1	0.98	1.11	0.34-1.58	2.34	0.89	0-8.67	7.59	6.82	0.82-15.6	0.28	0.28	0.18-0.36
Ga.	5	6.75	4.10	2.30-16.8	0.35	0.34	0.30-0.39	0.15	0	0-0.42	6.54	6.58	5.42-7.81	0.17	0.19	0.05-0.23
Ala.	5	110	7.42	5.77-502	1.52	0.59	0.18-5.78	0.08	0	0-0.39	10.9	3.68	2.70-25.7	0.61	0.68	0.29-0.92
Miss.	10	47.2	13.1	1.41-319	0.56	0.42	0.24-1.74	0.14	0	0-0.50	4.62	3.42	0-15.6	0.17	0.16	0.08-0.27
La.	10	8.19	5.12	0.67-33.1	0.87	0.67	0.13-3.41	0.06	0	0-0.38	3.65	3.92	1.38-5.17	0.25	0.25	0.13-0.36
N.C.	5	9.01	7.15	3.23-15.8	2.48	0.70	0.52-9.62	0.24	0.27	0-0.44	3.86	3.30	2.72-5.43	0.37	0.26	0.05-0.87
S.C.	5	10.2	7.27	5.55-23.7	6.67	0.60	0.31-30.7	0.05	0	0-0.26	4.36	4.13	2.30-7.75	0.57	0.33	0.17-1.10
Tenn.	5	11.3	13.0	3.39-17.0	1.43	1.10	0.40-3.42	0.37	0.32	0.29-0.52	8.25	7.86	4.55-12.5	0.35	0.26	0.20-0.66
Ark.	5	22.0	8.81	4.21-64.5	4.61	0.67	0.42-13.5	0.22	0	0-0.79	3.03	2.58	2.07-4.13	0.17	0.19	0.06-0.26
Md.	5	3.71	3.48	2.42-5.76	0.50	0.40	0.20-1.06	0.03	0	0-0.17	5.74	5.71	3.32-8.24	0.22	0.24	0.14-0.28
N. Va.	5	1.36	1.60	0.25-2.62	0.19	0.20	0-0.30	0.05	0	0-0.24	3.41	3.13	1.78-5.67	0.08	0.07	0.05-0.14
Ky.	5	2.36	1.86	1.12-4.33	1.13	0.44	0.24-2.86	0.17	0.20	0-0.27	4.85	4.88	4.31-5.43	0.09	0.08	0.05-0.14
Mo.	4	1.95	1.97	1.37-2.50	1.86	0.34	0-6.78	0.11	0	0-0.44	3.40	2.78	1.92-6.13	0.13	0.15	0.05-0.17
R.I.	5	15.6	11.7	1.29-47.6	0.88	1.04	0-2.68	0	0	—	8.58	3.38	1.47-19.5	0.13	0.13	0.05-0.22
N.J.	10	4.14	2.82	0.64-10.2	0.33	0.27	0.20-0.60	0.03	0	0-0.28	2.20	2.12	0-4.77	0.19	0.16	0.08-0.46
Pa.	5	2.64	1.68	1.30-6.00	0.39	0.30	0.20-0.83	0.21	0	0-0.80	2.61	1.88	1.51-5.17	0.10	0.07	0.07-0.17
Maine	5	3.43	0.48	0.31-15.2	0.18	0.19	0.13-0.23	0.04	0	0-0.23	2.43	2.60	1.10-3.51	0.07	0.05	0.05-0.12
Vt.	5	1.72	0.53	0.44-5.33	0.24	0.22	0.21-0.33	0	0	—	3.64	3.47	2.91-4.63	0.08	0.08	0.05-0.12
N.H.	5	3.35	2.10	1.05-8.48	0.23	0.24	0-0.37	0.11	0	0-0.29	1.03	1.41	0-2.21	0.09	0.08	0.07-0.12
N.Y.	5	2.64	0.89	0.59-6.08	0.32	0.39	0-0.62	0	0	—	6.72	5.00	2.36-14.4	0.15	0.13	0.08-0.23
Mich.	5	1.43	1.43	0.79-1.86	0.17	0.23	0-0.31	0	0	—	2.45	2.38	1.59-3.68	0.09	0.11	0.05-0.12
Wis.	5	6.92	2.68	0.39-26.0	0.22	0.25	0-0.47	0.14	0	0-0.47	4.83	3.65	1.51-12.5	0.10	0.09	0.05-0.15
Iowa	5	1.79	1.76	0.55-3.10	0.13	0	0-0.53	0.10	0	0-0.53	5.54	3.65	1.71-12.5	0.06	0.06	0.05-0.08

Data for chlorinated hydrocarbons apply to breast muscle, lipid weight; data for mercury apply to liver, wet weight. N = number of woodcock in sample. Sample sizes for mercury are one less than the number indicated in the following States: Tenn., Fla., R.I., Vt., La., N.H., and N.J.

TABLE 4.—Comparison of pools and averages of residue data for chlorinated hydrocarbons in breast muscle, and mercury in liver, of U.S. woodcock, 1970-71

	RESIDUE LEVELS, PPM ^{1,2}						
	DDE	DDD	DDT	DIELDRIN	HEPTACHLOR EPOXIDE	PCB'S	MERCURY
Means							
Averages	0.808	0.344	0.178	0.258	0.066	0.703	0.079
Pools	0.976	0.400	0.190	0.313	0.082	0.694	0.078
Variances							
Averages	0.2255	0.0728	0.0201	0.0548	0.0129	0.0357	0.0033
Pools	0.2644	0.0902	0.0169	0.1031	0.0190	0.0630	0.0030
Correlation Coefficients ³	0.630**	0.609**	0.303	0.436	0.764***	0.579**	0.946***

Data for chlorinated hydrocarbons represent lipid weight, data for mercury represent wet weight. Residue levels in pools and arithmetic averages of individual residue levels were transformed by log₁₀ (x + 1) prior to calculation of these means, variances, and correlation coefficients. Sample size is 20 for chlorinated hydrocarbons and 15 for mercury. Significance levels: ** = 0.01 ≥ P > 0.001; *** = P ≤ 0.001.

Comparison of sample variances (Table 4) shows that in five of seven cases the pool variance is larger than the average variance. None of these differences produce a significant F value when tested. Together they suggest that pool data are less reliable. If this difference is real, it may be because each State average comes from five analyses, whereas each pool comes from a single analysis. However, the mechanism is not obvious. The authors' limited data suggest that pools and averages with a sample size of five are not equivalent and that pool values are larger and more variable.

NORTH-SOUTH VARIATION IN RESIDUES

Gross inspection of the data indicated that levels of some residues increase from north to south. To examine this relationship the authors assigned each State a value from 1 to 5 as an index of latitude: 1—Florida, Georgia, Alabama, Mississippi, Louisiana; 2—North Carolina, South Carolina, Tennessee, Arkansas; 3—Maryland, West Virginia, Kentucky, Missouri; 4—Rhode Island, New Jersey, Pennsylvania; 5—Maine, Vermont, New Hampshire, New York, Michigan, Wisconsin, Minnesota. These values were then analyzed for correlation with the 23 States' average levels of chlorinated hydrocarbons (breast muscle, lipid weight) and mercury (liver, wet weight); Table 5 shows results. Number of individual birds for each State ranged from 4 to 10 with an average of 5.6 for chlorinated hydrocarbons and 5.3 for mercury.

Table 5 confirms that residues in general are negatively correlated with latitude. Furthermore, except for PCB's, the size of the correlation coefficients is positively correlated with mean residue level (Table 2, wet weight values); hence low levels are probably responsible for the smaller coefficients of DDD through heptachlor epoxide (there were 4 States where no individual muscle samples contained heptachlor epoxide and 18 where none contained detectable mirex). However, this explanation does not account for the low PCB coefficient. Whereas the insecticides presumably increase toward the South

due to greater agricultural usage, PCB's originate from various sources (6,7) not necessarily related to latitude, and this may explain the weaker relationship. The strong correlation of mercury with latitude (Table 5) presumably reflects greater ambient mercury in woodcock habitats with decreasing latitude. How the natural and personmade sources of mercury combine to produce such a distribution is not known.

CORRELATIONS OF RESIDUES WITH ONE ANOTHER

Among the eight chemical residues, levels of PCB's are most often significantly correlated with levels of other chemicals; this is true in six of seven cases (Table 6). DDT and its metabolites are closely associated with one another and with dieldrin and PCB's. The absence of heptachlor epoxide and mirex from many samples (Table 2) probably accounts for their lack of correlation with other residues. Mercury, in spite of its relative abundance (Table 2), is significantly associated with only three other materials. However, because mercury is assimilated and stored differently than the chlorinated hydrocarbons, a lesser degree of association is expected.

WING RESIDUES AS INDICATORS

Wings of woodcock obtained annually from hunters to evaluate the species' population levels and reproductive success (8) are now also being used to survey geographic trends in residues of chlorinated hydrocarbons (9). Dilworth et al. (4) have shown a highly significant correlation between DDT and metabolites in wing and breast muscle. Our data (Table 7) allow quantification of both wing-to-breast-muscle and wing-to-carcass relationships. Calculation of the mean difference and its 95-percent confidence interval makes it possible to predict accurately residue levels in breast muscle or carcass from amounts found in wings for this group of 40 woodcock. Of course, how these relationships might be altered by variations in overall residue levels is not known.

Wing, muscle, and carcass samples contain different percentages of fat. For our sample these values (mean \pm 1 standard error) are: wing, 14.4 ± 0.3 percent; muscle, 1.9 ± 0.1 percent; and carcass, 9.3 ± 0.1 percent. To compensate for this variable, calculations were made on lipid weight data. Nevertheless, results in Table 7 show significant differences among the three tissues for DDD, DDT, and PCB's. Therefore, quantification is needed beyond the determination of a significant correlation coefficient if wing residues are to be used to predict residue levels in other tissues.

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TABLE 5.—Correlations between average residue levels in U.S. woodcock and latitude index for 23 States of collection, 1970-71¹

CHEMICAL	CORRELATION COEFFICIENT ²
Heptachlor epoxide	-0.408
PCB's	-0.431*
Mirex	-0.528*
DDT	-0.530*
Dieldrin	-0.543**
DDD	-0.550**
Mercury	-0.659***
DDE	-0.670***

¹ Ppm values transformed by $\log_{10}(x + 1)$.

² Significance levels: * — $0.05 \geq P > 0.01$; ** = $0.01 \geq P > 0.001$; *** = $P \leq 0.001$.

TABLE 6.—Correlation matrix for residue levels of 8 chemicals in 122 individual U.S. woodcock, 1970-71

CHEMICAL	RESIDUE LEVELS, PPM ^{1,2}							
	MERCURY	DDE	DDD	DDT	PCB'S	MIREX	HEPTACHLOR EPOXIDE	DIELDRIN
Mercury	1	0.324***	0.202*	0.116	0.250*	0.082	0.063	0.114
DDE		1	0.803***	0.644***	0.436***	0.106	0.176	0.434***
DDD			1	0.749***	0.361***	0.043	0.096	0.486***
DDT				1	0.455***	0.046	0.064	0.356***
PCB's					1	-0.127	0.209*	0.208*
Mirex						1	-0.080	0.0003
Heptachlor epoxide							1	0.180
Dieldrin								1

Residue levels of chlorinated hydrocarbons (breast muscle) and mercury (liver) were transformed by $\log_{10}(x + 1)$ prior to computations. Data for chlorinated hydrocarbons represent lipid weight; data for mercury represent wet weight.

Significance levels: * = $0.05 \geq P > 0.01$; *** = $P \leq 0.001$.

TABLE 7.—Levels of residues in U.S. woodcock wings as indicators of levels in breast muscle and in carcass, 1970-71

CHEMICAL	RESIDUE LEVELS, PPM ^{1,2}			
	MEAN	t (PAIRED DATA)	MEAN DIFFERENCE $\pm 95\%$ CONFIDENCE INTERVAL	CORRELATION COEFFICIENT
DDE				
Muscle	0.584			
Wing	0.615	1.57	0.031 \pm 0.040	0.955***
Carcass	0.640	1.10	0.025 \pm 0.046	0.949***
DDD				
Muscle	0.210			
Wing	0.115	4.75***	0.095 \pm 0.040	0.779***
Carcass	0.172	3.28**	0.056 \pm 0.034	0.862***
DDT				
Muscle	0.114			
Wing	0.275	5.44***	0.161 \pm 0.060	0.492***
Carcass	0.183	4.92***	0.092 \pm 0.038	0.839***
PCB's				
Muscle	0.708			
Wing	0.593	4.24***	0.115 \pm 0.055	0.737***
Carcass	0.538	1.80	0.054 \pm 0.061	0.730***
Dieldrin				
Muscle	0.192			
Wing	0.199	0.342	0.007 \pm 0.042	0.937***
Carcass	0.134	1.56	0.064 \pm 0.083	0.581***
Heptachlor epoxide				
Muscle	0.075			
Wing	0.055	0.961	0.020 \pm 0.042	0.626***
Carcass	0.059	0.693	0.004 \pm 0.013	0.932***

Residue levels in ppm lipid weight were transformed by $\log_{10}(x + 1)$ prior to computations. Sample size is 40.

Significance levels: ** = $0.01 \geq P > 0.001$; *** = $P \leq 0.001$.

LITERATURE CITED

- (1) Pearce, P. A., and J. C. Baird. 1970. DDT closes New Brunswick woodcock season. *Canadian Field-Naturalist* 85(1):82.
- (2) Dilworth, T. G., P. A. Pearce, and J. V. Dobell. 1973. DDT in New Brunswick woodcock. In manuscript.
- (3) Armour, J. A., and J. A. Burke. 1970. Method for separating polychlorinated biphenyls from DDT and its analogs. *J. Ass. Offic. Anal. Chem.* 53(4):761-768.
- (4) Monk, H. E. (chairperson), J. A. Pickard, N. A. Smart, S. H. Yuen, E. W. Atkins, A. J. Beidas, T. E. Burke, H. Crossley, H. Egan, P. W. Lloyd, and E. J. Miller. 1961. Recommended methods of analysis of pesticide residues in foodstuffs. Report by the Joint Mercury Residues Panel. *Analyst* 86:608-614.
- (5) McLane, M. A. R., L. F. Stickel, and J. D. Newsom. 1971. Organochlorine pesticide residues in woodcock, soils, and earthworms in Louisiana, 1965. *Pestic. Monit. J.* 5(3):248-250.
- (6) Dustman, E. H., L. F. Stickel, L. J. Blus, W. J. Reichel, and S. N. Wiemeyer. 1971. The occurrence and significance of polychlorinated biphenyls in the environment. *Trans. 36th N. Amer. Wildlife Natur. Resources Conf.*, pp. 118-133.
- (7) Risebrough, R., with V. Brodine. 1970. More letters in the wind. *Environment* 12(1):16-27.
- (8) Clark, E. R. 1971. The status of American woodcock—1971. U.S. Bureau of Sport Fish. and Wildl., Migr. Bird Popul. Station Admin. Rep., pp. 1-18.
- (9) McLane, M. A. R., L. F. Stickel, E. R. Clark, and D. L. Hughes. 1973. Organochlorine residues in woodcock wings, 11 states—1970-71. *Pestic. Monit. J.* 7(2):100-103.

*Studies on the Distribution and Flux of Pesticides in Waterways Associated with a Ricefield—Marshland Ecosystem*¹

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ABSTRACT

In coastal prairie and marshland in Chambers County, Tex., authors studied the distribution and flux of chlorinated hydrocarbon pesticides in waterways associated with a ricefield—marshland ecosystem. Aldrin applied with seed rice entered the aquatic ecosystem through drainage of flooded ricefields. Chemical alteration of the pesticide was observed; dieldrin was the primary breakdown product. All insecticides were distributed unevenly, exhibiting a predilection for biotic components of the ecosystem. Residue analyses of representative species of the aquatic biota indicated significant biological accumulation and passage of these refractory compounds along the food chain. Rapid localization and concentration of pesticides in living organisms was observed. Reproductive tissues exhibited a marked affinity for the pesticides. Decline of assimilated residues in both biotic and abiotic components appeared to follow a first-order reaction curve. Contamination of the aquatic environment with toxaphene during the study period resulted in a massive kill of aquatic organisms. Neither long-term effects nor significant biological magnification of toxaphene was observed. Other chlorinated hydrocarbon pesticides of unknown origin were detected, including DDE, DDD, and DDT.

Introduction

The toxicity of chlorinated hydrocarbon pesticides to aquatic organisms has been documented by many investigators (1-8). Effects of the pesticidal chemicals range from acute intoxication resulting in death of the organism to more subtle sublethal effects. Though only

slightly soluble in water, chlorinated hydrocarbon pesticides enter the aquatic environment dissolved in minute amounts or in greater amounts adsorbed to suspended sediment particles (9). Rudd (10) asserted that water is the primary means of residue transport from a treated area to an untreated one. The presence in surface waters of such persistent, broadly toxic compounds results in exposure of the entire aquatic biota to the residues. Furthermore, in the laboratory, fish and other aquatic organisms have shown a marked ability to accumulate pesticides from the milieu. This has been attributed primarily to two factors: direct absorption of insecticides from water, and assimilation and concentration of residues from food substances. Butler (11) noted the phenomenon of direct absorption of residues by oysters. Chadwick and Brocksen (12) reported that accumulation of pesticides by fish was dependent on the concentration of pesticides in water. However, Murphy (13) asserted that the method of uptake was dependent on the size of the organism. In addition, accumulation of pesticides by organisms in natural aquatic ecosystems has been documented (14-16). This phenomenon of accumulation of pesticides by living organisms appears to be universal (17) and is primarily attributable to the chemical properties of these globally dispersed refractory compounds.

The effects of accumulating pesticides are for the most part unknown. Sublethal amounts of these compounds in water have been shown to retard growth (3), decrease reproductive success (18), and alter behavior (19) in aquatic organisms. Most investigations have confined themselves, however, to laboratory studies on isolated

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components of an aquatic ecosystem or isolated characteristics of an insecticide. At present, few data exist on the distribution, localization, and impact of various pesticides in natural aquatic ecosystems. Studies of residues in a few complete ecosystems have been undertaken (16,20).

The marshland—estuarine environment is one for which virtually no data exist on the dynamics or short-term effects of chlorinated hydrocarbon pesticides. As the habitat for a great and diverse group of aquatic species, the estuarine environment is a vitally important biological system. The authors' purpose was to investigate the dynamics and distribution of certain chlorinated hydrocarbon pesticides in a marshland—estuarine ecosystem. The primary pesticide in the investigation was aldrin applied in cultivation of rice and introduced into the aquatic ecosystem by drainage of flooded ricefields. In addition, 11 other chlorinated hydrocarbon pesticides were monitored in the organisms of this aquatic community.

Study Area

The study area was composed of approximately 8,000 hectares of coastal prairie and marshland in Chambers County, Tex., adjacent to East Galveston Bay (Fig. 1). The marshlands were used primarily for cattle grazing and the lower prairie was used for rice cultivation. Runoff from the marsh and rice-growing areas passed through a series of personmade drainage canals and natural bayous into East Bay. Salinity of drainage waters varied from 0.5 to 19 parts per thousand (ppt) during the study. Aquatic organisms inhabiting the waters were typically euryhaline—estuarine species. The marshland primarily discussed in this paper was a 300-hectare section of the above area which had been drained; it was cultivated with rice between March and August 1971. Portions of the lowlands not involved in rice cultivation were designated as control areas.

Materials and Methods

Aquatic organisms were trapped or netted in the main drainage points of treated ricefields and stored at 4°C or quick-frozen (-20°C) until time of extraction and analysis. Small organisms (*Palaeomonetes*, *Brevoortia*, etc.) were collected to give a sample size of 30 to 60g. The lower value represented the smallest sample in this study. Routinely, dip nets and seines were used for benthic forms. Cast and gill nets were used for fish and commercial crab traps were used effectively for crabs and some fish. Preparation for extraction was a modification of the method described by A. Wilson of the U.S. Environmental Protection Agency, Gulf Breeze Environmental Research Laboratory, Gulf Breeze, Fla. (*personal communication*). Samples were weighed and

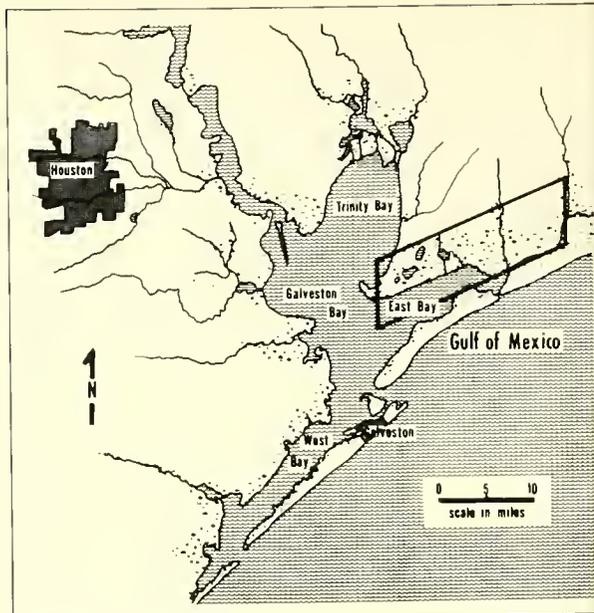


FIGURE 1.—Location of ricefield—marshland study area on Texas coast

placed in mason jars to which anhydrous Na_2SO_4 was added in an exact multiple of the sample weight (usually 3×). The mason jar was capped with a cutting assembly (Osterizer Corp.) and the sample was ground until a homogenous mixture was obtained. The ground sample was frozen (-20°C) for 15 to 20 minutes and reground until a free-flowing powder mixture was obtained. Repeated freezing and regrinding was often necessary to achieve such a powder. The tissue— Na_2SO_4 homogenate was either extracted immediately or wrapped in aluminum foil and stored in a freezer (-20°C). Analysis was of whole-body residues except when an organism was too large. In such cases representative tissues were analyzed, as indicated in the text and tables.

Pesticide residues were extracted in Soxhlet extractor with petroleum ether as described by A. Wilson (*personal communication*). A weighed quantity of tissue-desiccant homogenate equivalent to approximately 30 g tissue was extracted for 4 hours with 250 ml petroleum ether (Nanograde, Mollinkrodt) at a temperature high enough to produce cycling of the solvent every 5-10 minutes (approximately 90°C). Following extraction, the petroleum ether was reduced to approximately 15 ml over steam using a three-ball Snyder column and was quantitatively transferred to a separatory funnel for partitioning over acetonitrile. The petroleum ether fraction was adjusted to 25 ml and partitioned twice over 50 ml acetonitrile. Each time the mixture was manually agitated for 1 minute and allowed to separate. The acetonitrile was collected in a crystallizing dish and evaporated just to dryness on a slide warmer (40°C).

Prolonged drying or excess heating was avoided to prevent loss of pesticides due to volatilization.

The residue was resuspended in petroleum ether and subjected to column chromatography on florisil (Floridin Co., Berkeley Springs, W. Va.). A two-fraction preparative chromatographic separation involved transfer of the residue to 10 g of florisil in a 400-by-20-mm glass chromatography column. Elution was effected with 150 ml of a 6-percent solution of anhydrous ethyl ether in petroleum ether followed by elution with 150 ml of a 15-percent solution of ethyl ether in petroleum ether. The florisil required heating at 120°-135°C for at least 5 hours before use. This procedure separated dieldrin and endrin from other chlorinated pesticide residues (21). The 6-percent eluate was reduced to suitable volume over steam and subjected to gas-liquid chromatography (GLC). The 15-percent eluate required further preparation. The fraction, reduced to approximately 20 ml over steam, was quantitatively transferred to a 400-by-20-mm glass chromatography tube containing 10 g of a 1:1 by weight mixture on magnesium oxide and Celite 545 (Johns Manville Co.). Elution was effected with 100 ml petroleum ether over vacuum sufficient to produce an elution rate of approximately 35 ml/min. The eluate was reduced to suitable volume, quantitatively transferred to a graduate cylinder, and adjusted to a known volume with petroleum ether prior to analysis by GLC.

Pesticide residues were recovered from core samples (2.5 by 15 cm) of soil by triple extraction with acetonitrile. Extraction was performed with wet soils to maximize recovery (22). A portion of each sample was retained and dried to constant weight at 130°C for determination of weight. Samples weighing 250-300 g were placed in mason jars with 100 ml acetonitrile and mixed for 2 minutes in a high-speed blender. After the soil had settled the acetonitrile was decanted into an evaporating dish through a funnel containing anhydrous Na₂SO₄ to absorb water. Extraction was repeated a second and a third time using 100 ml acetonitrile and blending for 2 minutes. Following decantation of the third extract, the soil was poured into the funnel, rinsed with acetonitrile, and discarded. The acetonitrile was evaporated to dryness on a slide warmer. The residue was resuspended in petroleum ether and subjected to a two-fraction purification on florisil. In this case, both the 6-percent and 15-percent fractions were subjected to GLC without further purification.

Dip samples of water were collected in 1-gal. brown glass bottles and refrigerated until time of extraction. All analyses were completed within 30 hours after collection. Samples of 1,500 ml were extracted in a separatory funnel by shaking for 5 minutes with 100-150 ml petroleum ether. The water and petroleum ether were allowed to separate and the petroleum ether was collected in an Erlenmeyer flask. Extraction was

repeated a second and a third time. The aqueous phase was discarded and the petroleum ether phase was dehydrated with anhydrous Na₂SO₄. The extract was reduced to a known volume over steam. No further purification of this extract was necessary prior to analysis by GLC. This methodology gave 100-percent recovery of dieldrin from spiked samples. Salinity estimates were accomplished with standard hydrometers measuring density ranges from 1.000 to 1.030, or by chloride measurement using ampimetric titration with a chloridometer.

Residue analysis was by GLC with a Varian Aerograph Model 2100 dual-channel chromatograph equipped with tritium electron-capture detectors. Detection by electron capture allowed quantitation of organochlorine insecticides at amounts ranging from 10⁻¹¹ g for lindane to 10⁻¹⁰ g for *p,p'*-DDT. Readout was on a Varian Aerograph Model 20 dual-pen recorder. On-column injection into an all-glass system was incorporated to prevent decomposition of certain organohalogen insecticides (23). Columns were 6-foot capillary U-tubes with 2-mm internal diameter. Packing material consisted of 80/100 mesh Gas Chrom Q (Applied Science Laboratories, State College, Pa.) solid phase with silicone oil liquid phases including 3 percent DC-200, 5 percent QF-1, a 2:1 mixture of 5 percent QF-1 and 5 percent DC-200, and a 3:1 mixture of 3 percent DC-200 and 10 percent OV-17.

Nitrogen was used as carrier gas at 65 psi and rate (soap film flowmeter) of 40 ml/min. During operation the column temperature was maintained at 190°C. The injector was maintained at 215°C. Sufficient sensitivity was achieved by operating the tritium detectors at 215°C. The detectors operated on a 90-volt direct-current mode. Though linear range of electron-capture detectors is limited (24), linearity was obtainable in the range of pesticide concentrations assayed (10⁻¹¹ to 10⁻⁹ g).

Quantitation of data was based on comparison of printout of sample extract peak height with the peak heights of standard solutions of pesticides. Standards were injected following every third sample extract. Standard solutions were made using analytical grade chlorinated hydrocarbon pesticides obtained from the Pesticide Repository, Perrine, Fla. (See Appendix for common and systematic names of pesticides used in analysis.) Analysis was confirmed by using two liquid phases of different polarity such as DC-200 and QF-1. Another method employed binary solvent systems as described by Bowman and Beroza (25); this relies on solubility ratios of pesticides in immiscible solvents.

Results

Chlorinated hydrocarbon pesticides entered the aquatic ecosystem in the form of aldrin applied as a dressing on

seed rice (0.28 kg aldrin/hectare (ha.)). The cultivation process involved flooding ricefields to which aldrin-treated seed rice had been applied aerially, followed in 24-48 hours by discharging flood waters into drainage canals. Residue analyses of drainage canal water samples and ricefield soil samples taken before and after pesticide application are presented in Tables 1 and 2, respectively.

Aldrin had been applied to the field; yet dieldrin, rather than aldrin, was the primary residue detected. This was not unexpected since dieldrin, a persistent chlorinated hydrocarbon pesticide in its own right, is the epoxidation product of aldrin. The epoxidation process was doubtlessly hastened by environmental conditions of the ricefields, including elevated temperatures, high moisture levels, pH, Eh, and soil structure (26,27).

Concentrations of aldrin and dieldrin in water were extremely small. This is impressive, considering that these residues were the primary source of aldrin and

TABLE 1.—Pesticide residues detected in water from ricefield drainage canals before and after pesticide application

TIME, WK ¹	RESIDUE, PPB (μG/L) ²	
	ALDRIN	DIELDRIN
-2	ND	ND
-1	ND	ND
0.5	0.270	0.440
4	ND	0.172
8	ND	0.062
12	ND	0.040
13	ND	0.023
14	ND	0.034
15	ND	0.031

¹ Represents no. of weeks before (-) or after planting of aldrin-treated seed rice.
² ND = none detected (<μg/liter).

TABLE 2.—Pesticide residues detected in ricefield soil before and after pesticide application

TIME, WK ¹	RESIDUE, PPB (μG/KG) ^{2,3}	
	ALDRIN	DIELDRIN
-4	ND	ND
-1	ND	ND
2	—	2.8
4	10.9	10.1
5	8.3	5.1
8	ND	2.4
12	ND	2.7
15	ND	2.2

¹ Represents no. of weeks before (-) or after planting of aldrin-treated seed rice.
² Samples analyzed: composite core 2.5 by 15 cm, dry weight
³ ND = none detected (<μg/kg).

dieldrin in most other components of the ecosystem. Based on field size (129.6 ha.) and application rate (0.28 kg/ha.), it was estimated that the total aldrin input into the field was 36.6 kg. Flood waters were 0.15 m deep, totaling 19.4×10^7 liters of water on the field. If aldrin were stable and completely soluble in water, a concentration of 186 parts per billion (ppb) would have been observed. Instability and insolubility of the chemical resulted in levels of 0.49 ppb aldrin and 0.58 ppb dieldrin in samples of unfiltered flood waters. Thus approximately 95 g aldrin and 113 g dieldrin were carried from the field when it was drained. It was this small amount that accounted for the residues appearing in biotic components of the aquatic ecosystem represented by the drainage canal.

Following contamination, the decline of pesticide levels in water exhibited a pattern similar to that observed in many of the biotic and abiotic components of the ecosystem. As illustrated in Figure 2, the rate of dieldrin decline in water was proportional to the concentration of the pesticide present: i.e., a first-order reaction. Aldrin declined more rapidly, as stated earlier: after the fourth week following application, the insecticide was no longer detectable in water. The brief persistence of aldrin was no doubt the result of epoxidation of that compound to dieldrin. This characteristic of aldrin in water was important in evaluating and understanding pesticide assimilation by aquatic organisms.

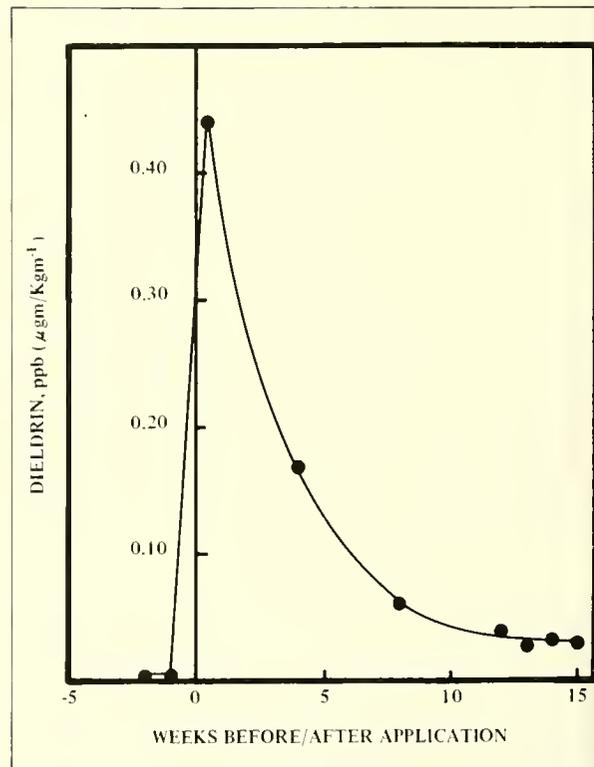


FIGURE 2.—Dieldrin residues in ricefield drainage water before and after planting of aldrin-treated rice

Though 11 additional chlorinated hydrocarbon pesticides were monitored (chlordane, *p,p'*-DDD, *p,p'*-DDE, *p,p'*-DDT, endrin heptachlor, heptachlor epoxide, lindane, methoxychlor, mirex, toxaphene), only toxaphene was detectable in water samples during the study period. Because of the chemical properties of toxaphene, it was not possible to quantitate the data obtained. Toxaphene residues and their effects on aquatic biota are mentioned later in this section. In the control marshland drainage system, water samples were taken regularly during the study period. No chlorinated hydrocarbon pesticide residues were detected.

Both aldrin and dieldrin were accumulated in soil (Table 2). The rapid decline in aldrin concentration was probably caused by loss through volatilization and decomposition; the rapid increase in dieldrin during the first 4 weeks presumably was caused by significant epoxidation of aldrin to dieldrin. The rate of loss of dieldrin from soil following the fourth week appeared to be proportional to the amount of residue in the soil. This would conform to Kearney et al. (28), who reported that loss of pesticides from soils followed a first-order reaction. The possibility of pesticide translocation by transported particulates has been suggested by Keith (9). Though the data are incomplete, pesticide analysis of bottom sediments from the ricefield drainage canal indicated localization of dieldrin of the same order of magnitude as that in ricefield soil (Table 3).

TABLE 3.—Pesticide residues detected in drainage canal bottom sediments before and after pesticide application

TIME, WK ¹	RESIDUE, PPB ($\mu\text{G/L}$) ^{2,3}	
	ALDRIN	DIELDRIN
-4	ND	ND
-2	ND	ND
2	ND	5.4
8	ND	2.4
15	ND	ND

¹Represents no. of weeks before (—) or after planting of aldrin-treated seed rice.

²Samples analyzed: composite core 2.5 by 15 cm, dry weight.

³ND = none detected ($< \mu\text{g/kg}$).

Within the aquatic ecosystem represented by the ricefield—marshland drainage canals, certain representative species were chosen as monitor organisms. These species were collected and analyzed regularly throughout the study. In addition to information gathered for specific monitored organisms, pesticide data were obtained for numerous other organisms representing all levels of the food web. These organisms represented species which could not be collected regularly in the study or control areas or those which were sporadically present in the areas due to habit, life cycle, or migratory behavior.

PALEMONETES VARIANS

Representative of plankton and nekton feeders was the

grass shrimp (*Palaemonetes varians*). Chosen because of its presence in waterways of all study areas, this organism exhibited euryhaline characteristics necessary to withstand salinity changes that were likely to occur in the waterways during the study period. Before rice was planted, residue baseline in *P. varians* consisted of dieldrin in varying amounts below 20 ppb. No aldrin was detected. Within a week after water had drained from treated fields into the waterways, the dieldrin residue in the shrimp increased to 25-50 times that of baseline. A steady but much slower decline in dieldrin residues followed, as illustrated in Figure 3.

Aldrin was detected in *Palaemonetes* the first day of field draining and for approximately 4 weeks following. The rapid assimilation of pesticide suggested a direct absorption of residue from water. On the first day of exposure, aldrin levels were 9.4 ppb, about 40 times that of the surrounding water. Dieldrin levels were approximately the same as aldrin levels. Ten days after field drain, aldrin levels had increased to 21.7 ppb; dieldrin had increased to over 500 ppb. After 4 weeks only dieldrin was detected. At its highest level, dieldrin was accumulated to a concentration over 1,000 times the maximum concentration detected in water.

The large increase in dieldrin accompanied by only slight increase of aldrin in *P. varians* during the first week could be attributed primarily to two factors. First, aldrin concentration in the water decreased much more rapidly than did the dieldrin concentration. This difference would be mirrored in residue levels present in an organism which absorbed residues directly. Second, aldrin was probably rapidly metabolized to dieldrin by

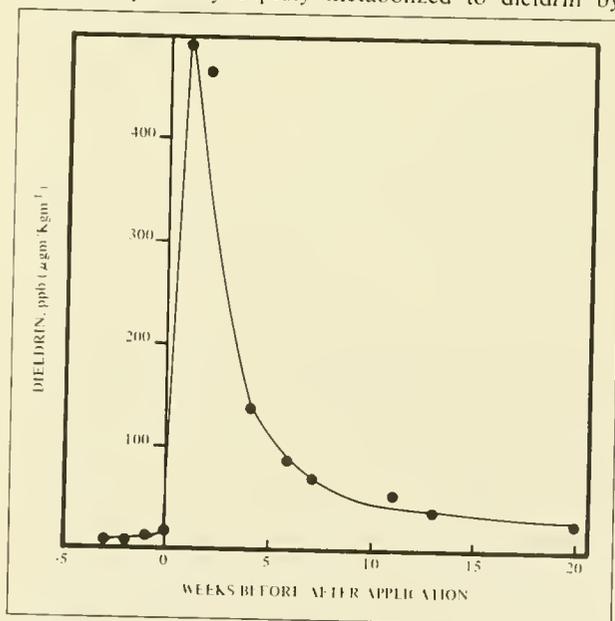


FIGURE 3.—Dieldrin residues detected in grass shrimp (*Palaemonetes varians*) before and after planting of aldrin-treated rice

P. varians following ingestion or absorption. Metabolic epoxidation of aldrin to dieldrin appears to be the major pathway of aldrin metabolism in living organisms (29).

CALLINECTES SAPIDUS

The blue crab (*Callinectes sapidus*) was chosen as a monitor organism representing a carnivorous scavenger. Dieldrin was detected in *Callinectes* collected in the aldrin-contaminated drainage system (Fig. 4). As with *Palaemonetes*, *Callinectes* showed dieldrin to be the primary pesticide assimilated. Levels approximately 2,000 times the water concentration were observed in this animal. Maximum concentration of 900 ppb was reached during the first week after drainage of the field. This was followed by a first-order decline over the next 20 weeks. In *C. sapidus*, aldrin was detected only during the week of field drain at a level slightly greater than 18.0 ppb.

LEPISOSTEUS OCULATUS

The spotted gar (*Lepisosteus oculatus*) represented a top carnivore of the aquatic ecosystem. Such a position within the food web should allow for biological concentration of pesticides present in the organisms of the ecosystem. The presence of aldrin, dieldrin, DDT, and its primary breakdown products was, therefore, not surprising (Table 4). Though often detected in small amounts in other environmental components, DDT, DDE, and DDD reached their highest concentration in *L. oculatus*.

It is noteworthy that aldrin was present in *Lepisosteus* much longer than in other aquatic organisms. Though usually not evident after the second to the fourth week in most food organisms of the gar, aldrin was detected for 7 weeks in *L. oculatus*. A likely explanation of this phenomenon is that, though undetectable in the food organisms, aldrin was actually present in minute quantities. The pesticide became detectable when biologically concentrated by *L. oculatus*.

Another significant discovery was the slower rate of insecticide accumulation in *Lepisosteus* after aldrin drained into the waterways. The concentration of dieldrin increased slowly over a 4- or 5-week period and then declined slowly over the next 10 weeks (Fig. 5). The slow decline in dieldrin concentration was similar to that observed in all organisms which incorporated residues: it followed a first-order reaction curve. The lag in accumulation was produced by the food chain effect. As Murphy (13) pointed out, a large fish primarily accumulates residues by consumption of certain food rather than by absorption from water. *L. oculatus*, therefore, probably incorporated aldrin and dieldrin through assimilation of the pesticides in its food supply. This required a multistep process which included release of pesticides into water, incorporation of residues by organisms of lower trophic levels, and ingestion of food organisms by *Lepisosteus*. The rise in pesticide levels in

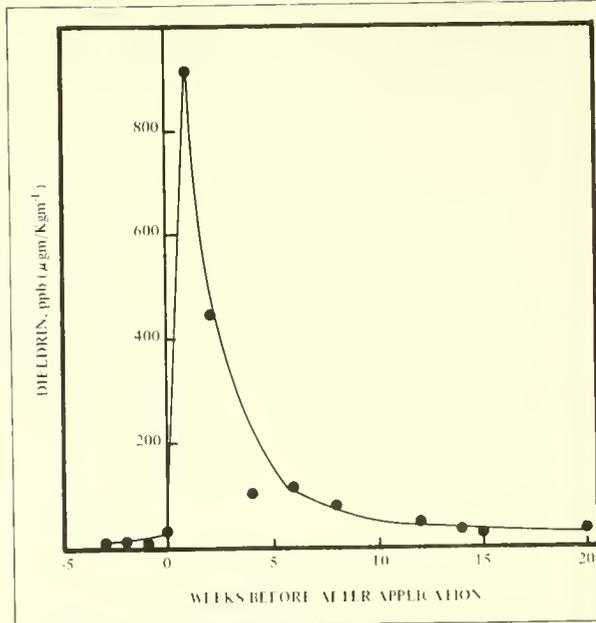


FIGURE 4.—Dieldrin residues in blue crab (*Callinectes sapidus*) before and after planting of aldrin-treated rice

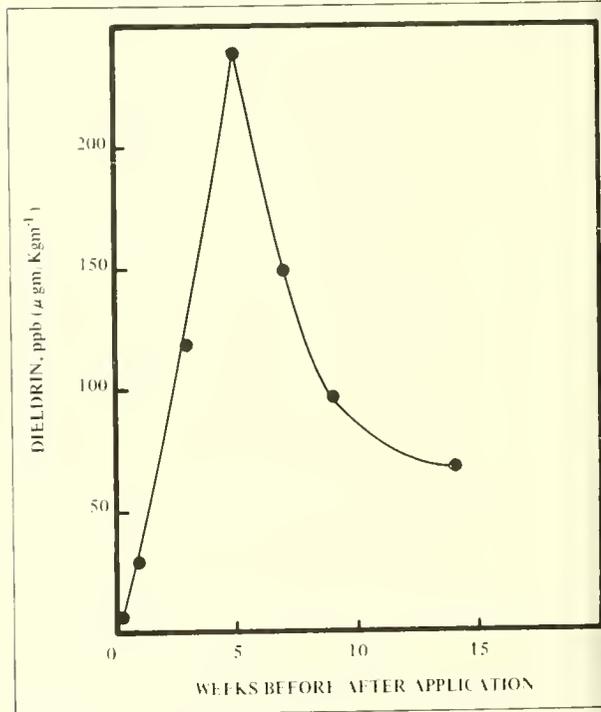


FIGURE 5.—Dieldrin residues in spotted gar (*Lepisosteus oculatus*) before and after planting of aldrin-treated rice

L. oculatus must by its nature lag behind the rise in residue levels in the lower trophic levels; therefore, such time shifts would be expected.

LEPOMIS MACROCHIRUS

Numerous other fish were present in the study area but were collected only on a sporadic basis. Two species

Lepomis macrochirus (bluegill) and *Brevoortia* sp. (menhaden), were collected with some regularity. Residue data for these and the other fish collected irregularly are listed in Table 5. Residues in *L. macrochirus* showed characteristics commensurate with its position in the food chain; i.e., between the lower trophic level of *Palaemonetes* and the higher level of *Lepisosteus*. Like *Palaemonetes*, *L. macrochirus* revealed aldrin residues only while the chemical was present in the surrounding water. Dieldrin residue levels in *L. macrochirus*, however, more closely resembled those of *Lepisosteus*, reaching a peak after 4 weeks and slowly declining thereafter. DDT and metabolites were present in several *L. macrochirus*, but at levels much lower than in *Lepisosteus*.

TABLE 4.—Chlorinated hydrocarbon pesticides detected in potted gar (*Lepisosteus oculatus*) after pesticide application

TIME, WK ¹	RESIDUE, PPB (μG , KG) ² :				
	ALDRIN	DIELDRIN	DDE	DDT	DDD
0	7.4	4.9	368.0	21.7	57.6
0	28.4	11.9	524.0	172.0	198.0
0	14.7	9.6	113.0	68.0	82.1
1	5.7	31.4	88.0	trace	29.0
3	3.9	96.8	58.0	14.2	19.3
3	7.1	153.0	107.0	34.7	79.7
5	16.3	275.0	145.0	42.2	101.0
5	12.1	198.0	82.7	5.9	14.3
7	2.6	110.0	59.0	ND	6.4
7	15.1	209.0	181.0	22.2	65.1
9	ND	98.0	191.0	ND	ND
14	ND	69.5	87.5	—	—

¹Represents no. of weeks after planting of aldrin-treated seed rice. 0 = week of planting.
²Samples analyzed: 1:1 mixture of liver and muscle, wet weight.
 ND = none detected ($< \mu\text{g}/\text{kg}$).

BREVOORTIA

Highest recorded levels of aldrin and dieldrin in aquatic organisms were in *Brevoortia* sp. Assimilation of pesticide was rapid: extremely high levels were reached during the first day of exposure. This is understandable in view of the findings of Murphy (13) concerning uptake of residues by fish. In contrast to large fish, small fish assimilate residues primarily by absorption from water rather than by consumption of any foods. *Brevoortia* collected were in the 10-40-mm range and probably absorbed the pesticide directly from the water. As a result, pesticides were assimilated with exceptional efficiency and little time lag.

DIVERSE FISH

Pesticide data from the diverse fish listed in Table 5 are significant from the standpoint of survey. Dieldrin residues were observed in all fish collected after aldrin had been introduced into the habitat, and the residues

persisted for a substantial length of time. These fish represent food sources of many organisms of higher trophic levels.

As mentioned previously, residues of toxaphene were detected in waters of the study area. This was the result of contamination of the drainage canals during aerial application of an unknown concentration of toxaphene to a ricefield in the study area as treatment for grasshopper infestation. The application of toxaphene was discovered following residue analysis of fish carcasses sampled from a massive fish kill which followed the spraying. The extreme sensitivity of fish to toxaphene (5) and the unusually high solubility of toxaphene in water (3 ppm) were factors which indicated acute toxaphene poisoning as the source of the fish kill. The number of fish killed was estimated in the tens of thousands and included catfish, menhaden, bluegill, carp, mullet, and numerous species of minnows and fry. The population of grass shrimp was so reduced after the toxaphene application that no further sampling of the organism was possible for the following 6 weeks.

Because of the nature of toxaphene, residue levels could not be quantitated. Only minute quantities of toxaphene were detected in the water following the fish kill. Furthermore, the limited persistence of toxaphene prevented accumulation of residues in most organisms of the ecosystem. Residues were detected in several aquatic feeding birds (Louisiana heron: *Hydranassa tricolor*; lesser yellow legs: *Totanus flavipes*; and black skimmer: *Rynchops nigra*), in two species of live fish (gar, and flounder: *Platichthys flesus*), and in certain aquatic insects (dytiscids). Blue crabs sampled contained no detectable residues, nor were toxaphene residues detected in any other terrestrial organisms of the area.

The significance of the input of toxaphene into the ecosystem was difficult to evaluate. Reduction of organisms was temporary and repopulation occurred within days or weeks. No long-term changes in species composition and diversity were noted. The lack of persistence of the pesticide prevented significant biological accumulation of the residue.

RESIDUES AND REPRODUCTION

The increased metabolic activity accompanying reproduction and the high lipid content of eggs would favor accumulation or deposition of pesticides in both reproductive organs and eggs. The deposition of pesticides in reproductive materials could have an important effect on the reproductive success of an organism and ultimately could affect the natural history of the species.

Levels of pesticides were determined for body tissues and eggs of two *Lepisosteus oculatus* collected in the study area and are reported in Table 6. In the case of nearly every residue present, a tenfold increase in con-

TABLE 5.—Pesticide residues present in bluegill (*Lepomis macrochirus*), menhaden (*Brevoortia sp.*), and other species of fish before and after pesticide application

TIME, WK ¹	ORGANISM	RESIDUE, PPB (μG/KG) ^{2,3}				
		ALDRIN	DIELDRIN	DDE	DDT	DDD
-20	<i>L. Macrochirus</i>	ND	7.7	ND	ND	ND
-10	"	ND	34.0	12.0	ND	ND
0	"	24.5	92.0	39.8	13.3	17.4
0	"	28.6	45.0	21.6	ND	7.5
4	"	ND	410.0	30.8	ND	ND
10	"	ND	64.6	—	—	—
15	"	ND	7.3	ND	ND	ND
-20	<i>Brevoortia sp.</i>	ND	4.7	5.7	ND	ND
0	"	550.0	1380.0	25.2	ND	ND
0	"	830.0	2200.0	29.5	ND	ND
8	"	ND	81.4	ND	ND	ND
8	"	6.1	160.0	16.9	ND	ND
10	"	ND	80.0	13.8	ND	ND
11	"	ND	32.5	—	—	—
-2	<i>Micropogon undulatus</i> (croaker)	ND	2.9	33.6	ND	ND
8	<i>Syngnathus sp.</i> (pipefish)	46.8	555.0	48.6	ND	ND
12	<i>Mugil sp.</i> (mullet)	ND	104.0	15.2	ND	ND
13	"	ND	53.0	—	—	—
13	<i>Ictalurus punctatus</i> (catfish)	—	107.0	—	—	—
13	<i>Platichthys flesus</i> (flounder)	—	235.0	—	—	—

¹ Represents no. of weeks before (—) or after planting of aldrin-treated seed rice.

² Samples analyzed: whole body, wet weight.

³ ND = none detected (<μg/kg).

TABLE 6.—Pesticide residues detected in tissues and eggs of *Lepisosteus oculatus* (spotted gar) after pesticide application

TIME, WK ¹	TISSUE	RESIDUE, PPB (μG/KG) ^{2,3}				
		ALDRIN	DIELDRIN	DDE	DDD	DDT
8	Liver-muscle	2.6	110.0	59.0	ND	6.4
8	Eggs	22.3	1210.0	715.0	54.6	131.0
8	Liver-muscle	15.1	209.0	181.0	22.0	65.1
8	Eggs	49.8	1280.0	1220.0	148.0	290.0

¹ Represents no. of weeks after planting of aldrin-treated rice.

² Samples analyzed: tissue, wet weight.

³ ND = none detected (<μg/kg).

centration was seen in eggs over the concentration in other body tissues. Such a phenomenon might be the result of high lipid content of eggs or possibly an active excretion of pesticides into reproductive materials. Both the dieldrin level and the high content of DDE could critically affect reproductive success of these fish. Envi-

ronmental levels of dieldrin producing 50 percent mortality in various fish were reported by Moore (30) to range from 100 to 250 ppb. The level of dieldrin in the microenvironment of the embryos in these fish eggs exceeded those levels.

Discussion

Our data suggest that the introduction of an organochlorine insecticide such as aldrin into a natural ecosystem is followed by certain predictable physical and chemical events. In the case of aldrin, specifically, one of the first events is a chemical alteration of the insecticide structure. In the present study epoxidation of aldrin to dieldrin occurred in both biotic and abiotic components of the ecosystem. The extent of the conversion of aldrin to dieldrin was evidenced by the fact that the primary, and often only, residue detected in certain components of the ecosystem was dieldrin. Though detected in certain components early in the study, aldrin was noticeably absent in all components later on.

Insecticide residues within the ecosystem became unevenly distributed, exhibiting a predilection for biotic components. The phenomenon of biological magnification was evident at all trophic levels. Concentrations of residues in organisms ranged from 500 to 10,000 times the maximum residue concentration in water. Evidence of accumulation and passage of pesticides along food chains exists in the temporal relationships of biocide assimilation. Biological magnification and passage of insecticides along the food chain requires a stepwise process whereby residues are assimilated in lower trophic levels and subsequently passed to higher and higher levels. Such a process would exhibit a chronological sequence in which residues first appear in the lower trophic levels. Only after a delay allowing for intermediate links in the chain would the residues become available for assimilation by organisms of the higher trophic levels.

This phenomenon was evident in the organisms of the study area as illustrated in Figures 1-4. The higher the trophic level represented, the greater was the time lag before maximum residue concentration was reached. Delays occurred at each of several levels prior to assimilation of residue in the higher trophic levels. The assimilation and concentration of residue followed an orderly pattern which resembled closely that of energy flow through food chain relationships.

In all cases, the maximum accumulation occurred within a short time following introduction of the insecticide into the ecosystem. Peak levels were reached in all monitored organisms within days or weeks. The dissipation or degradation of residue following biological concentration exhibited certain common characteristics in almost every component of the environment. Kinetic:

of insecticide loss resembled those of radioactive decay in that they were concentration-dependent. Loss of pesticide from water and most organisms appeared to follow a first-order reaction curve in which the rate of loss was directly proportional to the concentration of residue present. Mathematically this can be described as:

$$-\frac{dP}{dT} = PK$$

in which K = constant, P = residue concentration,

and $-\frac{dP}{dT}$ = negative rate of change of P per unit

time. A similar phenomenon was noted for residues in soil by Kearney et al. (28). This pattern of decline is evident in the graphic representation of residues in components of the ecosystem as illustrated in Figures 1-4. It would appear that concentration-dependent rate of decay or loss of insecticide occurred in both biotic and abiotic components of the aquatic ecosystem.

Summary

The chlorinated hydrocarbon insecticide aldrin applied to the rather discrete confines of a ricefield exhibited a dynamic behavior which resulted in dispersion of residues throughout the entire associated aquatic ecosystem. Though chemical alteration (aldrin → dieldrin) was extensive, dieldrin persisted in an active state for several months. Pesticides were rapidly concentrated in living organisms, apparently by both direct absorption of residues from the milieu and indirect assimilation of residues through the food web. Pesticides showed a tendency to concentrate selectively in certain tissues, notably reproductive tissues. This would indicate the need for careful study and evaluation of effects of such chemicals on fecundity and reproductive success of all organisms inhabiting areas of pesticide use.

Accumulation of aldrin and dieldrin in both biotic and abiotic components of the ecosystem was followed by a decline, the kinetics of which resembled a first-order reaction. This resulted in a rapid depletion or loss of extremely high levels of pesticide concentrated by organisms, but allowed for long-term persistence of low levels of chemically active compounds. Studies of long-term effects of small, sublethal doses of pesticide would seem to be the most logical method for evaluating the ultimate effect of chlorinated hydrocarbon pesticides on living systems.

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LITERATURE CITED

- (1) Anderson, B. G. 1959. The toxicity of organic insecticides to *Daphnia*. In *Biological Problems in Water Pollution*. Robert A. Taft Sanitary Engineering Center, Cincinnati, Ohio. pp. 94-95.
- (2) Butler, P. A. 1962. Effects on commercial fisheries. In *Effects of Pesticide on Fish and Wildlife in 1960*. Bureau of Sport Fisheries and Wildlife Circular 143. Fish and Wildlife Service. U.S. Dept. of Interior.
- (3) Butler, P. A. 1969. The significance of DDT residues in estuarine fauna. In *Chemical Fallout*. (Miller and Berg, ed.). Chas. C. Thomas Publisher, Springfield, Ill.
- (4) Graham, R. J. 1959. Effects of forest insect spraying on trout and aquatic insects in some Montana streams. In *Biological Problems in Water Pollution*. Robert A. Taft Sanitary Engineering Center, Cincinnati, Ohio. pp. 62-65.
- (5) Henderson, C., Q. H. Pickering, and C. M. Tarzwell. 1959. The toxicity of organic phosphorus and chlorinated hydrocarbon insecticides to fish. In *Biological Problems in Water Pollution*. Robert A. Taft Sanitary Engineering Center, Cincinnati, Ohio. pp. 76-88.
- (6) Loosanoff, V. L. 1959. Some effects of pesticides on marine arthropods and mollusks. In *Biological Problems in Water Pollution*. Robert A. Taft Sanitary Engineering Center, Cincinnati, Ohio. pp. 89-93.
- (7) Nicholson, H. P. 1967. Pesticide pollution control. *Science* 158:871-876.
- (8) Wurster, C. F., Jr. 1968. DDT reduces photosynthesis by marine phytoplankton. *Science* 159:1474-1475.
- (9) Keith, J. A. 1966. Reproduction in a population of herring gulls (*Larus argentatus*) contaminated by DDT. *J. Appl. Ecol.* 3 (Suppl.):57-70.
- (10) Rudd, R. L. 1964. *Pesticides and the Living Landscape*. U. of Wis. Press, Madison, Wis.
- (11) Butler, P. A. 1966. Pesticides in the marine environment. *J. Appl. Ecol.* 3 (Suppl.):253-259.
- (12) Chadwick, G. G., and R. W. Brocksen. 1969. Accumulation of dieldrin by fish and selected fish-food organisms. *J. Wildl. Manage.* 33(3):693-700.
- (13) Murphy, P. G. 1971. The effect of size on the uptake of DDT from water by fish. *Bull. Environ. Contam. Toxicol.* 6:38-45.
- (14) Hunt, E. G., and A. I. Bischoff. 1960. Inimical effects on wildlife of periodic DDD application to Clear Lake. *California Fish and Game* 46:91-106.
- (15) Hunt, E. G. 1966. Biological magnification of pesticides. In *Scientific Aspects of Pest Control*. Nat. Acad. Sci. Nat. Res. Council. Publ. 1402. Washington, D.C. pp. 251-262.
- (16) Woodwell, G. M., C. F. Wurster, Jr., and P. A. Isaacson. 1967. DDT residues in an east coast estuary: a case of biological concentration of a persistent insecticide. *Science* 156:821-823.
- (17) George, J. L., and D. E. H. Frear. 1966. Pesticides in the Antarctic. *J. Appl. Ecol.* 3 (Suppl.):155-167.
- (18) Grosch, D. S. 1967. Poisoning with DDT: Effect on reproductive performance of *Artemia*. *Science* 155: 592-593.

- (19) Cairns, J., N. R. Foster, and J. J. Loos. 1967. Effects of sublethal concentrations of dieldrin on populations of guppies. *Proc. Acad. Natur. Sci. Philadelphia* 119: 75-91.
- (20) Meeks, R. L. 1968. The accumulation of ^{36}Cl ring-labeled DDT in a freshwater marsh. *J. Wildl. Manage.* 32:376-398.
- (21) Johnson, L. Y. 1962. Separation of dieldrin and endrin from other chlorinated pesticide residues. *J. Ass. Offic. Agr. Chem.* 45:363.
- (22) Saha, J. G. 1971. Comparison of several solvents for extracting root absorbed radioactive dieldrin from wheat. *J. Econ. Entomol.* 64(1):50-53.
- (23) Bonelli, E. J., and K. P. Dimick. 1964. Gas chromatography and electron capture for analysis of pesticides. In *Lectures on Gas Chromatography*. (Mattick and Szymanski, ed.). Plenum Press, New York.
- (24) Cieplinski, E. W. 1964. Instrumental aspects of pesticide analysis by gas chromatography. In *Lectures on Gas Chromatography*. (Mattick and Szymanski, ed.). Plenum Press, New York.
- (25) Bowman, M. C., and M. Beroza. 1965. Extraction p-values of pesticides and related compounds in six binary solvent systems. *J. Ass. Offic. Anal. Chem.* 48(5):943-954.
- (26) Harris, C. R., and E. P. Lichtenstein. 1961. Factors affecting the volatilization of insecticides from soils. *J. Econ. Entomol.* 54:1038-1045.
- (27) Kiiigemagi, U., H. E. Morrison, J. E. Roberts, and W. B. Bollen. 1958. Biological and chemical studies on the decline of soil insecticides. *J. Econ. Entomol.* 51: 198-204.
- (28) Kearney, P. C., R. G. Nash, and A. R. Isensee. 1969. Persistence of pesticide residues in soils. In *Chemical Fallout*. (Miller and Berg, ed.). Chas. C. Thomas Publisher. Springfield, Ill. pp. 54-67.
- (29) Bann, J. M., T. J. DeCino, N. W. Earle, and Y. Sun. 1956. The fate of aldrin and dieldrin in the animal body. *J. Agr. Food Chem.* 4:937-941.
- (30) Moore, N. W. 1967. A synopsis of the pesticide problem. *Advan. Ecol. Res.* 4:75-125.

Selected Chlorinated Hydrocarbons in Bottom Material from Streams Tributary to San Francisco Bay¹

LeRoy M. Law and Donald F. Goerlitz

ABSTRACT

As part of a study of the environmental quality of San Francisco Bay, bottom material from 26 streams tributary to the Bay were analyzed for chlordane, DDD, DDE, DDT, and PCB residues. These compounds were present in essentially all streams tested. Chlordane proved to be ubiquitous, with a concentration range similar to that of the other compounds. Noteworthy was the occurrence in one stream of polychlorinated naphthalene residues. Compounds occurring in concentrations above 20 $\mu\text{g}/\text{kg}$ were identified in most instances by combined gas chromatography/mass spectrometry.

Introduction

San Francisco Bay is one of the principal aquatic resources of the State of California. Millions of people residing on or near the shores of the Bay utilize its waters for recreation, waste disposal, mining of commercially valuable salts and minerals, marine navigation, fishing, and general aesthetic enjoyment. The Bay receives waters from many sources, large and small, which drain a densely urbanized area developed agriculturally and industrially. In order to assess the potential contamination of the Bay from chlorinated hydrocarbon compounds, the U.S. Department of the Interior—Geological Survey initiated a study in February 1972 to obtain background information. Of special interest was the input attributable to the numerous streams that discharge into San Francisco Bay.

The worldwide distribution of residues of DDT and PCB's (polychlorinated biphenyls) is well established (1-11). Furthermore it has been demonstrated (12) that PCB's are accumulated and concentrated in certain organisms by as much as five orders of magnitude greater than the organism's aquatic environment. Woodwell and coworkers (13) have studied the biological concentration of DDT residues in organisms of increasing trophic levels and found it to be more than three orders of magnitude. Most chlorinated hydrocarbon pesticides are only slightly soluble in water and usually enter the hydrologic environment sorbed onto particulate matter (14). Even when dispersed in aqueous media they sorb onto sediment (15). For example, Bevenue et al. (16) found that the ratio of chlorinated pesticides associated with sediment to that in solution was 9,000 to 1. PCB's, because of their similarity in chemical properties to some insecticides, can be expected to behave in a water/sediment mixture in a like manner. Depending upon flow conditions sorbed compounds may be either in transport or deposited as part of the streambed matrix. Hence it was decided to survey the numerous Bay-area streams by analyzing the bottom material.

Nisbet and Sarofim (17) have estimated that of the 5×10^5 tons of PCB's produced in the United States during 1930-70, approximately 3.9×10^5 tons, or 78 percent, have been lost to the environment. Riseborough and de Lappe (18), in discussing the mass balance of pollutants, state that in the last 15 years, 6×10^{10} g (6.6×10^4 tons) per year of DDT have been manufactured in the United States for both domestic use and export. Because DDT is intentionally applied to the earth, vir-

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tually all of it has been lost to the environment, whereas PCB's are leaked to the environment by usage. In view of these large production figures the chlorinated hydrocarbon compounds DDT and PCB were considered the most likely pollutants to be found. Therefore, these compounds were chosen for study and this report summarizes the findings.

Sampling and Analytical Procedure

In February and March 1972, bottom material from 26 streams that discharge into San Francisco Bay was collected for analysis. Sampling sites are shown in Figure 1. The bottom material was collected in wide-mouth glass bottles equipped with Teflon-lined screw-top closures. Samples of soft bottom material were obtained by scooping directly with the glass bottle. When the texture of the bottom material prevented this method, samples were obtained by scooping the material with a chromium-plated garden trowel and then placing the sample in a bottle. All implements and bottles had been freed of any contaminants that would interfere with analysis.

Upon receipt in the laboratory the samples were wet-sieved through a screen with a 2-mm-pore diameter to isolate the material most likely to be transported during high flow. The immersed-screen method described by Guy (19) was followed, using water collected with the

hed material instead of distilled water. The liquid phase was separated from the solid material that passed through the screen by allowing the mixture to stand for several hours and decanting as much water as possible. Finally, the sieved sample was stored at 4°C to inhibit microbial degradation until extraction was initiated.

The procedure used in this study was a slightly modified version of the Geological Survey method for analyzing aquatic sediments for insecticides (20). A 25-g subsample of the wet bottom material was placed in a glass-stoppered flask and shaken for 20 minutes with 20-ml redistilled pesticide-grade acetone. Fifty ml of redistilled pesticide-grade hexane was added to the acetone/bottom-material slurry, and shaken for an additional 5-10 minutes. The extractant was decanted into a separatory funnel containing 500 ml of organic free distilled water. In a similar manner the extraction was repeated two more times, the only difference being that the volume of acetone used was reduced from 20 ml to 10 ml. The combined extracts were washed with three 500-ml volumes of distilled water and placed over anhydrous sodium sulfate to dry. After drying, the solvent volume was reduced to a few milliliters using a Kuderna-Danish evaporative concentrator and finally to a few tenths of a milliliter by evaporation under a stream of warm dry nitrogen. Mean recovery for the insecticides DDD, DDE, and DDT was 92, 99, and 99 percent, respectively. Mean recovery for PCB was 100 percent.

The compounds were initially isolated from interfering coextractives by adsorption chromatography. The concentrated extract was placed on a 1-by-8-cm column of alumina deactivated 9 percent by weight with water and eluted with 20 ml of hexane. The eluate volume was reduced to a few tenths of a milliliter and transferred to a second 1-by-8-cm chromatographic column of silica gel deactivated 3 percent by weight with water. Sufficient hexane was added to the column to total exactly 25 ml of eluate. At this point the elution solvent was changed to benzene and an additional 10 ml of eluate was collected separately. The PCB's were thereby isolated in the first fraction collected from the silica-gel column, and the DDT family and chlordane were in the second fraction

Finally the extracts were treated with metallic mercury, following the procedure of Goerlitz and Law (21), for the removal of sulfur interferences. The purified extracts were subjected to gas-chromatographic analysis for identification and quantitation of components. Two Varian Aerograph Model 600D gas chromatographs were used. The instruments were fitted with concentric-type tritium foil electron-capture detectors and connected to Honeywell recorders through an Infotronics Model CRS 100 electronic integrator. One chromatograph was equipped with a glass column 1.8 m long by 1.8 mm i.d., packed with 60-80-mesh Chromosorb W-HP coated with OV-1 3 percent by weight. The other chromatograph was

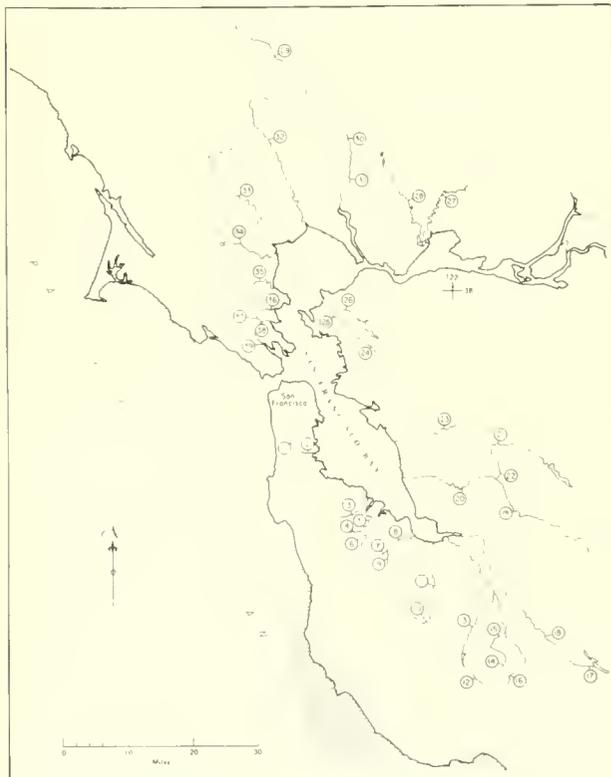


FIGURE 1.—Map of San Francisco Bay area showing stream bed sites sampled for chlorinated hydrocarbons

equipped with a glass column of the same dimensions, packed with 100-120-mesh Supelcoport coated with OV-17 1.5 percent by weight and QF-1 1.95 percent by weight. Operating conditions for both chromatographs were: oven temperature, 195°C; inlet temperature, 210°C; and nitrogen carrier gas flow rate, 30 ml/min.

The DDT family of pesticides were measured by comparing the area under the chromatographic peaks with the area of appropriate standards. Multiple peak residues such as chlordane and PCB's were quantitatively measured by comparing the sum of the areas of the two most prominent peaks with the appropriate analytical standards. The approximate minimum detectable concentrations of the compounds reported, employing the stated analytical conditions, are as follows: DDE: 0.05×10^{-6} $\mu\text{g}/\text{kg}$; chlordane, DDD, *o,p'*-DDT, and *p,p'*-DDT: 0.1×10^{-6} $\mu\text{g}/\text{kg}$; and PCB: 1×10^{-6} $\mu\text{g}/\text{kg}$. When the concentration of any component of interest was great enough, combined gas chromatography/mass spectrometry was used to confirm the identity of the compound. A Finnigan Instrument Corporation Model 1015 quadrupole mass spectrometer and Systems Industries System 150 computerized controller and data output system were used. The mass spectrometer was connected to a Varian Aerograph Model 1700 gas chromatograph via a glass jet separator. The gas chromatograph was equipped with a glass column 1.2 m by 2 mm i.d., packed with Gas Chrom Q coated with OV-1 3 percent by weight. The temperature of the column oven was programmed at a rate of 6°C/min from 175° to 235°C and then held isothermally until completion of analysis. Helium was used as a carrier gas at a flow rate of 30 ml/min.

Results and Discussion

Results of the analysis of bottom material samples from San Francisco Bay Area streams are given in Table 1. Residue concentrations, uncorrected for percent recovery, are expressed as $\mu\text{g}/\text{kg}$ based on the oven-dried weight of the bottom material, determined on a separate subsample. Site numbers referred to in Table 1 are the numbered sampling sites on the map in Figure 1. All residue identities in Table 1 were established by elution order when the sample extracts were subjected to column chromatography and by peak matching when analyzed by electron-capture gas chromatography. When concentration values were great enough, a gas chromatograph/mass spectrometer (GC/MS) was used to confirm the identity of a residue. Those residues that were confirmed by GC/MS are noted in Table 1.

Because this study was exploratory in design and scope, quantitative conclusions should not be drawn; however, certain generalizations can be observed. Chlorinated hydrocarbon residues were found in all stream bed samples analyzed, thus illustrating their widespread distri-

TABLE 1.—Chlorinated hydrocarbon residues found in San Francisco Bay Area streams

SITE No.	STREAM	RESIDUE CONCENTRATION IN $\mu\text{G}/\text{KG}$ ^{1,2}					PCB
		CHLORDANE	DDD	DDE	<i>o,p'</i> -DDT	<i>p,p'</i> -DDT	
1	Colma Creek	39	3.0	2.0	1.7	3.2	3.9
2	Colma Creek	19	4.1	1.8	0.80	5.3	12
3	Belmont Creek	660	41	17	89	200	52
4	Cordilleros Creek	20	3.8	3.5	4.0	13	14
5	Cordilleros Creek	33	17	6.1	5.2	39	6.0
6	Redwood Creek	40	8.4	5.2	4.2	24	25
7	San Francisquito Creek	7.1	2.2	2.1	0.96	7.1	1.2
8	San Francisquito Creek	670	160	43	20	150	430
9	Los Trancos Creek	21	10	5.5	1.3	5.6	21
10	Stevens Creek	7.8	0.0	0.0	0.0	12.3	180
11	Stevens Creek	190	19	22	11	33	30
12	Los Gatos Creek	0.0	1.8	0.87	0.28	2.2	0.0
13	Los Gatos Creek	280	33	25	11	32	170
14	Guadalupe River	17	3.5	2.3	0.87	3.2	(3)
15	Guadalupe River	9.6	3.1	1.8	0.52	1.6	2.7
16	Alamitos Creek	46	18	26	2.2	14	610
17	Coyote Creek	83	86	40	5.7	31	14
18	Coyote Creek	71	17	11	2.6	4.3	12
19	Alameda Creek	13	5.6	4.5	0.16	0.57	11
20	Alameda Creek	52	12	9.2	2.4	2.1	30
21	Arroyo de la Laguna	200	27	23	4.5	7.3	160
22	Arroyo de la Laguna	22	3.5	4.3	0.77	1.3	33
23	San Lorenzo Creek	15	7.0	7.5	0.0	1.7	25
24	Wildcat Creek	87	18	4.1	2.7	6.5	21
25	Wildcat Creek	45	8.8	6.1	1.8	9.7	43
26	San Pablo Creek	65	2.0	3.4	2.0	3.6	27
27	Union Creek	200	45	16	2.6	2.8	140
28	Green Valley Creek	0.0	1.9	2.3	0.36	0.86	5.3
29	Napa River	10	2.2	2.7	0.78	2.3	8.8
30	Napa River	0.0	46	0.0	9.7	73	1400
31	Napa River	97	16	11	2.8	8.4	7.6
32	Sanoma Creek	4.3	0.98	1.0	0.25	1.9	5.0
33	Petaluma River	130	8.3	5.5	3.8	2.7	27
34	Navato Creek	62	3.5	3.6	2.4	10	10
35	Miller Creek	310	16	11	13	8.4	35
36	San Rafael Creek	800	120	61	38	51	350
37	Corte Madera Creek	140	12	11	8.7	48	81
38	Corte Madera Creek	66	42	42	6.7	41	11
39	Arroyo Corte Madera del Persidio	140	34	7.6	11	16	24

¹ Based on oven-dry weight of stream bed material uncorrected for percent recovery.

² Underlined values indicate mass spectrometric confirmation of residue identity.

³ The presence of 55 $\mu\text{g}/\text{kg}$ of polychlorinated naphthalenes (PCN) obscured any PCB's present. PCN was identified by gas chromatograph/mass spectrometer.

bution in the San Francisco Bay area. Initially only the presence of the DDT family of compounds and the PCB's had been anticipated with any certainty, due to their established ubiquity. This investigation soon showed the insecticide chlordane to be as prevalent as the other target compounds; it appeared in 92 percent of the 39

samples analyzed. Both the PCB's and chlordane evidenced a wide range in concentration, from 1 to greater than 1,000 $\mu\text{g}/\text{kg}$. In spite of this extreme range there does not seem to be a significant difference between the average residue concentrations of streams discharging into the Bay south of San Francisco and those discharging into the Bay north of San Francisco. Significantly, only 3 of the 39 streams tested contained residues of the DDT family in quantities greater than those of PCB or chlordane.

Although a widespread occurrence of PCB's had been expected, two sampling sites showed residue levels much higher than anticipated. On Stevens Creek site 10 had residue levels of 180 $\mu\text{g}/\text{kg}$; on Alamos Creek site 16 had levels of 610 $\mu\text{g}/\text{kg}$. Neither area has any apparent industrial or commercial development. The sample from site 14 on the Guadalupe River contained 55 $\mu\text{g}/\text{kg}$ of polychlorinated naphthalenes. This is an industrial compound similar in properties and uses to PCB's. This sample, too, came from an area of no apparent industrial activity. Nonachlor, a component of commercial-quality chlordane, was often found in relatively higher concentrations in bottom material samples than in freshly prepared standards. This suggests that nonachlor may be more resistant to degradation than either the α or γ isomers of chlordane.

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LITERATURE CITED

- (1) Giam, C. S., A. R. Hanks, R. L. Richardson, W. M. Sockett, and M. K. Wong. 1972. DDT, DDE, and polychlorinated biphenyls in biota from the Gulf of Mexico and Caribbean Sea—1971. *Pestic. Monit. J.* 6(3): 139-143.
- (2) Holden, A. V., and K. Marsden. 1967. Organochlorine pesticides in seals and porpoises. *Nature* 216:1274-1276.
- (3) Holmes, D. C., J. H. Simmons, and J. O'G. Tatten. 1967. Chlorinated hydrocarbons in British wildlife. *Nature* 216:227-29.
- (4) Karlog, O., I. Kraut, and Sv. Dalgaard-Mikkelsen. 1971. Residues of polychlorinated biphenyls (PCB's) and organochlorine insecticides in liver tissue from terrestrial Danish predatory birds. *Acta. Vet. Scand.* 12:310-312.
- (5) Koeman, J. H., M. C. ten Noever de Brauw, and R. H. de Vos. 1969. Chlorinated biphenyls in fish, mussels and birds from the River Rhine and the Netherlands coastal area. *Nature* 221:1126-1128.
- (6) Modin, J. C. 1969. Chlorinated hydrocarbon pesticides in California bays and estuaries. *Pestic. Monit. J.* 3(1):1-7.
- (7) Risebrough, R. W., P. Rieche, D. P. Peakall, S. G. Herman, and M. N. Kirven. 1968. Polychlorinated biphenyls in the global ecosystem. *Nature* 220:1098-1102.
- (8) Schmidt, T. T., R. W. Risebrough, and F. Gress. 1971. Input of polychlorinated biphenyls into California coastal waters from urban sewage outfalls. *Bull. Environ. Contam. Toxicol.* 6(3):235-243.
- (9) Södergren, A., B. Svensson, and S. Ulfstrand. 1972. DDT and PCB in South Swedish streams. *Environ. Pollut.* 3(1):25-36.
- (10) Tombergs, H. P. 1972. The PCB situation in Germany. *Environ. Health Perspect.* 1:179-180.
- (11) Zitko, V. 1971. Polychlorinated biphenyls and organochlorine pesticides in some freshwater and marine fishes. *Bull. Environ. Contam. Toxicol.* 6(4): 464-470.
- (12) Sanders, H. O., and J. H. Chandler. 1972. Biological magnification of a polychlorinated biphenyl (Aroclor® 1254) from water by aquatic invertebrates. *Bull. Environ. Contam. Toxicol.* 7(5):257-263.
- (13) Woodwell, G. M., C. F. Wurster, Jr., and P. A. Isaacson. 1967. DDT residues in an East Coast estuary: A case of biological concentration of a persistent insecticide. *Science* 156:821-824.
- (14) Bradley, J. R., Jr., T. J. Sheets, and M. D. Jackson. 1972. DDT and toxaphene movement in surface water from cotton plots. *J. Environ. Quality* 1(1):102-105.
- (15) Poirrier, M. A., B. R. Bordelon, and J. L. Laster. 1972. Adsorption and concentration of dissolved carbon-14 DDT by coloring colloids in surface waters. *Environ. Sci. Technol.* 6:1033-1035.
- (16) Bevenue, A., J. W. Hylin, Y. Kawano, and T. W. Kelly. 1972. Organochlorine pesticide residues in water, sediment, algae, and fish, Hawaii—1970-1971. *Pestic. Monit. J.* 6(1): 56-64.
- (17) Nisbet, I. C. T., and A. F. Sarofim. 1972. Rate and routes of transport of PCBs in the environment. *Environ. Health Perspect.* 1:21-38.
- (18) Risebrough, R. W., and B. de Lappe. 1972. Accumulation of polychlorinated biphenyls in ecosystems. *Environ. Health Perspect.* 1:39-45.
- (19) Guy, H. P. 1969. Techniques of water-resources investigations of the U.S. Geological Survey, Book 5, Ch. A1:28.
- (20) Goerlitz, D. F., and E. Brown. 1972. Techniques of water-resources investigations of the U.S. Geological Survey, Book 5, Ch. A3:33-35.
- (21) Goerlitz, D. F., and L. M. Law. 1971. Note on removal of sulfur interferences from sediment extracts for pesticide analysis. *Bull. Environ. Contam. Toxicol.* 6(4): 9-10.

Organochlorine Residues in Golden Eagles, United States— March 1964-July 1971¹

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ABSTRACT

Since 1964, golden eagles (*Aquila chrysaetos*) collected dead, dying, or incapacitated in the United States have been analyzed for organochlorine residues under the National Pesticides Monitoring Program. This paper reports residues found in 134 brain, heart, kidney, liver, and muscle (BHKLM), 73 brain, and 102 fat samples representing 169 golden eagles from 22 States. DDE was found most frequently, and usually in the greatest concentrations, in each sample type. Dieldrin was also common. Heptachlor epoxide, polychlorinated biphenyls (PCB's), DDD, DDT, endrin, DDMU (1-chloro-2, 2-bis [*p*-chlorophenyl] ethylene), and aldrin were found less frequently. Variability of residue levels was great for all types of samples, and no regional patterns were evident. The data suggest that exposure to organochlorine pesticides has remained relatively constant from 1965 through 1970. Exposure is apparently through diet and not sufficient to warrant concern for direct nonsynergistic acute toxic effects. Sublethal effects are not precluded, however.

Of the 188 eagles found, 63 were examined for immediate cause of mortality. The most frequent causes appeared to be shooting and contact with power lines.

Of the 169 eagles found, necropsy or residue analysis suggested deaths by unnatural causes for 63. Of these, deaths due to shooting or contact with power lines were most common; other factors included trapping, collision with vehicles, and chemical poisoning. The remaining 106 birds died from undetermined causes which undoubtedly included a high proportion of natural deaths.

Introduction

The golden eagle (*Aquila chrysaetos*), a carnivore that is terminal in its food chain, has been selected by the Bureau of Sport Fisheries and Wildlife, U.S. Department of the Interior, as one of the species to be surveyed under the National Pesticides Monitoring Program (1). Under this program, golden eagles found in the United States that are dead, dying, or severely incapacitated are sent through U.S. Game Management Agents or National Wildlife Refuge Managers to Wildlife Research Centers for gross examination or necropsy and for organochlorine residue analysis. This paper reports necropsy and residue findings for 169 golden eagles received in this manner from 22 States by the Denver Wildlife Research Center between March 1964 and February 1970.

Materials and Methods

Whole birds and tissue samples were usually received frozen at the laboratory and were stored frozen until analysis. Most whole birds were examined for gross evidence of death due to unnatural causes, including shooting, impact on power lines, and chemical poisoning. A few were decomposed extensively, precluding necropsy. The birds were then dewinged, debeaked, and skinned for tissue sample removal. Usually a composite of 5 g each of brain, heart, kidney, liver, and muscle (BHKLM) was selected. In some cases fat and/or brain samples were taken.

Samples to be analyzed were blend-desiccated with sodium sulphate (5 parts to 1 part of sample) and Soxhlet-extracted for 6 hours with 1:9 diethyl-ether:petroleum-

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ether. Extractants were evaporated, crude lipids were determined gravimetrically, and the sample was taken up in hexane and partitioned with acetonitrile by a procedure similar to that of Mills (2). Additional interfering substances were removed by liquid adsorption chromatography (2), co-sweep distillation (3), or both. Various other cleanup and separative techniques, such as treatment with fuming sulfuric acid or chromatography with magnesia or alumina columns, were used when necessary. Recovery of organochlorine insecticides from eagle tissue by the above technique was $90 \pm 10\%$.

Sample residues were usually determined by gas-liquid chromatography (GLC) using tritium-activated, concentric-tube, electron-capture detectors. The most frequently used GLC operating parameters are presented in Table 1. In most cases, a Dow-200 column was used for separation, identification, and quantitation, and a QF-1 (FS-1265) column was used for confirmation. When residue levels permitted, further confirmation was performed by thin-layer chromatography with laboratory-prepared plates or Eastman Chromatogram (F) alumina- or silica-gel films.

TABLE 1.—Normal operating parameters for gas-liquid chromatography, with tritium electron-capture detection

	COLUMNS (GLASS, 5' x 1/8" O.D.)	
	QF-1	Dow-200
Liquid phase	5%	5%
Mesh size, H.P. chromasorb W	80-100	80-100
N ₂ flow rate, ml/min	50	50
Temperature, °C	175	185
Retention time of aldrin, min	3.3	6.5

Plates and films were developed with 0.5% methanol and 2.5% benzene in 2,2,4-trimethyl pentane (v/v); spots were visualized by silver nitrate spraying and ultraviolet exposure. The sensitivity of this procedure was greater than 0.1 ppm for organochlorine residues and 1.0 ppm for PCB's.

Results and Discussion

Median values are presented instead of means because of the skewness of the data and the need for comparison with the literature. Residue levels reported in this study have not been corrected for percent recovery of pesticides from eagle tissues.

Organochlorine residues were determined in 134 BHKLM, 102 fat, and 73 brain samples representing 169 golden eagles. Table 2 shows the frequency of occurrence of the nine organochlorine compounds found in the samples, DDE being most ubiquitous. As shown in Tables 3-4, residues were generally greatest in the fat samples, intermediate in BHKLM samples, and least in the brain samples.

TABLE 2.—Frequency of occurrence of nine organochlorine residues in golden eagle samples

ORGANOCHLORINE RESIDUES	NUMBER OF SAMPLES CONTAINING RESIDUES ¹					
	BHKLM (134)		FAT (102)		BRAIN (73)	
	NO. WITH RESIDUES	% OF TOTAL	NO. WITH RESIDUES	% OF TOTAL	NO. WITH RESIDUES	% OF TOTAL
DDE	127	94.8	100	98.0	65	89.0
Dieldrin	68	50.7	69	67.6	19	26.0
Heptachlor epoxide	23	17.2	32	31.4	7	9.6
PCB's (polychlorinated biphenyls)	20	14.9	13	12.7	15	20.5
DDD	10	7.5	13	12.7	1	1.4
DDT	3	2.2	8	7.8	3	4.1
Endrin	2	1.5	5	4.9	0	0.0
DDMU	2	1.5	0	0.0	0	0.0
Aldrin	1	0.7	3	2.9	1	1.4

¹ Total number of golden eagles represented = 169.

Table 3 gives the median, range, and number of samples with each organochlorine insecticide residue for each sample type according to State. These data are generally too variable and sample size is too small to permit meaningful statistical comparisons between States or regions. From the data available, it appears that exposure of individual golden eagles to organochlorine insecticides is quite variable but falls within approximately the same range across the country.

As shown in Table 3, DDE was found in at least one golden eagle from each of the 22 collection States. Few of the samples contained alarmingly high residues, however. Four of the fat samples contained over 40 ppm DDE (50-84 ppm), two of the BHKLM samples contained over 20 ppm DDE (24-25 ppm), and four of the brain samples contained over 2 ppm DDE (2.3-9.9 ppm). According to the general guidelines given by Stickel et al. (4) in their study of DDE residues in cowbirds (*Molothrus ater*), these residues are not sufficiently high to cause direct, nonsynergistic acute toxicity to eagles.

Golden eagles from all 22 States contained a median of 0.3 ppm DDE in BHKLM, 3.0 ppm in fat, and 0.1 ppm in the brain for the years 1964-70. These are higher levels than those of DDT and DDD in all sample types, indicating that most exposure to DDT and metabolites was not recent or was dietary. The DDE levels, however, are considerably lower than the lowest median DDE residue of 4.92 ppm in the carcass and 0.92 ppm in the brain of bald eagles (*Haliaeetus leucocephalus*) as reported by Mulhern et al. (5) for the years 1966-68, and 7.80 ppm in the carcass and 1.00 ppm in the brain of bald eagles as reported by Reichel et al. (6) for the years 1964-65. The lower residue content in the golden eagle compared to that in the bald eagle probably reflects their differing diets. The golden eagle's preferred diet of terrestrial herbivores such as rabbits and rodents (7,8,9) places it at the end of a shorter food chain than that of the bald eagle, which frequently takes fish (10).

Reichel et al. (6) also presented residue values for 21 golden eagle samples collected in 1964 and 1965, mostly in South Dakota. These birds also contained residues lower than those in bald eagles, with median values of 0.49 ppm DDE and 0.09 ppm dieldrin in the carcass, and 0.10 ppm DDE and less than 0.05 ppm dieldrin in

the brain. The 40 golden eagle samples from South Dakota for the years 1964-70 presented in Table 3 contained similar residue levels: median values of 0.2 ppm DDE and less than 0.1 ppm dieldrin in BHKLM; less than 0.1 ppm DDE and 0.1 dieldrin in the brain.

TABLE 3.—Organochlorine residues in golden eagles, listed by compound and State—1964-70

Residues in ppm, wet-weight basis

STATE	BHKLM			BRAIN			FAT		
	MEDIAN	RANGE	N ¹	MEDIAN	RANGE	N ¹	MEDIAN	RANGE	N ¹
DDE									
Alaska	9.3	—	1	1.0	—	1	—	—	—
Ariz.	—	—	—	—	—	—	4.1	—	1
Ark.	—	—	—	—	—	—	0.3	—	1
Calif.	0.5	<0.1-5.2	6	0.2	<0.1-2.4	6	0.4	<0.1-16	5
Colo.	0.3	<0.1-6.5	12	<0.1	—	4	0.8	<0.1-15	10
Idaho	4.0	0.1-8.0	2	<0.1	<0.1-0.3	3	1.8	0.7-3.0	2
Ill.	0.1	—	1	—	—	—	1.6	—	1
Ind.	1.6	—	1	—	—	—	13	—	1
Iowa	<0.1	<0.1-0.1	2	—	—	—	—	—	—
Md.	3.2	0.7-5.7	2	2.3	—	1	84	—	1
Minn.	0.6	<0.1-7.9	7	0.4	<0.1-0.7	4	7.1	1.8-40	5
Mo.	0.4	0.3-3.1	3	0.8	0.2-1.4	2	<0.1	—	1
Nebr.	0.2	<0.1-2.6	26	<0.1	<0.1-1.1	11	2.5	<0.1-26.0	28
Nev.	0.3	—	1	0.1	—	1	—	—	—
N. Mex.	0.1	—	1	—	—	—	1.6	—	1
N. Dak.	0.3	<0.1-24	8	<0.1	<0.1-0.2	4	3.4	1.3-50	8
Okla.	0.5	—	1	—	—	—	10	—	1
Oreg.	—	—	—	1.2	—	1	28	1.3-55	2
Pa.	1.0	0.4-6.8	4	0.2	<0.1-0.5	4	29	6.6-38	4
S. Dak.	0.2	<0.1-25	41	<0.1	<0.1-4.6	18	4.4	1.0-28	23
Utah	0.4	<0.1-4.0	6	0.5	<0.1-1.9	3	3.6	0.3-55	4
Wis.	6.2	1.4-11	2	5.0	0.1-9.9	2	12	—	1
All States	0.3	<0.1-25	127	0.1	<0.1-9.9	65	3.0	<0.1-84	100
DIELDRIN									
Calif.	—	—	—	—	—	—	<0.1	—	1
Colo.	<0.1	<0.1-4.4	8	<0.1	—	3	0.8	<0.1-12	10
Idaho	<0.1	—	1	—	—	—	—	—	—
Ill.	0.1	—	1	—	—	—	1.3	—	1
Ind.	0.2	—	1	—	—	—	—	—	—
Iowa	<0.1	—	1	—	—	—	—	—	—
Minn.	0.1	<0.1-0.2	3	<0.1	—	2	0.7	0.4-1.9	4
Mo.	—	—	—	<0.1	—	1	<0.1	—	1
Nebr.	<0.1	<0.1-0.4	15	<0.1	<0.1-0.1	3	0.4	<0.1-2.2	22
Nev.	0.1	—	1	<0.1	—	1	—	—	—
N. Mex.	<0.1	—	1	—	—	—	<0.1	—	1
N. Dak.	<0.1	<0.1-1.5	4	<0.1	—	1	1.4	0.4-3.1	6
Okla.	<0.1	—	1	—	—	—	0.7	—	1
Pa.	0.2	—	1	—	—	—	2.4	—	1
S. Dak.	<0.1	<0.1-3.0	27	<0.1	<0.1-0.4	8	0.8	0.2-6.6	20
Utah	0.1	—	3	—	—	—	<0.1	—	1
All States	<0.1	<0.1-4.4	68	<0.1	<0.1-0.4	19	0.7	<0.1-12	69
HEPTACHLOR EPOXIDE									
Ark.	—	—	—	—	—	—	<0.1	—	1
Calif.	—	—	—	—	—	—	<0.1	—	1
Colo.	0.1	<0.1-0.2	3	<0.1	—	2	0.4	<0.1-1.2	8
Md.	—	—	—	—	—	—	1.4	—	1
Minn.	<0.1	—	1	—	—	—	—	—	—
Mo.	0.2	—	1	0.1	—	1	<0.1	—	1
Nebr.	<0.1	<0.1-0.1	11	0.1	—	1	0.7	<0.1-1.2	9
N. Dak.	0.4	—	1	—	—	—	1.1	0.5-2.4	3
S. Dak.	0.2	<0.1-12.2	6	0.3	<0.1-2.3	3	0.5	0.2-1.3	7
Utah	—	—	—	—	—	—	<0.1	—	1
All States	<0.1	<0.1-12.2	23	0.1	<0.1-2.3	7	0.4	<0.1-2.4	32

TABLE 3.—Organochlorine residues in golden eagles, listed by compound and State—1964-70—Continued

Residues in ppm, wet-weight basis

STATE	BHKLM			BRAIN			FAT		
	MEDIAN	RANGE	N ¹	MEDIAN	RANGE	N ¹	MEDIAN	RANGE	N ¹
PCB									
Calif.	2.1	<1.0-4.2	2	<1.0	—	1	9.5	—	1
Idaho	6.0	—	1	—	—	—	—	—	—
Ill.	—	—	—	—	—	—	6.4	—	1
Md.	—	—	—	<1.0	—	1	3.0	—	1
Minn.	10	<1.0-19	2	<1.0	<1.0-1.0	2	<1.0	—	1
Mo.	10	—	1	5.0	—	1	—	—	—
Nebr.	<1.0	—	3	<1.0	—	3	<1.0	—	2
N. Dak.	1.0	—	1	—	—	—	6.0	2.0-10	2
Pa.	<1.0	—	3	<1.0	—	3	<1.0	—	3
S. Dak.	<1.0	<1.0-10	4	<1.0	<1.0-0.2	3	7.0	<1.0-14	2
Utah	5.0	<1.0-10	2	—	—	—	—	—	—
Wis.	7.0	—	1	6.0	—	1	—	—	—
All States	<1.0	<1.0-19	20	<1.0	<1.0-6.0	15	<1.0	<1.0-14	13
DDD									
Ark.	—	—	—	—	—	—	0.8	—	1
Calif.	—	—	—	—	—	—	1.0	—	1
Colo.	0.2	<0.1-0.3	2	—	—	—	<0.1	—	4
Nebr.	<0.1	—	2	—	—	—	<0.1	—	1
N. Mex.	<0.1	—	1	—	—	—	1.6	—	1
Okla.	0.1	—	1	—	—	—	0.5	—	1
Pa.	0.1	—	1	—	—	—	2.0	—	1
S. Dak.	0.2	<0.1-8.0	3	<0.1	—	1	0.9	<0.1-1.2	3
All States	<0.1	<0.1-8.0	10	<0.1	—	1	0.5	<0.1-2.0	13
DDT									
Ark.	—	—	—	—	—	—	<0.1	—	1
Colo.	0.2	—	2	—	—	—	<0.1	—	6
Idaho	—	—	—	<0.1	—	1	—	—	—
Minn.	—	—	—	<0.1	—	1	—	—	—
S. Dak.	<0.1	—	1	0.2	—	1	—	—	—
Utah	—	—	—	—	—	—	<0.1	—	1
All States	0.2	<0.1-0.2	3	<0.1	<0.1-0.2	3	<0.1	—	8
ENDRIN									
Colo.	<0.1	—	1	—	—	—	—	—	—
Md.	—	—	—	—	—	—	<0.1	—	1
Nebr.	<0.1	—	1	—	—	—	<0.1	—	3
N. Dak.	—	—	—	—	—	—	0.3	—	1
All States	<0.1	—	2	—	—	—	<0.1	<0.1-0.3	5
DDMU									
Colo.	0.6	0.5-0.6	2	—	—	—	—	—	—
ALDRIN									
Calif.	—	—	—	<0.1	—	1	—	—	—
Colo.	—	—	—	—	—	—	<0.1	<0.1-0.1	3
S. Dak.	<0.1	—	1	—	—	—	—	—	—
All States	<0.1	—	1	<0.1	—	1	<0.1	<0.1-0.1	3

¹ Number of specimens containing residue. Median is based on this number.

Dieldrin occurred in 69 (68%) of the 102 fat samples analyzed (Table 2). Only 68 BHKLM samples (51%) contained dieldrin, and 44 of these contained less than 0.1 ppm; the highest level of dieldrin was 4.4 ppm in a fat sample of a bird from Colorado (Table 3). Only 19 brain samples (26%) contained dieldrin, and 16 of these contained less than 0.1 ppm. The highest level found in the brain was 0.4 ppm in a bird from South Dakota. This is considerably lower than the minimum of 4 ppm

in the brain judged necessary for acute toxic effects by Stickel et al. (11). In contrast, Mulhern et al. (5) found that 8 of 69 bald eagles contained sufficiently high dieldrin levels in the brain to suggest dieldrin poisoning. The levels shown here in golden eagles do not preclude sublethal effects, however, as indicated by the studies of Lockie et al. (12), Hickey and Anderson (13), and Ratcliffe (14).

PCB's were first quantified in golden eagles in this laboratory in 1967 (Table 4). Their presence in 20 of 113 BHKLM samples from 1967-70 indicates their ubiquitous nature.

Heptachlor epoxide, DDD, DDMU, DDT, endrin, and aldrin were seen in a few samples, usually in small quantities. The highest median levels were 0.5 ppm for DDD in fat samples and 0.6 ppm for DDMU in BHKLM sam-

TABLE 4.—Organochlorine residues in golden eagles by year—1964-70

Residues in ppm, wet-weight basis

YEAR	BHKLM			BRAIN			FAT		
	MEDIAN	RANGE	N ¹	MEDIAN	RANGE	N ¹	MEDIAN	RANGE	N ¹
DDE									
1964	1.0	0.6-1.0	3	—	—	—	0.4	<0.1-6.5	8
1965	0.8	<0.1-25	6	<0.1	—	1	6.3	0.8-26	5
1966	0.4	<0.1-6.5	11	0.1	—	2	4.2	0.3-40	7
1967	0.2	<0.1-24	39	<0.1	<0.1-0.6	6	3.0	<0.1-84	30
1968	0.2	<0.1-9.3	39	0.1	<0.1-4.6	31	2.8	<0.1-55	30
1969	0.3	<0.1-8.0	25	<0.1	<0.1-1.4	22	3.7	0.3-35	18
1970	6.4	0.8-11	4	0.7	0.2-9.9	3	33	11.0-55	2
1964-70	0.3	<0.1-25	127	0.1	<0.1-9.9	65	3.0	<0.1-84	100
DIELDRIN									
1964	0.1	—	1	—	—	—	1.2	<0.1-12	8
1965	<0.1	<0.1-3.0	4	—	—	—	0.5	<0.1-2.2	5
1966	<0.1	<0.1-4.4	10	<0.1	—	2	1.6	<0.1-2.4	5
1967	<0.1	<0.1-2.3	24	<0.1	—	1	0.5	<0.1-3.1	24
1968	0.1	<0.1-0.6	17	<0.1	<0.1-0.4	9	1.2	<0.1-6.6	17
1969	<0.1	<0.1-0.4	12	<0.1	—	7	0.7	0.2-4.6	10
1970	—	—	—	—	—	—	—	—	—
1964-70	<0.1	<0.1-4.4	68	<0.1	<0.1-0.4	19	0.7	<0.1-12	69
HEPTACHLOR EPOXIDE									
1964	—	—	—	—	—	—	0.4	<0.1-1.2	8
1965	<0.1	—	1	—	—	—	0.8	0.5-1.1	2
1966	<0.1	<0.1-0.2	4	—	—	—	1.2	<0.1-2.4	2
1967	<0.1	<0.1-12.2	10	<0.1	—	1	0.7	<0.1-1.4	13
1968	0.1	<0.1-0.6	4	<0.1	<0.1-2.3	4	0.4	<0.1-1.2	4
1969	<0.1	<0.1-0.2	4	0.1	—	2	0.2	<0.1-0.4	3
1970	—	—	—	—	—	—	—	—	—
1964-70	<0.1	<0.1-12.2	23	0.1	<0.1-2.3	7	0.4	<0.1-2.4	32
PCB									
1964	—	—	—	—	—	—	—	—	—
1965	—	—	—	—	—	—	—	—	—
1966	—	—	—	—	—	—	—	—	—
1967	<1.0	<1.0-1.0	2	<1.0	—	1	5.0	<1.0-10.0	2
1968	<1.0	<1.0-10	7	<1.0	—	6	<1.0	<1.0-6.4	7
1969	<1.0	<1.0-10	7	<1.0	<1.0-5.0	6	<1.0	<1.0-9.5	3
1970	8.0	1.0-19	4	4.0	1.0-6.0	2	14	—	1
1964-70	<1.0	<1.0-19	20	<1.0	<1.0-6.0	15	<1.0	<1.0-14	13
DDD									
1964	—	—	—	—	—	—	<0.1	—	4
1965	8.0	—	1	—	—	—	—	—	—
1966	<0.1	<0.1-0.3	3	—	—	—	1.2	0.8-1.6	2
1967	<0.1	—	3	—	—	—	0.2	<0.1-1.0	4
1968	0.1	—	1	—	—	—	2.0	—	1
1969	0.1	<0.1-0.2	2	<0.1	—	1	1.0	0.9-1.2	2
1970	—	—	—	—	—	—	—	—	—
1964-70	<0.1	<0.1-8.0	10	<0.1	—	1	0.5	<0.1-2.0	1
DDT									
1964	—	—	—	—	—	—	<0.1	—	6
1965	—	—	—	—	—	—	—	—	—
1966	0.2	—	2	—	—	—	<0.1	—	1
1967	<0.1	—	1	<0.1	—	1	<0.1	—	1
1968	—	—	—	—	—	—	—	—	—
1969	—	—	—	0.1	<0.1-0.2	2	—	—	—
1970	—	—	—	—	—	—	—	—	—
1964-70	0.2	<0.1-0.2	3	<0.1	<0.1-0.2	3	<0.1	—	8

TABLE 4.—Organochlorine residues in golden eagles by year—1964-70—Continued

Residues in ppm, wet-weight basis

YEAR	BHKLM			BRAIN			FAT		
	MEDIAN	RANGE	N ¹	MEDIAN	RANGE	N ¹	MEDIAN	RANGE	N ¹
ENDRIN									
1964	—	—	—	—	—	—	—	—	—
1965	<0.1	—	1	—	—	—	<0.1	—	1
1966	<0.1	—	1	—	—	—	—	—	—
1967	—	—	—	—	—	—	<0.1	<0.1-0.3	4
1968	—	—	—	—	—	—	—	—	—
1969	—	—	—	—	—	—	—	—	—
1970	—	—	—	—	—	—	—	—	—
1964-70	<0.1	—	2	—	—	—	<0.1	<0.1-0.3	5
DDMU									
1964	0.6	0.5-0.6	2	—	—	—	—	—	—
1965	—	—	—	—	—	—	—	—	—
1966	—	—	—	—	—	—	—	—	—
1967	—	—	—	—	—	—	—	—	—
1968	—	—	—	—	—	—	—	—	—
1969	—	—	—	—	—	—	—	—	—
1970	—	—	—	—	—	—	—	—	—
1964-70	0.6	0.5-0.6	2	—	—	—	—	—	—
ALDRIN									
1964	—	—	—	—	—	—	<0.1	<0.1-0.1	3
1965	—	—	—	<0.1	—	1	—	—	—
1966	—	—	—	—	—	—	—	—	—
1967	<0.1	—	1	—	—	—	—	—	—
1968	—	—	—	—	—	—	—	—	—
1969	—	—	—	—	—	—	—	—	—
1970	—	—	—	—	—	—	—	—	—
1964-70	<0.1	—	1	<0.1	—	—	<0.1	<0.1-0.1	3

¹ Number of specimens containing residue. Median is based on this number.

ples (for median levels in birds from all States, see Table 3). Each of these insecticides had a median of less than 0.1 ppm in the brain.

The data in Table 4 suggest that exposure of golden eagles to organochlorine insecticides has not changed significantly from 1964 through 1970. The years with the largest sample sizes (1966-69) indicate no important changes in exposure. The median concentrations of DDE, which is represented by the largest number of samples, ranged only from 0.2 to 0.4 ppm in BHKLM samples, and from 2.8 to 4.2 ppm in the fat samples during these years. This is similar to the findings reported by Mulhern et al. (5) for bald eagles.

Cases in which necropsy or residue analysis indicated the probable cause of death are listed in Table 5. Of

TABLE 5.—Probable cause of death of 169 golden eagles as determined by necropsy or residue analyses

PROBABLE CAUSE OF DEATH	NUMBER
Shooting	18
Impact on power line or electrocution	15
1080 (sodium monofluoroacetate)	11
Trapping	10
Collision with vehicle	5
Strychnine	2
Cyanide	2
Unknown	106

the 63 eagles included, 33 died from shooting or contact with power lines (collision or electrocution). Six of the eagles killed by 1080 (sodium monofluoroacetate) were collected in 1966, three in 1968, and two in 1969. Most of the specimens examined died from undetermined causes, which undoubtedly included a high proportion of natural deaths.

LITERATURE CITED

- (1) Johnson, R. E., T. C. Carver, and E. H. Dustman. 1967. Residues in fish, wildlife, and estuaries. *Pestic. Monit. J.* 1(1):7-13.
- (2) Mills, P. A. 1959. Detection and semiquantitative estimation of chlorinated organic pesticide residues in foods by paper chromatography. *J. Assoc. Off. Agric. Chem.* 42:734-740.
- (3) Storherr, R. W., and R. R. Watts. 1965. A sweep co-distillation cleanup method for organophosphate pesticides. I. Recoveries from fortified crops. *J. Assoc. Off. Agric. Chem.* 48(6):1154-1158.
- (4) Stickel, W. H., L. F. Stickel, and F. B. Coon. 1970. DDE and DDD residues correlated with mortality of experimental birds. *Inter-Amer. Conf. Toxicol. Occup. Med.* pp. 287-294.
- (5) Mulhern, B. M., W. L. Reichel, L. N. Locke, T. G. Lamont, A. Belisle, E. Cromartie, G. E. Bagley, and R. M. Prouty. 1970. Organochlorine residues and autopsy data from bald eagles. *Pestic. Monit. J.* 4(3): 141-144.

- (6) Reichel, W. L., E. Cromartie, T. G. Lamont, B. M. Mulhern, and R. M. Prouty. 1969. Pesticide residues in eagles. *Pestic. Monit. J.* 3(3):142-144.
- (7) Boeker, E. L., and T. D. Ray. 1971. Golden eagle population studies in the Southwest. *Condor* 73(4):463-467.
- (8) McGahan, J. 1968. Ecology of the golden eagle. *Auk* 85(1):1-12.
- (9) McGahan, J. 1967. Quantified estimates of predation by a golden eagle population. *J. Wildl. Manage.* 31(3):496-501.
- (10) Imler, Ralph H., and E. R. Kalmbach. 1955. The bald eagle and its economic status. U.S. Fish Wildl. Serv. Circ. 30.
- (11) Stickel, W. H., L. F. Stickel, and J. W. Spann. 1969. Chemical fallout; current research on persistent pesticides. *Proc. First. Rochester Conf. Toxicity*, pp. 174-204.
- (12) Lockie, J. D., D. A. Ratcliffe, and R. Balharry. 1969. Breeding success and organochlorine residues in golden eagles in West Scotland. *J. Appl. Ecol.* 6(3):381-389.
- (13) Hickey, J. J., and D. W. Anderson. 1968. Chlorinated hydrocarbons and eggshell changes in raptorial and fish-eating birds. *Science* 162(3850):271-273.
- (14) Ratcliffe, D. A. 1970. Changes attributable to pesticides in egg breakage frequency and eggshell thickness in some British birds. *J. Appl. Ecol.* 7(1):67-107.

Toxaphene Content of Estuarine Fauna and Flora Before, During, and After Dredging Toxaphene-Contaminated Sediments¹

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ABSTRACT

*This paper evaluates toxaphene concentrations in selected estuarine fauna, flora, sediment, and dredge spoil before, during, and after the dredging of Terry Creek, Brunswick, Ga., in autumn 1972. This is the second effort to widen the channel of the creek, which receives the effluent from a nearby toxaphene-manufacturing plant: a 1971 dredging effort was aborted by the State of Georgia. The current study employed safeguards inspired by the 1971 State action: enclosure of dredge spoil in diked areas of unproductive marshland to prevent runoff, and weekly monitoring of Terry Creek biota and sediment to detect the possible role of toxaphene in any resulting disturbance to the balance of nature. Monitoring of dredge spoil, fauna, and flora showed toxaphene concentrations to be higher during dredging than before or after. Eastern oysters (*Crassostrea virginica*), reported to be among the best biological monitors, did not demonstrate large changes in toxaphene content resulting from the dredging. The high toxaphene concentration in oysters ranged between 2.0 and 5.0 ppm. The best indicators evaluated were salt marsh cordgrass (*Spartina alterniflora*) and mummichog (*Endulus heteroclitus*). The highest content found in *S. alterniflora* was 7.5 ppm; the highest concentration in *E. heteroclitus* was over 200 ppm.*

Introduction

A unique occasion to study the dispersal of the chlorinated hydrocarbon, toxaphene, and the relation of its concentration to waterway maintenance dredging arose near Brunswick, Ga. Terry Creek, which receives the effluent from a toxaphene-manufacturing plant, was the

site of a recent dredging operation. An earlier operation (1) had been aborted after 100 yards of dredging, when the State of Georgia objected that toxic products in the undiked spoil sediment might drain through the marshland on which the spoil was being deposited. Such drainage would contaminate both the potentially productive marshland and the estuarine ecosystem into which it drained. The current study initiated safeguards against such a contingency: enclosure of dredge spoil in diked areas of marshland which had been identified by remote sensing techniques (2,3) as less productive than the marshland initially used as deposit sites; and weekly monitoring of Terry Creek biota and sediment to detect the possible role of toxaphene in any resulting disturbance to the balance of nature.

The monitoring program which the U.S. Army Corps of Engineers, Savannah District, outlined in response to the State of Georgia was designed to document at weekly intervals the possible role of toxaphene in any ecologic disturbance resulting from the dredging of Terry Creek. Toxaphene concentrations were measured in selected estuarine fauna, flora, sediment, and dredge spoil during dredging. Findings were compared to the authors' earlier baseline studies of pesticide concentrations in the estuarine ecosystem, which revealed toxaphene in many portions of the food web and highly concentrated in the sediments of the creek (4).

Methods

Terry Creek was dredged by hydraulic pumping and 5 x 10⁶ cubic yards of spoil was placed in two diked

¹ Contribution No. 30, University of Georgia Marine Institute, Sapelo Island, Ga. 31327.

areas on a nearby salt marsh (areas C and D, Fig. 1). Collection sites for environmental samples are indicated in the same figure: A) Back River Bridge; B) mouth of Terry Creek; C) west dredge spoil area near the toxaphene plant outfall; D) east dredge spoil area near Back River; and E) main channel of Terry Creek. Field collections were obtained at weekly intervals beginning one week before dredging operations started on September 7, 1972, and terminating 8 weeks later, 1 week after the completion of all dredging on October 26, 1972. Additional baseline data on the toxaphene content of Terry Creek organisms were collected during 1970 and 1971 and followup collections continued at monthly intervals for several months. Environmental samples included finfish collected by otter trawl and cast net in the main channel of Terry Creek; salt marsh cordgrass (*Spartina alterniflora*) collected near the dredge spoil dike areas; sediment collected from the mouth of Terry Creek and from within each of the diked spoil areas; and oysters (*Crassostrea virginica*) collected from Back River Bridge.

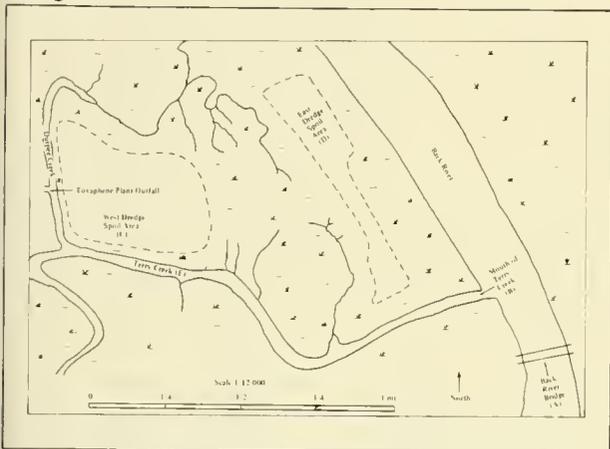


FIGURE 1.—Geographic location of collection sites near Terry Creek, Brunswick, Ga., 1972

Samples were processed and analyzed for toxaphene according to authors' methods in the earlier baseline studies (4) and the technique of Wilson (5). Specific details are summarized in Table 1. Chromatograms of environmental samples were so similar to chromatograms of technical grade toxaphene standard that no polychlorinated biphenyls were indicated. All concentrations are expressed in parts per million (ppm) wet weight except *S. alterniflora* which is based on dry weight. Prior to analysis, *S. alterniflora* plant parts were given four rinses in tap water to remove surface salt deposits. Each leaf and stem was then blotted dry with tissue to remove residual rinse water. The relative recovery from oysters and sediment was above 85 percent and 90 percent, respectively. Data were not corrected for this error and concentrations below 0.25 ppm were considered insignificant with the exception of those in-

cluded in water samples. Concentrations less than 0.0010 ppm were considered below the limits of detection.

TABLE 1.—Summary of column packing and operating parameters used for toxaphene analysis

Column:	5 ft by 1/8 in., glass, packed with 3% DC-200 on Gas Chrom Q, 80/100 mesh
Temperature:	Detector 210°C Injector 210°C Oven 190°C
Carrier:	Purified nitrogen at a flow rate of 40 ml/min

Results

Results of toxaphene analyses in fauna, flora, and sediment reveal that toxaphene was generally higher in dredge spoil sediment than in any other samples processed (Table 2). Comparisons of concentrations in mummichog (*Fundulus heteroclitus*), white shrimp (*Penaeus setiferus*), marsh grass, and sediment show that, except for dredge spoil within the diked areas, concentration rarely exceeded 10.0 ppm (Fig. 2-10).

Butler (6) demonstrated that shellfish can produce biological magnification of pesticide levels up to 70,000 times those of surrounding water. Yet the levels in oysters collected at Back River Bridge (Fig. 1) adjacent to the mouth of Terry Creek never exceeded 2.0 ppm during the dredging operation.

Toxaphene concentrations in dredge spoil from the western enclosure close to the toxaphene plant outfall (Fig. 1) neared 1,000 ppm (Fig. 5). The highly contaminated sediment in both the western and eastern enclosures was held within two dikes (Fig. 1) and did not appear to influence the surrounding biota.

Background toxaphene concentrations in 1970-71 collections of fauna, flora, and sediment exhibited higher values than 1971-72 concentrations. The latter values remained about the same before and after dredging, reflecting in part the pollution abatement practices initiated at the toxaphene production plant which greatly decreased the quantities of toxaphene in the plant effluent.

Discussion

Toxaphene contamination appears to be best indicated by the marsh grass (*S. alterniflora*). Various species of fish are also good indicators of the increased toxaphene in the suspended material and water. Although Butler (6) has suggested that shellfish are among the best biological monitors for pesticide residues, the results of this study suggest that marsh grass and finfish accumulate toxaphene to a greater degree than oysters (*Crassostrea virginica*) when all are collected from the same geo-

TABLE 2.—Toxaphene concentrations, ppm, found during fall 1972 monitoring of Terry Creek dredging operation¹

	REPLI- CATE NO.	CRUISE No. 1 (SEPT. 2)	CRUISE No. 2 (SEPT. 14)	CRUISE No. 3 (SEPT. 21)	CRUISE No. 4 (SEPT. 28)	CRUISE No. 5 (OCT. 5)	CRUISE No. 6 (OCT. 12)	CRUISE No. 7 (OCT. 19)	CRUISE No. 8 (OCT. 26)
Mummichog (<i>Fundulus heteroclitus</i>)	1	10.45	NSC	NSC	10.52	NSC	131.14	12.07	NSC
	2	8.97	NSC	NSC	3.41	NSC	217.14	5.18	NSC
Salt marsh cordgrass (<i>Spartina alterniflora</i>)	1	0.82	1.13	0.73	2.04	0.81	3.93	7.33	1.69
	2	0.76	1.56	0.56	2.54	0.91	3.68	6.26	2.92
Eastern oyster (<i>Crassostrea virginica</i>)	1	1.20	1.42	1.55	1.21	1.26	1.19	1.70	0.94
	2	1.37	1.33	1.71	1.15	1.23	1.24	1.79	0.95
Sediment (near entrance to Terry Creek)	1	5.47	5.56	0.87	2.11	5.55	3.97	2.11	2.64
	2	4.42	4.20	0.94	2.68	7.24	4.06	2.23	3.74
Dredge spoil from east enclosure (Back R.)	1	NSC	0.81	60.08	5.70	NSC	NSC	NSC	NSC
	2	NSC	0.79	150.79	5.12	NSC	NSC	NSC	NSC
Dredge spoil from west enclosure (Dupree C.)	1	NSC	NSC	NSC	NSC	93.39	756.40	51.64	241.64
	2	NSC	NSC	NSC	NSC	119.52	812.64	142.42	331.55
Water sample	1	ND	NSC	0.0013	0.0013	0.0016	0.0014	NSC	NSC
	2	ND	NSC	NAS	NAS	NAS	NAS	NSC	NSC
Anchovy (<i>Anchoa mitchelli</i>)	1	NSC	8.61	NSC	20.46	8.96	9.89	12.85	10.51
	2	NSC	NAS	NSC	16.60	NAS	10.13	11.96	NAS
Shrimp (<i>Penaeus setiferus</i>) head and thorax	1	NSC	1.21	4.80	3.22	3.03	2.88	4.19	10.69
	2	NSC	1.51	4.65	2.24	2.85	NAS	4.30	2.41
Shrimp (<i>Penaeus setiferus</i>) abdomen (edible tail)	1	NSC	0.58	0.86	1.22	0.92	1.49	0.74	2.51
	2	NSC	0.58	0.90	0.88	0.73	NAS	0.64	0.83
Star drum (<i>Stellifer lanceolatus</i>)	1	NSC	2.43	2.09	NSC	2.72	NSC	NSC	1.42
	2	NSC	2.61	3.24	NSC	2.48	NSC	NSC	1.09

¹ NSC—no sample collected; NAS—not adequate sample; ND—not detectable.

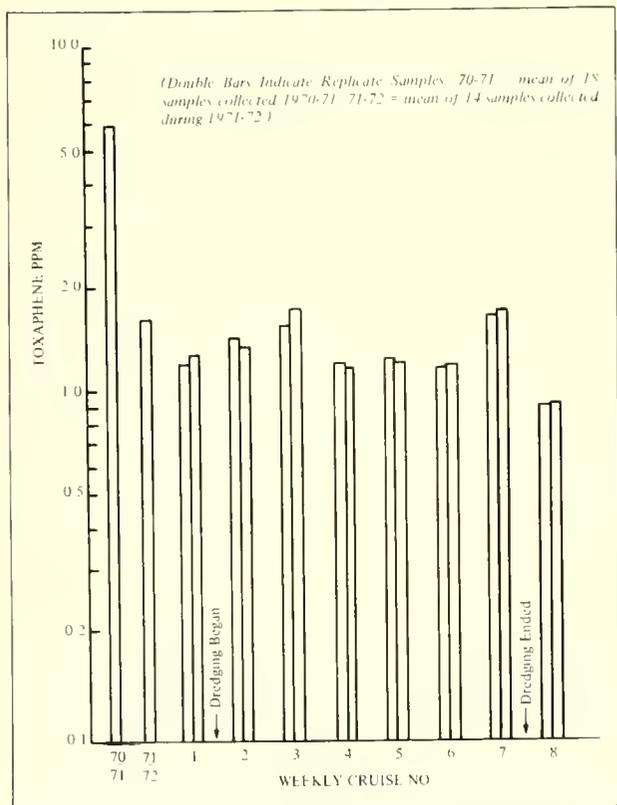


FIGURE 2.—Toxaphene concentration, ppm, in oysters (*Crassostrea virginica*) from Back River Bridge, Terry Creek, Brunswick, Ga., 1972

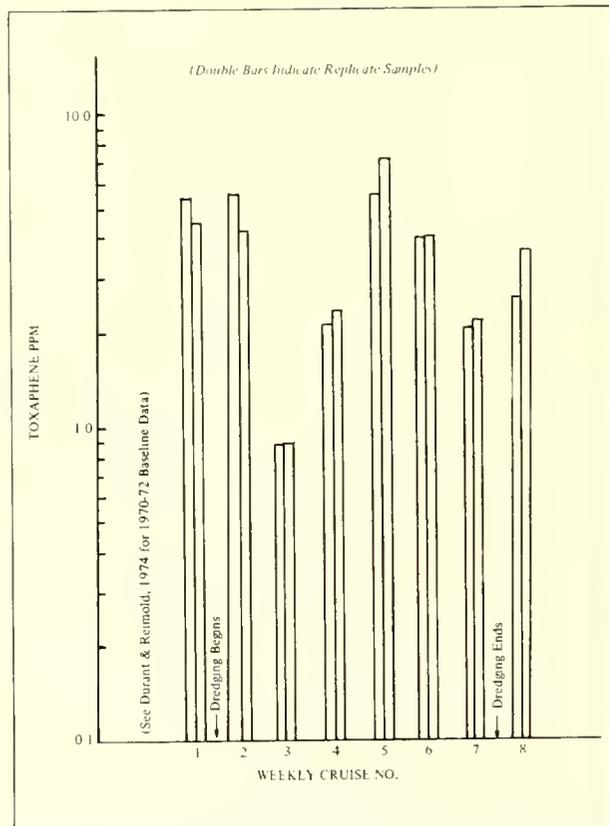


FIGURE 3.—Toxaphene concentration, ppm, in surface sediment from mouth of Terry Creek, Brunswick, Ga., 1972

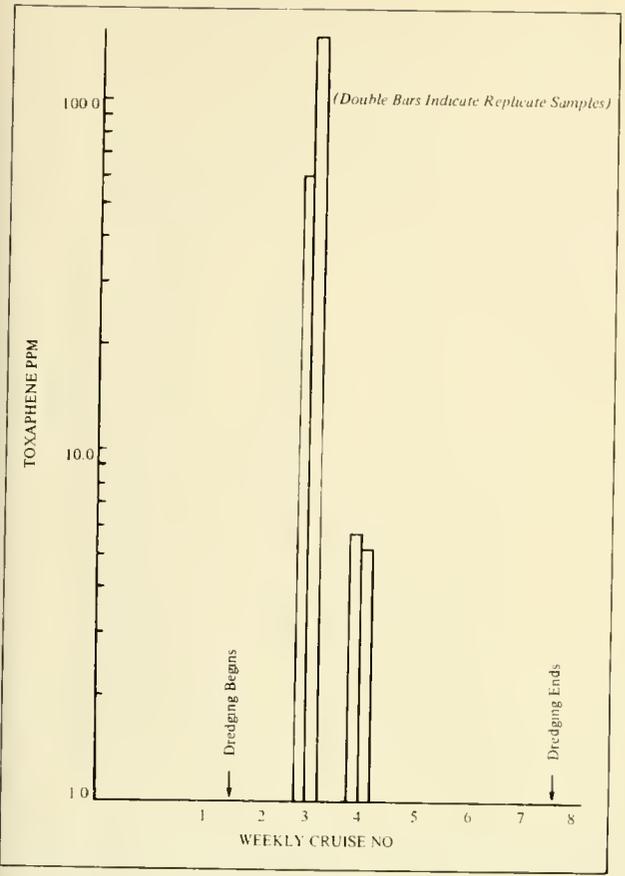


FIGURE 4.—Toxaphene concentration, ppm, in dredge spoil from east enclosure near Terry Creek, Brunswick, Ga., 1972

graphic location. The authors submit that different organisms may be able to preferentially concentrate different residues. Although relatively high concentrations of toxaphene were found in anchovy (*Anchoa mitchelli*), it was frequently absent from the trawl catch.

The high toxaphene content of *S. alterniflora* is of interest since it represents a translocation of toxaphene from the sediments into the plant tissue. *S. alterniflora* is a halophyte and probably translocates toxaphene along a pathway similar to the movement of salt. This is unique because it is one of the only known instances of toxaphene translocation in high concentrations among primary producers.

Altogether, over 125 samples were analyzed for toxaphene during the 8-week study. In addition, qualitative visual examination of the Terry Creek area was made at weekly intervals to assess potential fish kill. Fewer than 20 dead fish were recovered during the 8 collection trips of 4 to 5 hours each. Those recovered and positively identified included tongue-fish (*Symphurus sp.*) harvest fish (*Peprilus sp.*), silver perch (*Bairdiella sp.*), sea catfish (*Arius sp.*), and one menhaden (*Brevoortia sp.*).

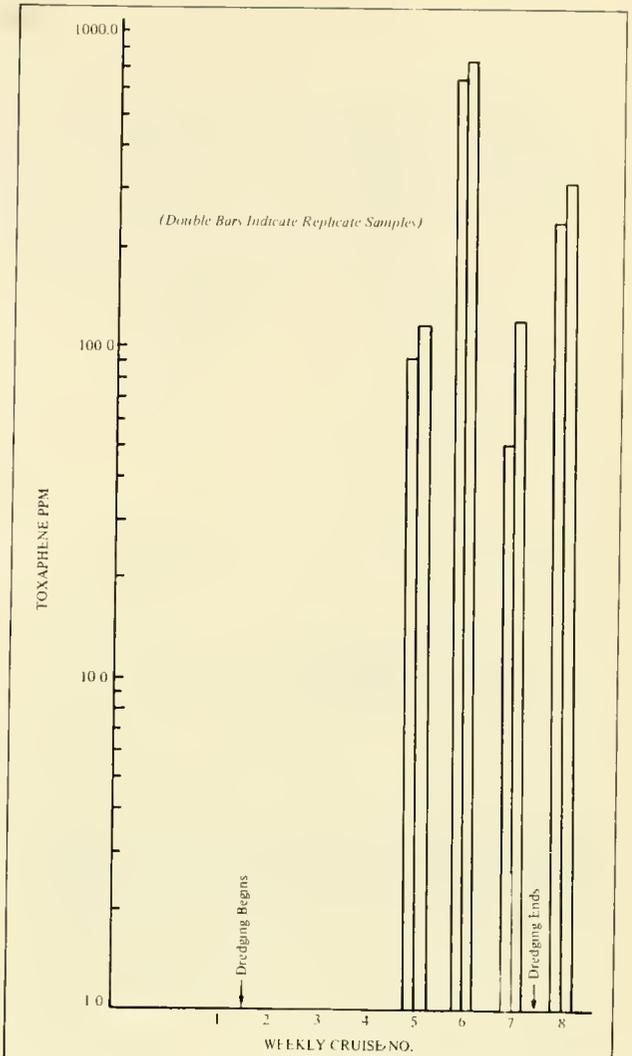


FIGURE 5.—Toxaphene concentration, ppm, in dredge spoil from west enclosure near Terry Creek, Brunswick, Ga., 1972

Local shrimp boats that dock in Terry Creek frequently offloaded and sorted catches during the study; this may well have been the source of dead fish, especially since the authors' sampling indicated that the species were not indigenous to Terry Creek. At no time were fish observed to be dying (alive but floating on the surface on their sides), nor did they show other signs of distress during the nearly 100 person-hours of field sampling in Terry Creek.

It is the conclusion of this study that dredging did not dramatically alter the biological balance of the estuary by toxaphene contamination when toxaphene residues were isolated in diked enclosures. As reported by the authors in the baseline studies (4), the combination of ultraviolet radiation and biological degradation should render the impounded sediments nontoxic in a few years.

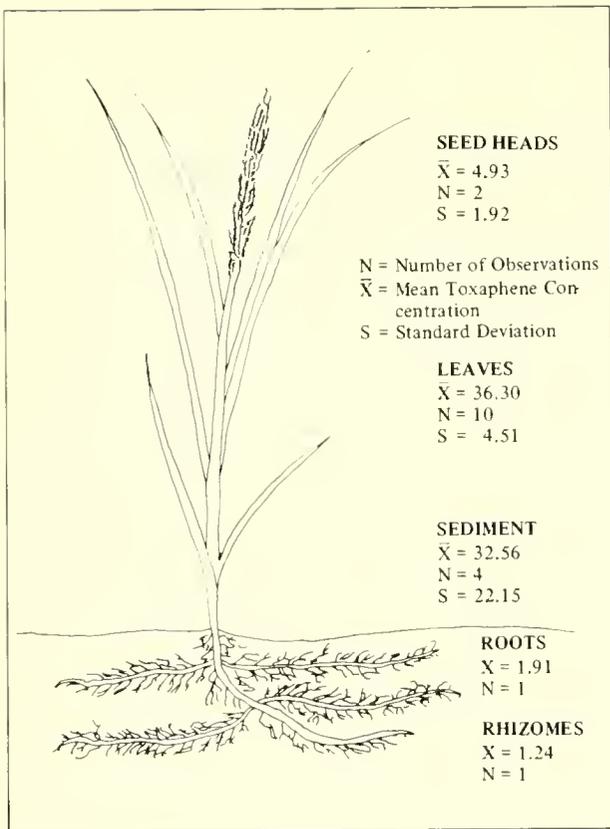


FIGURE 6.—Toxaphene concentration, ppm, in marsh grass (*Spartina alterniflora*) and surrounding sediments collected from Terry Creek Marsh, Brunswick, Ga., 1970-72

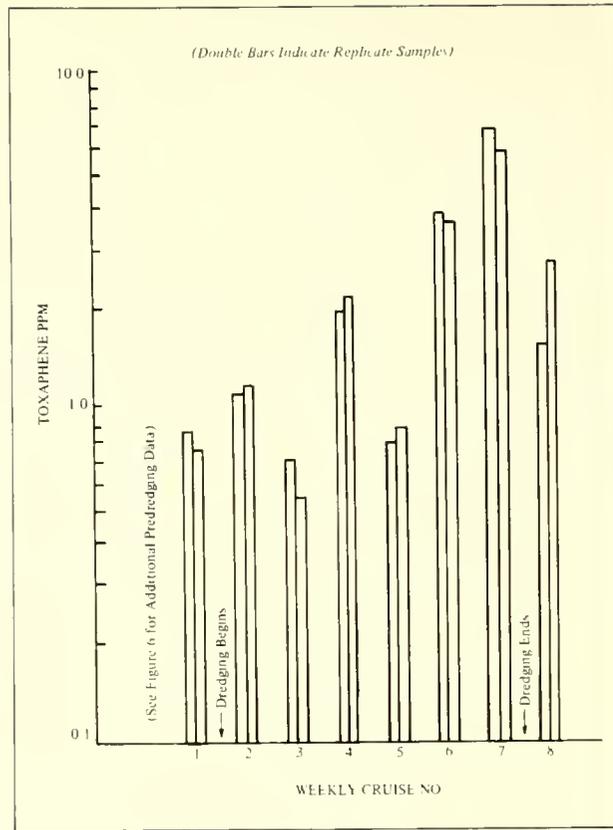


FIGURE 7.—Toxaphene concentration, ppm, in marsh grass (*Spartina alterniflora*) leaves and stems from bank of Back River near Terry Creek, Brunswick, Ga., 1972

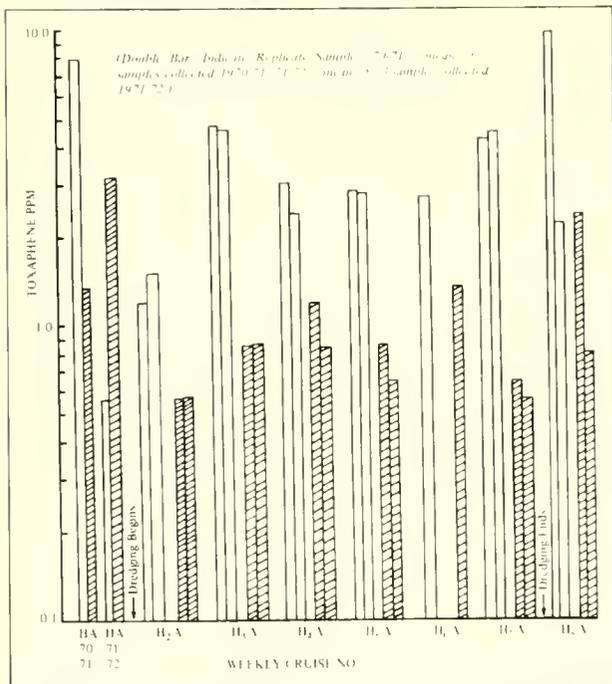


FIGURE 8.—Toxaphene concentration, ppm, in white shrimp (*Penaeus setiferus*) from Terry Creek, Brunswick, Ga., 1972

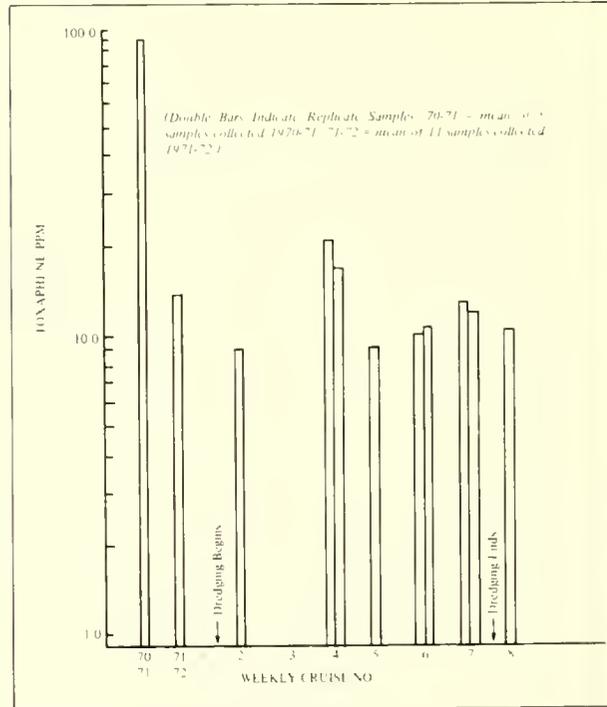


FIGURE 9.—Toxaphene concentration, ppm, in anchovy (*Anchoa mitchelli*) from Terry Creek, Brunswick, Ga., 1972

Acknowledgments

This research was supported by a grant from Hercules, Inc., to the University of Georgia Marine Institute and a contract between the Savannah District U.S. Army Corps of Engineers and the University of Georgia Marine Institute. The authors also wish to acknowledge the assistance of J. E. Durant and P. C. Adams for analysis and collection of the data.

LITERATURE CITED

- (1) Durant, C. J., and R. J. Reimold. 1972. Effects of estuarine dredging of toxaphene-contaminated sediments in Terry Creek, Brunswick, Ga.—1971. *Pestic. Monit. J.* 6(2):94-96.
- (2) Reimold, R. J., J. L. Gallagher, and D. E. Thompson. 1973. Remote sensing of tidal marsh. *Photogr. Eng.* Vol. 39, pp. 477-488.
- (3) Reimold, R. J., and R. A. Linthurst. 1974. Remote sensing—wetlands. Preprint No. 2143. Am. Soc. Civ. Eng. N.Y., N.Y. 19 pp.
- (4) Reimold, R. J., and C. J. Durant. 1972. Survey of toxaphene levels in Georgia estuaries. Georgia Marine Science Center, Technical Report Series No. 72-2. Skidaway Island, Ga.
- (5) Wilson, A. J., Jr. 1967. Pesticide analytical manual for BCF contracting agencies. USDI Bur. Commer. Fish. Gulf Breeze, Fla., pp. 1-11.
- (6) Butler, P. A. 1969. Monitoring pesticide pollution. *Bio-science* 19(10):889-891.

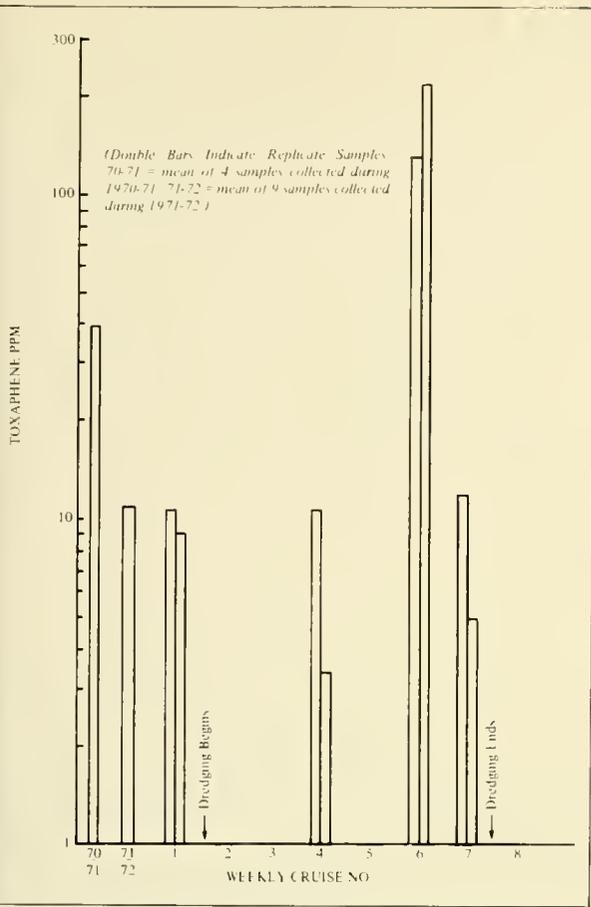


FIGURE 10.—Toxaphene concentration, ppm, in *Fundulus heteroclitus* from Terry Creek, Brunswick, Ga., 1972

GENERAL

Resmethrin Residues in Foliage after Aerial Application

Theresa L. Andrews¹

ABSTRACT

The residue present after aerial application of 0.05 and 0.15 lb per acre of the synthetic pyrethroid, resmethrin, was analyzed on three kinds of foliage and in water samples. The compound was identified by thin-layer chromatography (TLC) detecting from 0.06 to 0.25 ppm. The residue on aspen and Douglas fir showed that the initial deposit was light, and no detectable amount was found after seven days. The highest residue, 1 ppm, was found on willow taken the day of insecticide application. No detectable quantities were found in the water samples.

Introduction

As part of the U.S. Department of Agriculture Forest Service program to evaluate potential insecticides, a preliminary safety evaluation was conducted on the synthetic pyrethroid, resmethrin. The study was done on the Pike National Forest near Colorado Springs, Colorado, in cooperation with the U.S. Department of Interior Bureau of Sport Fisheries and Wildlife. This continuing program is designed to ascertain the hazards of insecticides to nontarget organisms such as birds, aquatic and terrestrial invertebrates, and fish.

This paper describes the method of detection, amount of deposit, and persistence of the insecticide resmethrin after spray application by helicopter at two dosage levels. This chemical was found to possess a high degree of activity on several forest insects (1).

Methods and Materials

Resmethrin is the proposed common name for 5-benzyl-3-furyl-methyl (\pm -cis, trans-chrysanthemate), a mixture of synthetic pyrethroid first described by Elliot, et al. (2). This mixture of isomers has been called NRDS 104,

SBP-1382, and NIA 17370. It is available commercially from S. B. Pennick and Co., New York, as SBP-1382.

Natural pyrethrins are easily analyzed by electron-capture gas chromatography, but resmethrin cannot be detected in this manner. The hydrogen flame detector could be used to detect 3 μ g of resmethrin. However, it was impossible to detect this quantity from plants because the extractives interfered with the hydrogen flame detection system.

Early investigation of the photostability of resmethrin was carried out by using Rhodamine B as a chromogenic detector on thin-layer chromatography (TLC). The greatest sensitivity was achieved with Isatin in sulfuric acid as a chromogenic agent. This chromogen was originally used to detect thiophene (3), and was developed for the detection of resmethrin at a 0.1- μ g level by Abernathy, et al. (4). Isatin sprayed on 10 μ l of control solutions of resmethrin in ethyl acetate (w/v) containing 0.1, 0.2, 0.5, 0.75, 1.0, and 2.5 μ g produced a stable, measurable, and readily detectable red spot on TLC plates. However, plant extracts produced interfering color in the presence of hot sulfuric acid. By moving the interfering materials to the front of the TLC with n-hexane, resmethrin could be identified on silica gel G (250 μ).

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Twenty grams of local plant material (willow, poplar, Englemann spruce, and Douglas fir) were treated with resmethrin at rates of 1.0, 5.0, 10, and 20 μg as preliminary plant fortified controls. The stems, needles, or leaves were cut into small segments and placed in Mason jars containing 20 ml of ethyl acetate. The jars were placed in an enclosed dry ice bin for 10 minutes. The ethyl acetate was decanted, and the frozen material was macerated with mortar and pestle and washed twice with 20 ml of ethyl acetate. The ethyl acetate fraction was evaporated under vacuum to around 5 ml and transferred to centrifuge tubes. The volume was evaporated with nitrogen to about 0.5 ml and centrifuged to remove the small particles. The clear supernatant was transferred, and the precipitate was washed three times with 1 ml of ethyl acetate. The samples were evaporated under nitrogen to the desired volume of 100 μl of which 10 μl was spotted on a TLC plate.

These samples were chromatographed in duplicate with 10 μl of the corresponding control standards of 0.1, 0.5, 1.0, and 2.0 μg of resmethrin on each plate. The plates were first developed with n-hexane to remove any interfering materials. After the plates were air-dried, two different solvent systems were used to move the resmethrin: one consisting of benzene, and the other of chloroform, ether, and ethyl acetate (2:1:2). After the plates were developed, they were sprayed with 0.5% satin in concentrated sulfuric acid (w/v). These fortified plant samples gave a red spot equal in color intensity and size to the 10 μl quantities of the control standard solutions. The R_f values for resmethrin were $0.50 \pm 6\%$ for benzene and $0.85 \pm 6\%$ for the chloroform, ether, ethyl acetate solution.

Resmethrin was applied by a helicopter on two separate plots at two dosage levels: 0.05 lb and 0.15 lb per 0.5 g of mineral oil per acre. Field samples of willow, aspen, and Douglas fir were collected from three different areas in the plots at three different times: immediately after spray application, three days later, and one week later. Samples of water were also taken from streams in these plots. All samples were immediately placed with dry ice until extracted.

Forty grams of each of the field plant samples were extracted and handled the same as the previous plant controls. All samples including controls were spotted on a TLC plate in a 10 μl volume. If quantities less than 0.06 ppm were found in 10 μl , no further concentration by evaporation of the plant extract was performed. If quantities greater than 0.25 ppm were found, then solutions were diluted so that 10 μl contained from 0.25 to 1.0 μg resmethrin.

Controls of 100 grams of laboratory tap and distilled water were fortified with 10 or 20 μg of resmethrin. Duplicate samples were placed in sealed quart jars in a

dry ice bin for periods of one hour, and for one, three, and seven days. The pH of the water varied from 6.7 to 6.9. These samples were washed three times with ethyl acetate in the same manner as the plant material. Since resmethrin is insoluble in water, no difficulties were encountered with the extraction procedure using 500 μl of ethyl acetate. The ethyl acetate was evaporated to a volume of 100 μl of which 10 μl was spotted on a TLC plate.

The field samples of water were taken from the lower, middle, and upper parts of a stream in each plot. Forty grams of each water sample was extracted three times with 500 ml of ethyl acetate. The samples were analyzed in duplicate in the same manner as the water controls. The small amount of debris in the field stream samples presented no problems during extraction. The pH varied from 5.4 to 5.8.

Results and Discussion

Immediately after the resmethrin was sprayed, no detectable residues were found on the aspen at the lower dose rates, but at the 0.15-lb rate, 0.8 ppm was found (Table 1). Only the willow samples showed a deposit as high as 1 ppm. The initial deposit was light; after seven days, no detectable residues were found. The <0.05 ppm designation was used when very faint traces were visible on the TLC. The results suggest that after aerial application of resmethrin at 0.05 and 0.15 lb/acre, no substantial residue remains after seven days.

TABLE 1.—Resmethrin residues, ppm, found days after aerial application on three types of plant foliage

PLANT	DAYS AFTER APPLICATION			CONTROL FORTIFIED WITH 0.5 PPM RESMETHRIN ¹
	0	3	7	
RATE: 0.05 LB/ACRE				
Aspen	0	0	0	—
	0	0	0	—
	0	0	0	0.4
Willow	1.0	0.3	<0.05	—
	1.0	0.3	0	—
	1.0	0.3	<0.05	0.5
Douglas fir	0.3	0	0	—
	0.3	0	0	—
	0.8	0	0	0.4
RATE: 0.15 LB/ACRE				
Aspen	0.8	0	0	—
	0	0	0	—
	0.4	0	0	0.5
Willow	0.8	0.5	<0.05	—
	0.5	0	0	—
	0.5	0.4	<0.05	0.5
Douglas fir	0.3	0	0	—
	0.5	0	0	—
	0.5	0	0	0.4

¹ Average of six samples analyzed with an accuracy of $\pm 7\%$.

Recovery of the 10 and 20 μg of the fortified water controls with resmethrin on the TLC plates were measured and remained unchanged within a 10 percent error. The water samples from the field showed no detectable quantities of resmethrin. Although the lesser application rate of 0.05 lb/acre of resmethrin had a fatal effect on most of the aquatic insects in the 1-hour postspray period, no toxic effects were observed in fish held in cages in the stream (5). The fact that no resmethrin was recovered from the aquatic samples even though insect mortality was high obviously indicated substantial degradation, considerable dilution of the insecticide, or insufficient understanding of resmethrin within the environment.

LITERATURE CITED

- (1) *Unpublished report. March 1, 1971.* Pacific Southwest Forest and Range Experiment Station, Berkeley, Calif.
- (2) *Elliot, M., A. W. Farnham, N. F. James, P. Needham, and B. C. Pearson. 1967.* A new potent insecticide. *Nature* 213, (5075) 493-494.
- (3) *Curtis, P. F., and G. T. Phillip. 1962.* Isatin as a chromogenic agent for detection of thiopene. *J. Chromatogr.* 9 (11): 366.
- (4) *Abernathy, C. O., J. E. Casida, and I. Yamamoto. 1971.* Division of Entomology, University of California, Berkeley, Calif. Unpublished results.
- (5) *Shea, P. J. 1971.* Unpublished report. Pacific Southwest Forest and Range Experiment Station, Berkeley, Calif.

Detection of DCPA Residues in Environmental Samples

F. M. Miller and E. D. Gomes

ABSTRACT

DCPA was detected in river water, five species of fish, and air in the lower Rio Grande Valley of Texas. Its presence was determined by electron-capture gas-liquid chromatography and confirmed by several analytical methods. Analyses of water samples taken over a 2-year period usually indicated less than 1 ppb DCPA in water during both years. Residues in one freshwater and four saltwater fish species varied from less than 1 ppb to 8 ppm. DCPA was found in air samples for several months following use in a vegetable-growing area.

Introduction

DCPA (Dimethyl tetrachloroterephthalate) is a herbicide that is sold under several brand names for control of grasses and weeds in turf and gardens and for use in commercial agriculture. In the lower Rio Grande Valley, DCPA is used primarily as a pre-emergence herbicide on onion soils and to a lesser extent on cabbage and cotton crops.

This chlorinated hydrocarbon pesticide is of low solubility, is adsorbed by organic matter in soil, and does not leach in any of the general soil types. Its average half-life is 100 days in most soil types and it is relatively nontoxic to animal species that have been tested (1).

During 1969 onion soils were sampled in 10 states; 46.5 percent had traces (0.94 ppm) of DCPA. This is in contrast to a nationwide sampling of croplands during 1969 in which only 0.1 percent of the 1,729 samples tested showed traces of DCPA (2,3). The herbicide has also been detected in air samples from an onion-growing area in Colorado (4).

This report, which presents data from several studies, indicates rather widespread environmental contamination by a chlorinated pesticide. Aquatic sampling of the two major streams in this area was initiated in 1971 to detect differences in pesticide contamination over a period of time. In 1972 selected tissues from two large samples of speckled trout were analyzed to determine the level of chlorinated hydrocarbon pesticides present. Air samples were analyzed for pesticides during 1972 as a part of a national monitoring program (5). Several miscellaneous samples were taken after analytical confirmation of DCPA. Because contamination of streams and fish has not been reported previously, all available data are presented in this paper. All studies were conducted in the lower Rio Grande Valley of Texas, an intensely agricultural area.

Methods and Materials

SAMPLING

Two sampling sites, one on each of the two major waterways in the lower Rio Grande Valley, were monitored in 1971 for chlorinated hydrocarbon pesticides. One sample of unfiltered water, bottom sediment, and menhaden (*Brevoortia* sp.) was taken each month from the Arroyo Colorado at a brackish water location near the port which is east of Harlingen (Fig. 1). Only water and bottom sediment samples were taken at the second Rio Grande site near Los Indios. Bottom sediment and water samples were taken in solvent-rinsed containers near the bank; the menhaden were collected by cast netting near the middle of the stream.

In 1972 two large samples of spotted seatrout (*Cynoscion nebulosus*) were taken by bait casting in the Three

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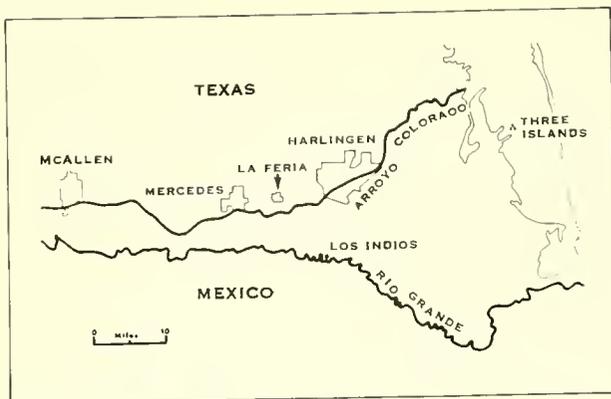


FIGURE 1. Map of Lower Rio Grande Valley showing sampling sites for DCPA

Islands area of the lower Laguna Madre. One sample was taken during May and the other was collected in July. The length, weight, and sex of each fish were recorded. Each speckled trout was dissected and the ovaries or testes, liver, and 10 g of edible flesh were removed and frozen until analyzed. Several Rio Grande perch (*Cichlasoma cyanoguttatum*) were collected at various freshwater locations along the Arroyo Colorado (Table 1, Fig. 1), and were dissected in the same manner to obtain similar tissues when possible. Collectors caught one mullet (*Mugil* sp.) while gathering menhaden. Two speckled trout and one red drum (*Sciaenops ocellata*) were collected and analyzed for residues of DCPA during 1973.

Air samples were taken from two locations in each of two cities from February 1972 until January 1973. One MisCo high-volume sampler was placed near the center and one on the periphery of each city. Approximately 61 cubic meters of air were sampled at each location over a 24-hour period. The combined samples from each city were analyzed as one sample. Weekly samples were taken alternately from each city.

ANALYTICAL PROCEDURES

A 1-liter water sample was extracted with 150 ml of hexane in a 2-liter separatory funnel. The contents were shaken vigorously for 2 minutes with venting and allowed to settle until the layers separated. The hexane layer was removed and another 150-ml portion of hexane was added to the water sample. Then the procedure was repeated. The two 150-ml extracts were combined and a small amount of sodium sulfate was added to absorb any water remaining in the extract. The sample was transferred to a 500-ml Kuderna-Danish evaporative concentrator and concentrated to 5 ml followed by Florisil cleanup (6).

Each 25-g bottom sediment sample was placed in a 250-ml Erlenmeyer flask, 150 ml of acetonitrile was added, and the sample was shaken for 1 hour at 3

agitations per second on a wrist-action shaker. The entire sample was filtered through a solvent-rinsed glass wool filter into a 1-liter separatory funnel containing 500 ml of water. The soil remaining on the filter was rinsed twice with 25 ml of acetonitrile. The acetonitrile/water mixture was partitioned twice with petroleum ether. The petroleum/ether extract was concentrated and passed through Florisil for cleanup.

Fish samples were analyzed by taking approximately 25 g of menhaden, 10 g of trout flesh, 5 g of perch flesh, and the entire ovaries, testes, or liver. Each sample was weighed and placed in a stainless steel Omni-mixer cup, 50 ml of acetonitrile were added, and the sample was blended at medium speed for 5 minutes. The ovaries were ground in a mortar with sodium sulfate and petroleum ether. The ground or blended extract was filtered through a solvent-rinsed, glass wool filter into a 1-liter separatory funnel. The sample filtercake was rinsed with 25 ml of acetonitrile; to this was added 130 ml of petroleum ether and the mixture was shaken for 2 minutes. Then 600 ml of water was added, the sample was shaken again for about 1 minute, the 2 layers were allowed to separate, and the aqueous layer was discarded. Approximately 200 ml of water was added again. The sample was shaken; the layers were allowed to separate; and the water was discarded again, removing the remaining acetonitrile. The petroleum ether extract was concentrated and cleaned on a Florisil column.

Air samples were collected by drawing atmospheric air through ethylene glycol. The samples were extracted with hexane and were cleaned on a Florisil column (7).

When Florisil cleanup was employed, DCPA eluted in the 15 percent fraction. This fraction was concentrated to 5 ml and analyzed by gas-liquid chromatography (GLC).

Routine pesticide analyses were accomplished with Micro-Tek 220 gas chromatographs that were equipped as follows:

Detector:	electron-capture tritium foil; 20 volts.
Columns:	1.5% OV-17/1.95% QF-1 on Chromosorb W 100/120 mesh H.P.; 4% SE-30/6% QF-1 on Chromosorb W, H.P.; 1.6% OV-210/6.4% OV-17 on Gas Chrom Q; 5% OV-210 on Gas Chrom Q.
Temperatures:	Inlet 225°C Detector 205°C Columns OV-17/QF-1, SE-30/QF-1, and OV-210/OV-17 at 200°C OV-210 at 175°C.
Carrier gas:	Nitrogen.
Flow rate:	OV-17/QF-1, 80 cc/min; OV-17/OV-210, 65 cc/min; SE-30/QF-1, 75 cc/min; OV-210, 60 cc/min.
Sensitivity:	½ FSD with 50 pg of aldrin.
Electrometer setting:	10x16.

TABLE 1.—DCPA Residues in Three Species of Fish

DATE COLLECTED	SITE OF COLLECTION	SPECIES	TISSUE	DCPA RESIDUE, PPB
November 1972	Arroyo Colorado, Harlingen	Mullet	skin flesh viscera	555 159 231
December 1972	Arroyo Colorado, Harlingen	Rio Grande Perch	liver ovaries flesh	468 420 217
		Rio Grande Perch	liver ovaries flesh	388 212 89
February 1973	Arroyo Colorado, La Feria	Rio Grande Perch	liver ovaries flesh	215 107 29
February 1973	Arroyo Colorado, Mercedes	Rio Grande Perch	liver flesh	190 0
March 1973	Arroyo Colorado, Mercedes	Rio Grande Perch (1 sample; 2 small fish)	flesh	90
March 1973	Three Islands, Laguna Madre	Redfish	liver testes flesh	18 132 0

Recovery studies were conducted with unfiltered arroyo water and trout flesh. Mean DCPA recovery from water samples was 97 percent, with 88 percent recovery from fish flesh. All results are presented as unadjusted values.

CONFIRMATORY TECHNIQUES

In addition to GLC analyses, three other confirmatory techniques were used. The extracts of several arroyo water samples (20 gallons) were pooled and the presence of DCPA was confirmed by infrared analysis. The KBr micropellet was scanned on a Perkin-Elmer 337 Grating Infrared Spectrophotometer.

Several fish and water samples were analyzed by a thin-layer chromatography/GLC technique (TLC-GLC) (7). Since there was not enough DCPA to develop on the TLC plate, the R_f value was determined. A portion of the Al_2O_3 on the TLC plate was removed at the indicated point, extracted with hexane, and analyzed on the gas chromatograph.

Two samples were analyzed by GLC/mass spectrometry (GLC-MS) (8). The first sample, a pooled extract of menhaden, was cleaned up by thin-layer chromatography. When the fish extract showed many interfering substances, a second and much cleaner sample was obtained by extracting 10 gallons of arroyo water.

Results and Discussion

Since 1971 routine samples of soil, water, and menhaden have been taken from the Arroyo Colorado and analyzed by GLC. Some of the unfiltered water samples collected in 1971 showed a very prominent peak which eluted at the same retention time as that of heptachlor epoxide on OV-17/QF-1 and SE-30/QF-1 columns. Analyses of samples in the past have indicated little heptachlor or

heptachlor epoxide in the Rio Grande Valley. A closer look at this mystery peak revealed a difference of 0.05 relative retention time units from that of heptachlor epoxide on the OV-210/SE-30 column. At that time, the peak was tentatively identified as DCPA. The 1972 water samples showed greater concentrations of the chemical during the fall of the year. Air samples also revealed a substance with an identical retention time. During this same time period, some of the menhaden and trout being analyzed were demonstrating this peak in tissue, liver, and reproductive organs, indicating some persistence of the chemical in the aquatic and estuarine environment. Confirmatory procedures were initiated during the latter months of 1972.

CONFIRMATORY PROCEDURES

In 1972, the OV-210 GLC column proved to be of great importance in identifying DCPA. The most critical differentiation was between heptachlor epoxide and DCPA, which elute with almost the same relative retention time on columns other than the OV-210. Most of the commonly used chlorinated hydrocarbon pesticides elute in the same general sequence when using columns such as the OV-210/OV-17 (Fig. 2). With the OV-210 column, however, the relative retention times of some chlorinated hydrocarbons differ. Heptachlor epoxide increases slightly, but the retention time of DCPA is much greater than that of heptachlor epoxide (Fig. 2).

Several samples were analyzed by flame photometric detection, indicating that the substance was not a phosphorus- or sulfur-bearing compound. The TLC-GLC technique confirmed DCPA in several fish and water samples.

A relatively pure sample of DCPA was difficult to obtain, but its presence in arroyo water was confirmed by infra-

red spectrophotometry (Fig. 3). The subnanogram amounts of DCPA in arroyo water necessitated the extraction of 20 gallons of the water in order to collect enough DCPA for infrared analysis. GLC-MS analyses confirmed the presence of DCPA in water and fish samples.

WATER AND SEDIMENT

In 1971 DCPA was identified in unfiltered water samples by GLC (Table 2). Trace amounts were found only in water, and were not confirmed by other techniques. Similar low residue levels were found throughout 1972 and 1973. Although the monthly sample in September 1972 was negative, an additional sample taken on the same date at a nearby location revealed the highest recorded water value of 132 ppb. Another unfiltered sample taken at the Harlingen site later in September contained 0.91 ppb DCPA. Likewise, two additional samples taken during another negative month, December 1972, contained 0.35 and 0.40 ppb DCPA. It is obvious that monthly sampling does not give an

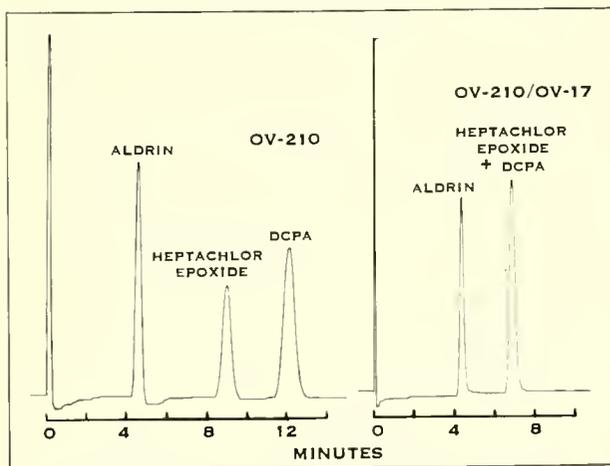


FIGURE 2.—Gas chromatograms showing differences in elution pattern between OV-210 and OV-210/OV-17 column materials

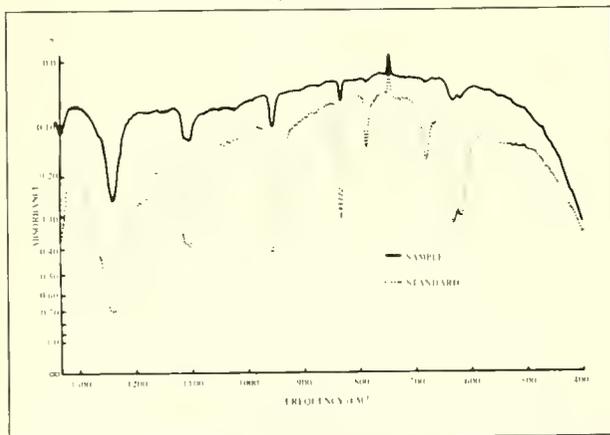


FIGURE 3.—Infrared spectral comparison of DCPA standard and water sample, showing confirmation of DCPA in arroyo water

accurate estimate of the amount of DCPA in the stream. Only one DCPA residue of 0.08 ppb was found in water samples from the Rio Grande, possibly because most of the lower Rio Grande Valley drains into the Arroyo Colorado rather than into the Rio Grande.

Only one bottom-sediment sample contained a trace (42 ppb) of DCPA. Water samples were analyzed without removing the particulate matter; it is not known whether the DCPA residues are in the water or in association with suspended particles.

MENHADEN

Monthly samples of menhaden did not reveal any DCPA residues until March 1972 (Table 2). Each sample included 25 g of the small fish with the heads and tails removed. Since specific tissues were not analyzed, these results cannot be directly related to the values for other fish. Based on current procedures, however, it appears that the menhaden contain greater amounts of DCPA than the other species of fish sampled to date. The higher residue values probably are not due to contamination from the gut contents because the gut was extracted separately on several occasions and residues were less than those in the remainder of the tissues.

As with the water residue, the amount of DCPA in menhaden varied widely. In November an additional sample taken at a site nearby contained 7.27 ppb DCPA; the regularly scheduled sample had only 0.52 ppb.

OTHER FISH

In May and July 1972, two large samples of speckled trout were collected for chlorinated hydrocarbon analysis. The May collection of 58 females and 8 males averaged 38 cm in length and 500 g in weight. Testing showed that 29 percent of the females and 50 percent of the males in this collection contained DCPA in one or more tissues (Table 3). Overall, the highest levels were found in the liver tissues, although these were not always positive when other tissues were. The greatest amounts recorded for liver, ovaries, testes, and flesh were 196, 85, 200, and 26 ppb, respectively.

The second sample of 9 females and 10 males averaged 38 cm in length and weighed 568 g. DCPA was not present in any of the tissues. No effort was made to determine whether the two samples were from the same fish population. Two speckled trout (427 g and 257 g) collected during March 1973 also had DCPA residues.

Several other species of fish (Table 1) were collected after the initial detection of DCPA in fish. Analysis of one mullet showed residues comparable to those found in menhaden of the same collection. Five samples of Rio Grande perch were collected at various locations along the Arroyo Colorado over a 4-month period. DCPA residues in the flesh varied from 0 to 217 ppb. One redfish had a trace of DCPA in the liver and testes.

TABLE 2.—DCPA residues in unfiltered water samples and menhaden from Arroyo Colorado near Harlingen, Tex.

MONTH	DCPA RESIDUES					
	1971		1972		1973	
	WATER, PPB	FISH, PPM	WATER, PPB	FISH, PPM	WATER, PPB	FISH, PPM
January	0.12	0	0	0	0.59	0.97
February	0.05	0	0.08	0	1.59	—
March	0	0	0	2.78	1.05	2.78
April	0.23	0	0.15	0	0.83	0.22
May	0.10	0	0	0	0.47	0.27
June	0.02	0	0.02	0	0.02	1.07
July	0	0	0	0	0.04	0
August	0	0	0.03	0	0.06	0
September	0	0	0	0.35	0.05	0
October	0	0	1.25	8.15	0.18	0.24
November	10.00	0	0.96	0.52	1.09	0.05
December	0	0	0	1.75	0.55	0

TABLE 3.—Residues of DCPA in spotted sea trout from Three Islands, Laguna Madre

DATE COLLECTED	NUMBER AND SEX OF FISH ANALYZED	TOTAL FISH WITH RESIDUES		TISSUE SAMPLED	FISH WITH RESIDUES		MEAN RESIDUE, PPB	
		No.	%		No.	%	PER SAMPLE	PER POSITIVE SAMPLE
May 1972	58 females	17	29	liver	8	14	8	60
				ovaries	14	24	8	36
				flesh	3	5	1	16
	8 males	4	50	liver	4	50	56	112
				testes	2	25	35	28
				flesh	0	0	0	0
July 1972	9 females	0	0	liver				
				ovaries				
				flesh	0	0	0	0
	10 males	0	0	liver				
				testes				
				flesh				
March 1973	1 female	1	—	liver	1	100	1	1
				ovaries	1	100	1	1
				flesh	0	0	0	0
	1 male	1	—	liver	1	100	472	472
			flesh	1	100	55	55	

AIR MONITORING

Weekly air monitoring of the lower Rio Grande Valley alternately sampling the Harlingen and McAllen areas showed no DCPA residues from February to September 1972. Of 17 weekly samples taken from September through December, 11 were positive for DCPA. Routine weekly air sampling was discontinued at the end of December, but three additional samples were taken during 1973. A trace of DCPA was found in early January 1973, but none was detected in samples taken later in January and in March.

As might be anticipated, the residues were found during the first part of the vegetable-growing season and residues were higher in the vegetable-growing area. Mean air sample values for the 4-month period with DCPA residues during the fall was $1.94 \mu\text{g}/\text{m}^3$ with extreme values of 0.90 and $8.62 \mu\text{g}/\text{m}^3$. Higher levels were

found in samples near McAllen, a vegetable-growing area, than in those from Harlingen during the same time period. Mean residues per positive sample were 4.73 and $2.59 \mu\text{g}/\text{m}^3$ for McAllen and Harlingen, respectively.

Conclusion

DCPA is a frequent, although intermittent, chlorinated hydrocarbon contaminant of the aquatic and estuarine environments of the lower Rio Grande Valley. How long it persists in these environments is unknown; it is probably very transient, because it is readily broken down by microorganisms in soils (9). Hexachlorobenzene (HCB) residues have not been found in environmental samples from this area although the commercial DCPA preparation may have up to 10 percent HCB in some formulations (10). The source of aquatic contamination

with DCPA is unknown at this time. It seems unlikely that windblown residues or contamination from a single spill could account for the presence of these residues over this period of time.

To date, DCPA has not been detected in water in amounts that might cause acute intoxication of fish. Investigation is needed, however, to determine subacute toxicity of this compound to fish at low levels. Investigation of the method by which DCPA enters the aquatic ecosystem is also needed.

Acknowledgments

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LITERATURE CITED

- (1) *Weed Science Society of America. 1970. Herbicide Handbook of the Weed Science Society of America. Second Edition. Department of Agronomy, University of Illinois, Urbana, Ill. 368 pp.*
- (2) *Wiersma, G. B., W. G. Mitchell, and C. L. Stanford. 1972. Pesticide residues in onions and soil—1969. Pestic. Monit. J. 5(4):345-347.*
- (3) *Wiersma, G. B., H. Tai, and P. F. Sand. 1972. Pesticide residue levels in soils. FY 1969—national soils monitoring program. Pestic. Monit. J. 6(3):194-201.*
- (4) *Tessari, J. D., and D. L. Spencer. 1971. Air sampling for pesticides in human environment. J. Ass. Offic. Anal. Chem. 54(6):1376-1382.*
- (5) *Stanley, C. W., J. E. Barney II, M. R. Helton, and A. R. Yobs. 1971. Measurement of atmospheric levels of pesticides. Environ. Sci. Technol. 5(5):430-435.*
- (6) *Mills, P. A. 1961. Collaborative study of certain chlorinated organic pesticides in dairy products. J. Ass. Offic. Agr. Chem. 44(2): 171-177.*
- (7) *Thompson, J. F., ed. 1971. Manual of Analytical Methods. Perrine Primate Research Laboratory, U.S. Environmental Protection Agency—Office of Research and Development, Perrine, Fla.*
- (8) *Biros, F. J., and A. C. Walker. 1970. Pesticide residue analysis in human tissue by combined gas chromatography—mass spectrometry. Agric. Food Chem. 18(3) 425-429.*
- (9) *Bone, H. T. 1970. The breakdown of dimethyl 2,3,5,6 tetrachloroterephthalate (DCPA) in soil and its effect on certain processes of soil microorganisms. Doctoral dissertation, plant pathology. The University of Wisconsin, Madison, 105 pp.*
- (10) *Wapensky, L. A. 1969. Collaborative study of gas chromatographic and infrared methods for Dacthal formulations. J. Ass. Offic. Anal. Chem. 52(6):1284-1292.*

Degradation of Four Organophosphate Insecticides in Grape Tissues

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ABSTRACT

Four organophosphate pesticides were applied to field-grown grapes at maximum recommended rates for pest control in Fresno County, Calif. Periodic sampling and analyses were carried out for each pesticide immediately before and following application on leaves, bark, cane, fruit, and soil. At harvest time 42 days after the initial application, azinphosmethyl and ethion residues were found on leaves at approximately 0 percent and 2.5 percent, respectively, of their original levels. Phosalone, applied 14 days after the azinphosmethyl and ethion treatment, still had about 30 percent of its original residue at harvest time; naled residues were not detected (<0.10 ppm) 4 days after application. Residues on cane and bark were quite stable and accounted for a relatively high percentage of the total residues found on the plant at harvest. Total extracted residues found on the plant at harvest amounted to approximately 280 ppm.

Introduction

During the summer of 1970, 51 acres of Thompson seedless grapes were set aside in Fresno County, Calif., for the purpose of spraying with four different organophosphate insecticides at rates normally recommended for pest control and within the minimum time period permitted by Federal regulation. Related data on cholinesterase depressions in farm workers exposed to pesticide residues are reported by Bailey, et al. (1). The article at hand deals only with the deposit and degrada-

tion of the respective chemicals following application. Very little, if any, published information is available concerning safe reentry times for field workers following application of pesticides on grapes. This study aimed to determine the degradation pattern of the chemical in the various grape tissues in the treated vineyard, and whether a potential problem exists for workers who might be exposed to that chemical. If a possible health problem exists, further studies will be necessary to determine safe reentry times following application.

Methods and Procedures

Four organophosphate pesticides were applied in five replicate plots on 51 acres in Fresno County, Calif., beginning August 27, 1970. One application of each insecticide was applied to each replicate plot on staggered days to see whether different days of application would give appreciably different residue levels. The four pesticides selected were ethion or Nialate^R, azinphosmethyl or Guthion^R, naled or Dibrom^R, and phosalone or Zolone^R. Some of the more toxic metabolites and degradation products were also analyzed. For example, dichlorvos or DDVP, 2,2-dichlorovinyl dimethyl phosphate, is a degradation product of naled and was thus analyzed with naled. Chemical structures of these pesticides and their oxygen analogs are shown in Figure 1. Table 1 shows the rate and formulation of each insecticide application, and the interval between treatment and harvest. Amounts actually applied were a little higher in the first two applications than those originally planned because of a miscalculation concern-

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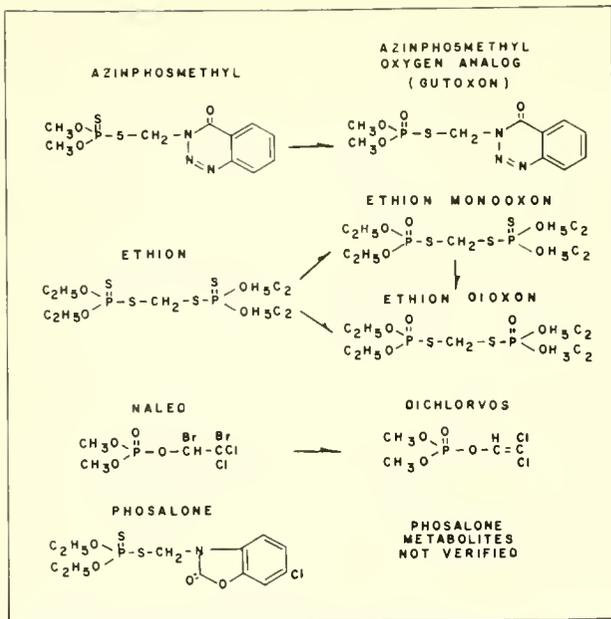


FIGURE 1.—Chemical structures of azinphosmethyl, ethion, naled, phosalone, and their oxygen analogs

TABLE 1.—Insecticides applied to grape fields in Fresno County, Calif., 1970

INSECTICIDE	FORMULATION ¹	ACTIVE INGREDIENT, LB/ACRE	DAYS: APPLICATION TO HARVEST
Ethion	25% WP	1.60	42
Azinphosmethyl	50% WP	1.90	42
Phosalone	3 lb/gal EC	3.00	28
Naled	8 lb/gal EC	1.00	14

¹ WP: wettable powder.

ing the spraying apparatus. But such an error is not unlike a typical field application. Periodic samplings, starting with a pre-application sample, were continued throughout the growing season until harvest. Samples were taken on leaves, bark, cane, fruit, and the surface inch of soil immediately below the plants. In all samplings, random samples were selected from inside and outside each plant.

Following sampling, specimens were immediately placed in a dry-ice chest and kept frozen at subzero temperatures until extracted into an organic solvent. A mixture of 10 percent methanol in chloroform was selected as the final organic solvent. As reported by Bowman and Beroza in 1968 (2), this solvent system was superior for extracting the oxygen analogs and degradation products as well as the parent materials for the many organophosphate pesticides studied. Samples of leaves, bark, and cane weighing 100 g were placed in a 2-liter Erlenmeyer flask and shaken with 1,000 ml of solvent on a rotary shaker for 30 minutes. The solvent was filtered through anhydrous sodium sulfate into a glass storage bottle and stored in the dark until analyzed.

Purification of samples was not considered necessary except to analyze ethion and the oxygen analogs. Interfering materials were removed from the ethion extracts by evaporating a portion of extract representing 10 g of crop to dryness, then adding 10 ml of benzene. A chromatographic column was prepared by placing a plug of glass wool into a 2.0-by-11.0-cm borosilicate glass chromatographic tube with a 250-ml reservoir attached to the top. The column was packed with 9 cm of activated florisil and topped with 2 cm of granular anhydrous sodium sulfate, then washed with 80 ml of benzene which was subsequently discarded. The sample was transferred to the column and eluted with 50 ml of 10 percent ethyl ether in benzene. The solvent was evaporated and the residue remaining was transferred with acetone to a McNaught and McKay-Shevky-Stafford sedimentation tube. The sample was then made to a known volume before injecting into the gas chromatograph.

Oxidized analogs of ethion and azinphosmethyl on leaves were also separated from their interfering materials by means of an activated florisil column. Four separate solvent mixtures were added to the column, with an increase in polarity with each subsequent solvent mixture. The first fraction included 200 ml of benzene; this was followed by 100 ml of 25 percent ethyl ether in benzene, 100 ml of 25 percent acetone in benzene, and a fourth and final fraction of 50 ml of acetone. Fractions one through three contained ethion monooxon and the last two fractions contained ethion dioxon, as well as the oxygen analog of azinphosmethyl commonly referred to as gutoxon. Because the third fraction of 25 percent acetone in benzene contained both ethion monooxon and ethion dioxon, the residue analysis of each product was cleaned separately. Metabolites of phosalone were not analyzed routinely because of interfering substances and the inability to isolate specific products. Analyses before and after cleanup were tried with gas liquid chromatography and thin-layer chromatography (GLC and TLC).

There were no detectable phosphorus compounds besides those already mentioned following the application of phosalone to the treated plots. Thin-layer chromatography, however, did reveal so many cholinesterase inhibiting spots on the chromatogram that separation and detection from known cholinesterase-inhibiting products was impossible. Since gas chromatography did not give any appreciable residues for the metabolites, it was assumed that the enzyme detection system used for thin-layer chromatography was that much more sensitive than that of gas chromatography. Because GLC measured only the phosphorus element as it passed through the gas-chromatographic column, it was concluded that the relative amount of the metabolites of phosalone was most likely insignificant.

Soil samples were handled somewhat differently than bark, cane, and leaf samples. They were moistened with water only until the soil became glossy, and were shaken on a rotary shaker for 30 minutes with the extracting solvent. The solvent was filtered through anhydrous sodium sulfate and handled in accordance with the other samples of bark, cane, and leaves. All fruit samples were analyzed for total residue by chopping the frozen grapes in a Hobart food chopper, transferring 100 g into a blender with 400 ml of stripping solvent, blending for 2 minutes, and shaking for 30 minutes. The organic solvent containing the residue was then filtered through anhydrous sodium sulfate into a glass storage bottle.

All extracts except gutoxon were analyzed on a gas chromatograph; most were analyzed at least twice using two different detectors. Recovery samples were also run on each date, and replicates were sampled from the control plots for each pesticide applied. Fortified recovery studies for each organophosphate pesticide were made at the time of extraction and just before analysis at the 1 ppm level.

The two detectors and gas chromatographs used throughout the study included a Varian Aerograph Model 204 gas chromatograph equipped with a cesium bromide thermionic flame detector (3,4) and a Micro-Tek Model MT 220 gas chromatograph equipped with a dual flame photometric detector (5,6). Both GLC systems are relatively specific for phosphorous-containing organic compounds. A chlorinesterase detection method (7) was also utilized following separation by thin-layer chromatography for detecting and confirming the presence of naled, dichlorvos, ethion monooxon, ethion dioxon, and gutoxon; this method was used with the gas chromatography procedure. Gutoxon was the only metabolite that was not analyzed by GLC. For this particular compound, only thin-layer chromatography was used. The developing solvent was benzene: ethyl acetate: methyl alcohol, 90:8:2.

The GLC columns used throughout the study were: a 6-ft-by- $\frac{1}{8}$ -in.-o.d. borosilicate glass packed with 10 percent DC 200 on 100/120-mesh Gas Chrom Q; a 6-ft-by- $\frac{1}{4}$ -in.-o.d. borosilicate glass packed with 3 percent OV-225 on 60/80-mesh Gas Chrom Q; a 3 $\frac{1}{2}$ -ft-by- $\frac{1}{4}$ -in.-o.d. borosilicate glass packed with 5 percent OV-225 on 60/80-mesh Gas Chrom Q; and a 6-ft-by- $\frac{1}{4}$ -in.-o.d. borosilicate glass packed with 10 percent OV-17 on 60/80-mesh Gas Chrom Q. The first two columns were used for separating and analyzing ethion, azinphosmethyl, and phosalone. The third column was used to separate naled and dichlorvos; the fourth column was used to separate ethion monooxon and ethion dioxon. Temperatures of the injection part and detector for the Micro-Tek gas chromatograph were 240°C and 290°C, respectively. Injection and detection temperatures for the Varian Aerograph were 227°C and 230°C, re-

spectively. Flow rates of the oxygen, air, hydrogen, and nitrogen carrier gases for the Micro-Tek were 20, 20, 200, and 90 ml/min, respectively. The Varian Aerograph flow rates of the air, hydrogen, and nitrogen (carrier) gases were 170, 16.5, and 20 ml/min, respectively. Column temperatures for both instruments for ethion, azinphosmethyl, and phosalone were held to 230°C; ethion monooxon and ethion dioxon samples were operated at 245°C. The naled and dichlorvos analyses were handled differently in that the column temperature was programmed with an initial temperature of 130°C for 2 minutes following injection. Then it was programmed at a rate of 30°C/min until a final temperature of 170°C was reached; it was held at that temperature for 6 minutes before cooling to the initial temperature of 130°C.

Results and Discussion

Several extraction solvents including acetonitrile, benzene, chloroform, and 10 percent methanol in chloroform were compared for the quantity of residue extracted and the variability of the residue between individual samples. The quantity of the residue in the substrates was about the same regardless of the solvent selected; however, the 10 percent methanol in chloroform gave results slightly more consistent than those produced by the other solvents. Extraction time of 30 minutes was also compared with another procedure (8) which included shaking the contents in 1:2 ratio of crop tissue to solvent for 2 minutes, letting it rest for 2 minutes, shaking for $\frac{1}{2}$ minute, and resting $\frac{1}{2}$ minute before transferring extract into a sample bottle. Again, residue levels were similar and well within the variations found between the replicates. However, there was a considerable degree of inconsistency between these samples and those produced by the 30-minute extraction period.

This study was concerned with maximum levels of residue that might be associated with surface exposure and includes residue levels that might be incorporated into the plant surface, as in the plant waxes or tissues just under the immediate surface. Therefore, residue levels reported here are probably higher than the actual surface residue to which a worker would be exposed in a field situation. Ascertaining how an individual is exposed to pesticides and which pesticides he is exposed to is very difficult. Much work needs to be done in this regard, but this was not the objective of the present study.

Authors of this study had anticipated looking at some of the toxic degradation products which are more polar than their parent compounds. Therefore, it was necessary to extract with a mixture including a polar

solvent. Ten percent methanol in chloroform (2) was used throughout the study.

Results from the fortified recovery studies ranged from 95 to 100 percent for all pesticides analyzed including the degradation products. The only two exceptions to this were ethion dioxon, which ranged from 80 to 95 percent recovery, and gutoxon, which could not be checked for a specific recovery because it was analyzed by thin-layer chromatography. Fortified extracts of gutoxon did look satisfactory even when fortified at 0.1 ppm. However, this was only a visual observation and quantitation was not attempted.

Soil, leaves, cane, and bark were sampled periodically following each insecticide application. Harvested grapes were also sampled. Figures 2-4 show in graphic form the residue levels found on the various tissue samples, except for soil samples. Residue levels in the soil were relatively low, ranging from about 3.0 ppm on the first day of application to 1.0 ppm at harvest for azinphosmethyl and phosalone. Ethion had about the same initial residue but degraded rather rapidly, with a final residue at 42 days of 0.15 ppm. Naled had an initial level of about 0.5 ppm; the second sampling four days later showed less than 0.1 ppm except for one sample which had 0.2 ppm. Fruit samples of grapes were harvested

and analyzed on two different dates, September 28 and October 8. Table 2 shows these residues and residues found on all tissues sampled at time of harvest. In all cases, residues found on the fruit were within the U.S. Government tolerance for each of the four pesticides surveyed.

As mentioned earlier, insecticides were not applied to the five replicate plots (R1-5) on the same day. The plot identified as R1 had its first application of ethion and azinphosmethyl on August 27, R2 and R3 on August 28, and R4 and R5 on August 31. The variability of residue between the three dates of application was less than the variability between samples with the same application on the same plot sampled the same day. Therefore, factors attributed to variation of application days were generally considered insignificant. The same was true of phosalone which was applied to R1, R2, and R3 plots on September 11. R4 and R5 plots received their first application of phosalone on September 14. Naled was applied to all five plots on September 24.

For each periodic sampling, Figures 2-5 show the highest, lowest, and average residue for each pesticide per

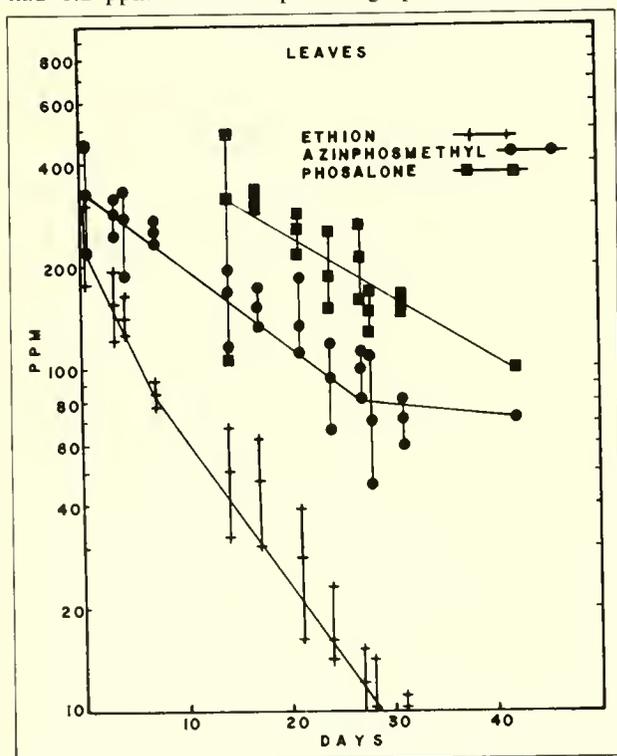


FIGURE 2.—Residues of ethion, azinphosmethyl, and phosalone extracted from grape leaves with an organic solvent wash from samples taken at time of application and throughout growing season. Each group of points represents range and mean of residues in samples after application

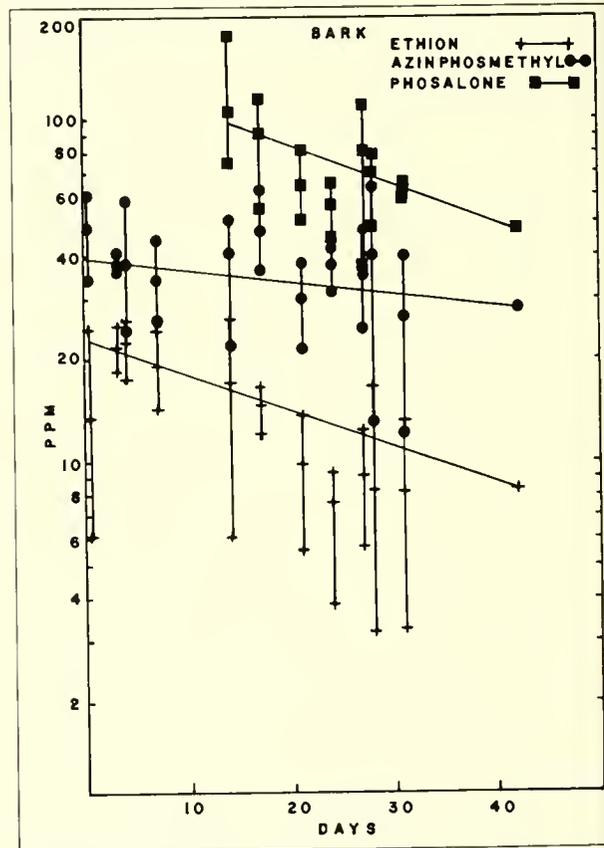


FIGURE 3.—Residues of ethion, azinphosmethyl, and phosalone extracted from grape bark with an organic solvent wash from samples taken at time of application and throughout growing season. Each group of points represents range and mean of residues in samples after application

TABLE 2.—Insecticide residues found on grape tissues at time of harvest

INSECTICIDE	TISSUE ANALYZED	RESIDUES FOUND, PPM
Azinphosmethyl	Leaves	71.3
	Bark	28.2
	Cane	6.60
	Fruit	2.56 ¹
	Soil	1.00
Ethion	Leaves	5.80
	Bark	8.20
	Cane	0.40
	Fruit	0.70 ¹
	Soil	0.15
Phosalone	Leaves	98.8
	Bark	47.0
	Cane	6.80
	Fruit	1.08 ¹
	Soil	1.00
Naled	Leaves	<0.10
	Bark	2.20
	Cane	<0.10
	Fruit	<0.10 ¹
	Soil	<0.10

¹ Represents average of residues taken on two days of harvest: Sept. 28 and Oct. 9

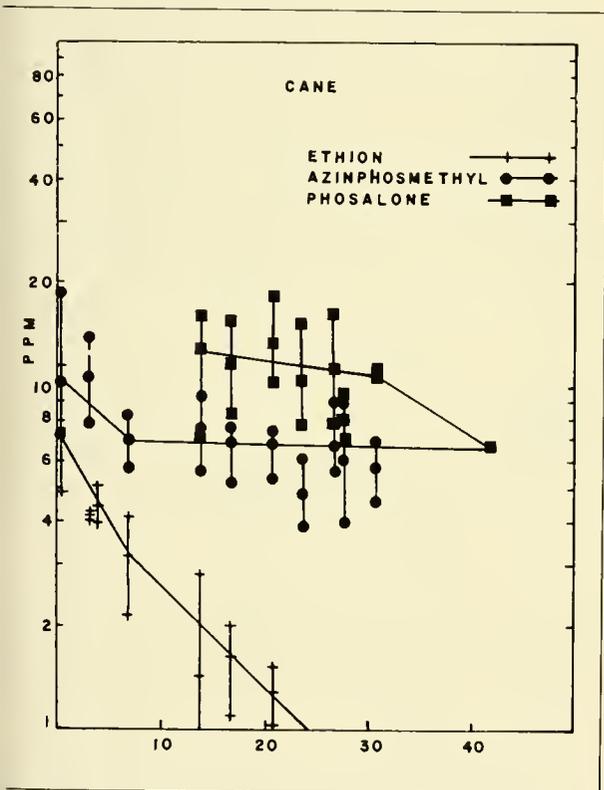


FIGURE 4.—Residues of ethion, azinphosmethyl, and phosalone extracted from grape cane with an organic solvent wash from samples taken at time of application and throughout growing season. Each group of points represents range and mean of residues in samples after application.

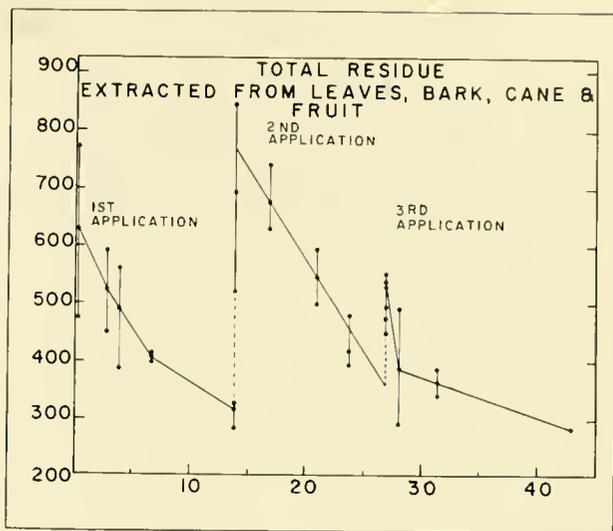


FIGURE 5.—Total insecticide residue extracted from leaves, bark, cane, and fruit of grape

period from the initial time of the azinphosmethyl and ethion application. All reported naled residues include dichlorvos, even though the two insecticides were analyzed individually. Table 3 shows the average levels of residue found on the four separate substrates from initial day of application until harvest. Even though residue levels among samples varied considerably, levels in relation to time followed first-order kinetics, particularly in leaf tissues. Variability was much greater between cane and bark samples than between soil and leaf samples. However, data did indicate that the rate of decline of each pesticide was considerably slower after the first few days, particularly for azinphosmethyl and phosalone. The irregularity between samples in the corky tissues can be explained by irregular absorption and adsorption and by exposure of the tissue to the spray. Irregularity is also explained by the variable exposure of the tissue to sunlight and other degradation processes. It is difficult to get complete random sampling of old and new tissues from each plant because of the irregularities mentioned which may also explain the variability between samples.

In all cases, the stability of the insecticides in the bark and cane was very significant. Even 42 days after application, about half the original residue remained with the exceptions of naled and ethion. Naled was not detected in the cane; however, it was detected in the bark 14 days after application. Even though the residue level was relatively small, with about 15 percent of the initial deposit remaining at harvest time, the rate of decay was only 50 percent from day 4 to day 15. It appears that once the pesticide is in contact with the corklike tissue, it is absorbed readily and becomes quite stable over a long period of time. This may or may not be significant in relation to the exposure of field

TABLE 3.—*Degradation of azinphosmethyl, ethion, phosalone, and naled in grape plant tissues*

DAYS: INITIAL APPLICATION (DAY 0) TO HARVEST	AVERAGE RESIDUE ON LEAVES, PPM				AVERAGE RESIDUE ON BARK, PPM				AVERAGE RESIDUE ON CANE, PPM				AVERAGE RESIDUE ON SOIL, PPM			
	AZINPHOS- METHYL	ETHION	PHOSALONE	NALED	AZINPHOS- METHYL	ETHION	PHOSALONE	NALED	AZINPHOS- METHYL	ETHION	PHOSALONE	NALED	AZINPHOS- METHYL	ETHION	PHOSALONE	NALED
0	322	225			48	13			10.4	7.5			2.8	1.4		
3	283	156			38	22			10.6	4.0			1.6	1.4		
4	271	139			38	22			8.1	4.5			3.7	2.4		
7	251	84			34	19			6.9	3.1			3.1	1.5		
14	167	49	310		41	17	106		7.5	1.4	13		1.5	0.56	2.9	
17	150	37	310		47	15	92		6.8	1.6	12		2.3	0.44	3.5	
21	132	28	252		30	10	65		6.9	1.3	13		1.1	0.20	2.5	
24	92	16	182		37	7.6	55		4.8	0.85	10		1.3	0.35	1.7	
27	98	12	210	36	35	8.9	80	14	6.6	0.90	11	1.1	1.6	0.28	2.1	0.27
28	69	10	144	<0.1	40	8.2	70	8.2	6.0	0.70	8.0	<0.10	1.7	0.40	1.8	<0.10
31	70	10	156	<0.1	26	8.2	62	5.6	5.7	0.60	10.5	<0.10	1.5	0.26	2.0	<0.10
42	71	5.8	99	<0.1	28	8.2	47	2.2	6.6	0.40	6.8	<0.10	1.0	0.15	1.0	<0.10

workers. Because high levels of residue are involved, however, the matter needs to be investigated.

The two oxygen analogs of ethion on grape leaves are shown in Table 4. All replicate samples analyzed for the metabolites were composited according to days from application. Residues of ethion monooxon and ethion dioxon were much lower than their parent compound the first few days following application. However, the relative amount of residues for the two products was much higher following the third day. The total amount of both ethion monooxon and ethion dioxon from the fourteenth day after application was approximately 50 percent of its parent compound and continued in this proportion throughout the growing season. Even though the percentage of these metabolites was quite high, the total amount of residue was much lower than other organophosphate pesticides studied. Gutoxon, the oxygen analog of azinphosmethyl, was analyzed only the first 14 days following initial application due to the background on the thin-layer plates following the phosalone application. None of the samples analyzed showed any detectable residues of gutoxon or other cholinesterase-inhibiting products in excess of 1 ppm for this period.

TABLE 4.—*Degradation of ethion, ethion monooxon, and ethion dioxon on grape leaves*

DAYS: INITIAL APPLICATION (DAY 0) TO HARVEST	RESIDUE ON LEAVES, PPM			
	ETHION	ETHION MONOOXON	ETHION DIOXON	ETHION MONOOXON + ETHION DIOXON
0	225	25	2.0	27
3	156	15	2.6	17.6
7	84	19	13	32
14	49	10	15	25
17	37	7.2	8.8	16
21	28	6.3	4.5	10.8
24	16	4.6	3.6	8.2
27	12	3.4	3.4	6.8
31	10	2.6	1.8	4.4
42	5.8	1.3	1.4	2.7

Table 5 and Figure 5 show the total residue less the metabolites on the leaves, bark, cane, and fruit from initial application until harvest. The day azinphosmethyl and ethion were applied, the average residue level was 626 ppm and after 14 days the sum of the residue in the plant dropped to about 300 ppm. On this day, phosalone was applied and the total residue rose to an average level of 688 ppm. Just prior to the naled application 14 days later, the residue level should have reached a level of about 350 ppm, according to projection from the graph. The naled application did not have a great effect on the total residue after the first day following application because of its rapid decay in most tissues. Perhaps the most significant fact displayed by this graph is the level of residue at or near time of harvest. This level approached nearly 300 ppm, about

TABLE 5. *Averages (ppm) of all four insecticides from initial application to harvest*

DAYS: INITIAL APPLICATION (DAY 0) TO HARVEST	LEAVES	BARK	CANE	FRUIT	TOTAL APPLI- CATION
FIRST APPLICATION					
0	547	61	18		626
3	439	60	15		514
4	410	60	13		483
7	335	53	10		398
14	241	56	9.3		306
SECOND APPLICATION					
14	501	166	21		688
17	497	154	20		671
21	412	105	21		538
24	290	100	16		406
27	350	119	17		486
THIRD APPLICATION					
27	328	144	22		494
28	223	126	15	12	376
31	236	102	17	14	369
42	175	85	14	4.4	278

one half the initial and total deposit of azinphosmethyl and ethion, and one third the highest residue level found on any one sample at any given time. Even though this residue level is high, it likely does not reflect the total measure of hazard to which an agricultural worker is exposed because a considerable portion of these materials were found in the bark and cane and, as mentioned previously, may not present an immediate hazard. This aspect of pesticide residue in such tissues needs to be considered in a worker-safety study. Studies should also be conducted to ascertain whether the high residues found in corklike tissue are, like leaf tissues, a potential hazard and, if so, in what manner and to what degree an individual would be exposed to them.

LITERATURE CITED

(1) *Bailey, J. B., D. Flaherty, and D. Mengle. 1973.* Pesticide residues on grape leaves evaluated for adverse effects on grape pickers. In manuscript.

- (2) *Bowman, M. C., M. Beroza, and D. G. Leuck. 1968.* Procedures for extracting residues of phosphorus insecticides and metabolites from field treated crops. *J. Agr. Food Chem.* 16:796-802.
- (3) *Oaks, D. M., K. P. Dimick, and H. C. Hartmann. 1966.* Aerograph Phosphorous Detector. *Aerograph Research Notes*, 1-13.
- (4) *Hartmann, H. C. 1966.* Phosphorus detector for pesticide analyses. *Bull. Environ. Contam. Toxicol.* 1:159-168.
- (5) *Brody, S. S., and J. E. Chaney. 1966.* Flame photometric detector: application of a specific detector for phosphorus and for sulfur compounds sensitive to subnanogram quantities. *J. Gas Chromatogr.* 4(2):42-46.
- (6) *Bowman, M. C., and M. Beroza. 1968.* Gas chromatographic detector for simultaneous sensing of phosphorus and sulfur containing compounds by flame photometry. *Anal. Chem.* 40:1448-1452.
- (7) *Winterlin, W. L., G. Walker, and H. Frank. 1968.* Detection of cholinesterase inhibiting pesticides following separation on thin layer chromatograms. *J. Agr. Food Chem.* 16:808-812.
- (8) *Magee, R. October 1970.* Uniform method for determining chemical degradation on tree foliage. Memorandum from Calif. Dept. of Agriculture.

APPENDIX

Chemical Names of Compounds Discussed in This Issue

ALDRIN	Not less than 95% of 1,2,3,4,10,10-hexachloro-1,4,4a,5,8,8a-hexahydro-1,4- <i>endo-exo</i> -5,8-dimethanonaphthalene
AROCLOR 1260	PCB, approximately 60% chlorine
AZINPHOSMETHYL (Guthion®)	0,0-dimethyl S[4-oxo-1,2,3-benzotriazin-3(4H)ylmethyl] phosphorodithioate
BHC (Benzene Hexachloride)	1,2,3,4,5,6-hexachlorocyclohexane (mixture of isomers). Commercial product contains several isomers of which <i>gamma</i> is most active as an insecticide.
CHLORDANE	1,2,3,5,6,7,8,8-octachloro-2,3,3a,4,7,7a-hexahydro-4,7-methanoindene. The technical product is a mixture of several compounds, including heptachlor, chlordene, and two isomeric forms of chlordane.
DCPA (Dacthal®)	Dimethyl-tetrachloroterephthalate
DDD	See TDE.
DDE	Dichlorodiphenyl dichloro ethylene. (Degradation product of DDT.) Main component: 1,1-dichloro-2,2-bis(<i>p</i> -chlorophenyl) ethylene <i>o,p'</i> -DDE 1,1-dichloro-2-(<i>o</i> -chlorophenyl)-2-(<i>p</i> -chlorophenyl) ethylene <i>p,p'</i> -DDE 1,1-dichloro-2,2-bis(<i>p</i> -chlorophenyl) ethylene
DDMU	(1-chloro-2,2-bis[<i>p</i> -chlorophenyl]ethylene)
DDT	α -bis(<i>p</i> -chlorophenyl) <i>B,B,B</i> -trichloroethane. Numerous isomers in addition to <i>p,p'</i> -DDT are possible, and some are present in the commercial product. <i>o,p'</i> -DDT [1,1,1-trichloro-2-(<i>o</i> -chlorophenyl)-2-(<i>p</i> -chlorophenyl) ethane]
DDVP	See dichlorvos.
DIBROM	See naled.
DICHLORVOS	2,2-dichlorovinyl dimethyl phosphate
DIELDRIN	Not less than 85% of 1,2,3,4,10,10-hexachloro-6,7-epoxy-1,4,4a,5,6,7,8,8a-octahydro-1,4- <i>endo-exo</i> -5,8-dimethanonaphthalene
ENDRIN	1,2,3,4,10,10-hexachloro-6,7-epoxy-1,4,4a,5,6,7,8,8a-octahydro-1,4- <i>endo-endo</i> -5,8-dimethanonaphthalene
ETHION	0,0,0',0'-tetraethyl S,S'-methylene bisphosphorodithioate
GUTHION	See azinphosmethyl.
HEPTACHLOR	1,4,5,6,7,8,8-heptachloro-3a,4,7,7a-tetrahydro-4,7- <i>endo</i> -methanoindene
HEPTACHLOR EPOXIDE	1,4,5,6,7,8,8-heptachloro 2,3-epoxy-3a,4,7,7a-tetrahydro-4,7-methanoindane
LINDANE	Gamma isomer of benzene hexachloride (1,2,3,4,5,6-hexachlorocyclohexane) of 99+% purity
METHOXYCHLOR	1,1,1-trichloro-2,2-bis(<i>p</i> -methoxyphenyl) ethane
MIREX	Dodecachlorooctahydro-1,3,4-metheno-1H-cyclobuta[cd]pentalene
NALED	1,2-dibromo-2,2-dichloroethyl dimethyl phosphate
NONACHLOR	Component of commercial quality chlordane
PHOSALONE	0,0-diethyl S-(6-chloro-2-oxo-benzoxazolin-3-yl) methyl phosphorodithioate
POLYCHLORINATED BIPHENYLS (PCB's)	Mixtures of chlorinated biphenyl compounds having various percentages of chlorine
RESMETHRIN	(5-benzyl-3-furyl methyl 2,2-dimethyl-3-(2-methylpropenyl)cyclopropanecarboxylate
TDE (DDD)	2,2-Bis (<i>p</i> -chlorophenyl)-1,1-dichloroethane (including isomers and dehydrochlorination products)
TOXAPHENE	Chlorinated camphene (67-69% chlorine); product is a mixture of polychlor bicyclic terpenes with chlorinated camphenes predominating
ZOLONE	See phosalone.

ERRATA

PESTICIDES MONITORING JOURNAL, Volume 7, Number 1. In the paper "Pesticide Residues in Natural Fish Populations of the Smoky Hill River of Western Kansas—1967-69," page 56, right column, third paragraph, second sentence, should read, "Dieldrin was

detected in a small percentage (15%) of the samples; most of these had only trace (<0.01 ppm) amounts."

In Table 4 of the same paper, sample numbers and dieldrin residues for Station 5 were misquoted. Correct values for Station 5 appear below:

TABLE 4.—Pesticide residues in fish and fish tissues from the Smoky Hill River, Kansas—1967-69—Continued
[T = <0.01 PPM]

SPECIES	TISSUE	NUMBER OF SAMPLES ¹	NUMBER OF TIMES DETECTED AND RANGE () IN PPM OF DETECTED RESIDUES ^{2,3}					
			DIELDRIN	HEPTACHLOR EPOXIDE	<i>o,p'</i> -DDT	<i>p,p'</i> -DDT	<i>p,p'</i> -DDE	<i>p,p'</i> -DDD
STATION 5								
toneroller	Whole body	8	3 (T-.01)	0	0	0	8 (T-.09)	0
ted shiner	Whole body	9	3 (T-.01)	0	0	0	8 (.01-.04)	0
lains Killifish	Whole body	7	1 (T)	0	0	0	4 (T-.01)	0
reen sunfish	Whole body	6	2 (T-.03)	0	0	1 (.02)	5 (T-.03)	0
arp	Flesh	4	0	0	1 (.07)	0	2 (.01)	0
iver carpsucker	Flesh	2	1 (T)	0	0	0	1 (.01)	0
hannel catfish	Flesh	6	1 (T)	0	1 (.07)	0	5 (T-.02)	1 (.02)
arp	Testes	4	1 (T)	0	0	0	4 (.01-.07)	0
	Ovaries	4	0	0	0	0	3 (.01-.02)	0
iver carpsucker	Testes	1	1 (T)	0	0	0	1 (.01)	0
	Ovaries	1	1 (T)	0	0	0	1 (.01)	0

For whole body analysis, individuals of one species from one station were pooled to make one sample. The sample of flesh consisted of a pooling of equal weights of flesh taken from each individual of one species; gonads were treated similarly, keeping sexes separate. Wet-weight basis.

Endrin, aldrin, and heptachlor residues were all zero values.

ESTICIDES MONITORING JOURNAL, Volume 7, Number 3/4. In the paper "Surveys of Mercury Levels

in Fish and Other Foods," page 131, left column, last line, should read "ppm total mercury in the whole fish."

The PESTICIDES MONITORING JOURNAL welcomes from all sources qualified data and interpretive information which contribute to the understanding and evaluation of pesticides and their residues in relation to man and his environment.

The publication is distributed principally to scientists and technicians associated with pesticide monitoring, research, and other programs concerned with the fate of pesticides following their application. Additional circulation is maintained for persons with related interests, notably those in the agricultural, chemical manufacturing, and food processing industries; medical and public health workers; and conservationists. Authors are responsible for the accuracy and validity of their data and interpretations, including tables, charts, and references. Accuracy, reliability, and limitations of the sampling and analytical methods employed must be clearly demonstrated through the use of appropriate procedures, such as recovery experiments at appropriate levels, confirmatory tests, internal standards, and inter-laboratory checks. The procedure employed should be referenced or outlined in brief form, and crucial points or modifications should be noted. Check or control samples should be employed where possible, and the sensitivity of the method should be given, particularly when very low levels of pesticides are being reported. Specific note should be made regarding correction of data for percent recoveries.

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PESTICIDES IN SOIL

Pesticide Residue Levels in Soils and Crops, FY-70—National Soils Monitoring Program (II)

A. B. Crockett,¹ G. B. Wiersma,¹ H. Tai,² W. G. Mitchell,²
P. F. Sand,³ and Ann E. Carey⁴

ABSTRACT

This data report is a summary of Fiscal Year 1970 results of the National Soils Monitoring Program. It includes data on pesticide applications, soil residues, and crop residues collected from 1,506 cropland sites in 35 States. Pesticide application data are summarized by all sites and by State. Soil residue data are itemized similarly, but also include data by cropping region. Tables generally give the number of sites, number of times a pesticide was applied or detected, percent occurrence, arithmetic mean application rate or residue level, and range of residues detected. For some data, geometric means or 50 percentile levels, both with 95 percent confidence intervals, are presented.

Pesticides applied most frequently were atrazine, 2,4-D, captan, and malathion. Farmers in cotton and corn cropping regions applied the most pesticides; those in grass hay and mixed hay areas applied the least. Dieldrin, DDTR, aldrin, chlordane, and heptachlor epoxide were the chlorinated hydrocarbon residues found in soil most frequently. Highest residue levels were found in the corn and cotton cropping regions; lowest levels were in the hay, general farming, and small-grain soils.

Introduction

The National Soils Monitoring Program is an integral part of the National Pesticide Monitoring Program (NPMP). The Program was initiated at the recommendation of the President's Science Advisory Committee report of 1964 entitled "Use of Pesticides." This committee recommended that appropriate Federal agencies "develop a continuing network to monitor residue levels in air, water, soil, man, wildlife, and fish" (1).

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The objective of NPMP is to determine levels and trends of pesticides and their degradation products in the various components of the environment (2). The initial goal, establishment of NPMP baseline or background levels of pesticide residues, will provide a basis for comparison of subsequently identified pesticide residue levels in an environmental component and, ultimately, detection of significant trends.

In determining levels and trends of pesticide residues, NPMP personnel have been guided by criteria of the Monitoring Panel of the Federal Working Group on Pest Management (2). The Panel has listed five areas of concern for individuals evaluating pesticide residue levels in environmental components. They are: any concentration of a pesticide known to be potentially harmful; increasing trends; levels exceeding standards; recognition of adverse effects on humans; and erratic variability, a statistically oriented observation that is potentially common to each stratum sampled.

This report is a summary of the pesticide application data and soil and crop residue data collected in Fiscal Year 1970 (FY-70) from 1,506 sites located in 35 States. Data were not collected from certain agricultural States because of budgetary limitations. States omitted were those abounding in wheat and other grains, which require fewer pesticides than do many nongrain crops. The FY-69 (3) and FY-70 findings have achieved the initial NPMP goal of establishing baseline data. Authors will identify significant trends as more data are accumulated.

Sampling

Sampling techniques involved in this study were generally the same as those employed by Wiersma, Sand, and Cox in a 1971 study (4). In FY-70, cropland sites in 35 States were sampled (Fig. 1). This included all but the following States: Alaska, Arizona, Colorado, Hawaii, Idaho, Kansas, Montana, Nevada, New Mex-

The hexane sample extract was shaken with 100 ml of acetonitrile in a 500 ml separatory funnel. The bottom acetonitrile layer was set aside. Nanograde acetonitrile (100 ml) was added to the hexane extract and the separation step described above was repeated two more times; then the hexane was discarded and the three acetonitrile layers were combined. The 300-ml acetonitrile extract, which contained essentially all the pesticides in the original hexane extract, was backwashed with 25 ml of acetonitrile-saturated hexane and the hexane layer was discarded. The acetonitrile sample extract was concentrated to approximately 10 ml under a three-ball Snyder column, and 100 ml of hexane was added. Addition of hexane and concentration to approximately 10 ml was performed three times, after which the sample was essentially in hexane. Remaining hexane extract was diluted to appropriate volume and held at low temperature for subsequent Florisil column cleanup and fractionation.

GAS-LIQUID CHROMATOGRAPHY

Analyses were performed on gas chromatographs equipped with tritium foil electron affinity detectors for organochlorine compounds and thermionic or flame photometric detectors for organophosphorous compounds. A multiple-column system employing polar and nonpolar columns was utilized to identify and confirm pesticides. Instrument parameters were as follows:

Columns: Glass, 6 mm o.d. by 4 mm i.d., 183 cm long, packed with one of the following: 9 percent QF-1 on 100/120 mesh Gas-Chrom Q; 3 percent DC-200 on 100/120 mesh Gas-Chrom Q; or 1.5 percent OV-17/1.95 percent QF-1 on 100/120 mesh Sepulcoport.

Carrier Gases: 5 percent methane-argon at a flow rate of 80 ml/min; prepurified nitrogen at a flow rate of 80 ml/min.

Temperatures:	Detector	200°C
	Injection port	250°C
	Column QF-1	166°C
	Column DC-200	170-175°C
	Mixed column	185-190°C

Sensitivity or minimum detection levels for organochlorine compounds ranged from 0.002 to 0.03 ppm except for combinations of polychlorinated biphenyls (PCB's), chlordane, toxaphene, and other chemicals which had minimum detectable levels of 0.05 to 0.1 ppm. Minimum detectable levels for organophosphorous compounds were approximately 0.01 to 0.03 ppm. When necessary, residues were confirmed by thin-layer chromatography or p-values.

RECOVERY STUDIES

For organochlorine pesticides, average recovery rate in soil was 90 to 110 percent. Recovery values for stalks and hay ranged from 80 to 95 percent, with an average of 89 percent; corresponding values for grains were 90 to 100 percent, with a 95 percent average. For organophosphate pesticides, average recovery values were 67.1 percent for soybeans, 86 percent for sorghum grain, and 60 percent for corn stalks. Residue levels in both crops and soils are expressed on a dry-weight basis and are corrected for percent recovery.

Results

Tables presented in this report are divided into three groups: pesticides applied to cropland, chlorinated hydrocarbon pesticide residues in cropland soil, and chlorinated hydrocarbon and organophosphate pesticide residues in crops. Pesticide application data are further subdivided by all sites and by State. Residues in soil are summarized by all sites and by States and cropping regions.

Most tables list the number of samples, the number of times a pesticide was applied or detected, percent occurrence of that particular pesticide, arithmetic mean, and range. Readers should exercise caution when interpreting the arithmetic mean because data are not normally distributed. The arithmetic mean tends to be considerably higher than the corresponding median; but because of the skewed distribution of these data, the mean may not be a good indication of central tendency. Hence geometric means and 50 percent estimates have been presented.

PESTICIDES APPLIED TO CROPLAND

When soil samples were collected from cropland, field personnel attempted to contact farmers to determine what pesticides had been applied to the sites during the year of sampling. These data were not always available: only 1,346 use records were collected from 1,506 sites. Tables summarizing application data show the number of sites using a pesticide, percent of sites using a particular pesticide, average rate of application for sites using the pesticide, and average amount of pesticide applied to all sites. The latter figure was determined by dividing the total amount of active ingredients applied to all sites by the total number of sites surveyed. All rate data are expressed in pounds per acre (lb/a). To convert to kilograms per hectares (kg/ha), multiply by 1.1208.

ALL SITES

Table 1 is a summary of the 1,346 sites surveyed from 35 States. The most common pesticides were atrazine, 2,4-D, captan, and malathion, which were used

on 11, 9, 8, and 6 percent of the sites, respectively. Aldrin and DDT were used on 4 percent of the sites.

BY STATE

Table 2 is a breakdown of the all-site data by State. Because some of the smaller Eastern States had very few samples, several were combined to obtain more representative data. State groups used were Mid-Atlantic: Delaware, Maryland, and New Jersey; New England: Connecticut, Maine, Massachusetts, New Hampshire, Rhode Island, and Vermont; and Virginia and West Virginia.

Considering the number of States sampled, it is not feasible to discuss pesticide applications of each State. It is, however, worthwhile to mention application frequencies of a few States.

Because Mississippi farmers produce large quantities of cotton, a crop which demands heavy pesticide treatment, they apply a large number of pesticides to much of their cropland. Growers used the following pesticides most frequently on the specified percentage of sites: methyl parathion, 48 percent; trifluralin, 42 percent; DDT, 32 percent; Cotoran (fluometuron), 26 percent; toxaphene, 23 percent; Bidrin (dicofthos), 19 percent; MSMA, 19 percent; folex, 16 percent; and diuron, 13 percent. In Illinois, a major corn-growing State, pesticides applied most frequently and the percentage of sites treated were: captan, 45 percent; malathion, 45 percent; Ramrod (propachlor), 24 percent; aldrin, 18 percent; atrazine, 16 percent; and heptachlor, 12 percent. In contrast to these States were Oklahoma, Minnesota, Kentucky, and the New England group, where no pesticide was applied to more than 8 percent of the sampling sites.

Herbicide 2,4-D was applied most frequently in South Dakota; of the sites sampled, 25 percent were treated. Atrazine was applied most frequently in Wisconsin and North Carolina: 25 and 26 percent of the sites, respectively, were treated. Captan was applied most frequently in the Mid-Atlantic States; 47 percent of the sites were treated.

BY CROP

Table 3 presents pesticide application data for several crops. The few pesticides applied to alfalfa and bur clover were not widely used. Of the many different pesticides applied to field corn, atrazine, captan, 2,4-D, and malathion were employed most frequently. Farmers used 45 different pesticides on cotton fields; of these compounds, 14 were applied to more than 10 percent of the sites. In contrast, field workers applied only two pesticides to both grass hay and mixed hay fields. Although 27 pesticides were applied to soybeans, only amiben and trifluralin were applied to more than 5 percent of the sites sampled.

CHLORINATED HYDROCARBON PESTICIDE RESIDUES IN CROPLAND SOIL

All 1,506 soil samples from the 35 States were examined for chlorinated hydrocarbon residues. A few samples were analyzed for additional pesticides, but these data were insufficient for consideration. In the future, soil residue analyses will be expanded to include more compounds.

Samples were not analyzed for PCB's because little was known about them at the time of analysis. A review of the gas chromatograph traces revealed that PCB residues were seldom present and, when they were, the residues existed only in very small quantities. PCB peaks were recognized and not confused with DDT.

ALL SITES

Table 4 summarizes chlorinated hydrocarbon soil residue data for all States, including the number of times a pesticide was detected, percent occurrence, arithmetic mean, geometric mean with 95 percent confidence interval, and range of detected residue values. The geometric mean was used because it gives a better indication of the central tendency of the data. It was calculated using a 0.01 addition to eliminate the problem of zeros and was later subtracted from the calculated mean.

The most widely distributed chlorinated hydrocarbon was dieldrin: 31 percent of the soil samples had detectable residues. It was followed by DDTR (DDE+TDE), aldrin, chlordane, and heptachlor epoxide, which were detected at 23, 13, 11, and 10 percent of the sites respectively.

DDTR existed in the highest concentration, with an arithmetic mean of 0.30 ppm and geometric mean of 0.0116 ppm. Although the arithmetic mean for dieldrin was much lower than that for DDTR, the geometric means are indistinguishable at the 95 percent confidence level. The very high residue value of 113 ppm as shown in the range of DDTR can have a major effect on an arithmetic mean. The effect of extreme values upon the geometric mean is considerably less.

BY STATE

Chlorinated hydrocarbon residues in soils of specific States (Table 5) are presented in the same manner as the all-sites data except for the geometric means.

Comparisons of the percent occurrence of aldrin, dieldrin, heptachlor epoxide, DDTR, and chlordane are presented in Figures 2 through 6. The key for each figure is based on the arithmetic average percent occurrence (\bar{x}) of the given pesticide for all sites. The four categories used are: greater than $2\bar{x}$, greater than \bar{x} but less than $2\bar{x}$, greater than $\frac{1}{2}\bar{x}$ but less than \bar{x} , and less than $\frac{1}{2}\bar{x}$.

Iowa and Illinois showed the highest percent occurrence of aldrin, dieldrin, and heptachlor epoxide (Fig

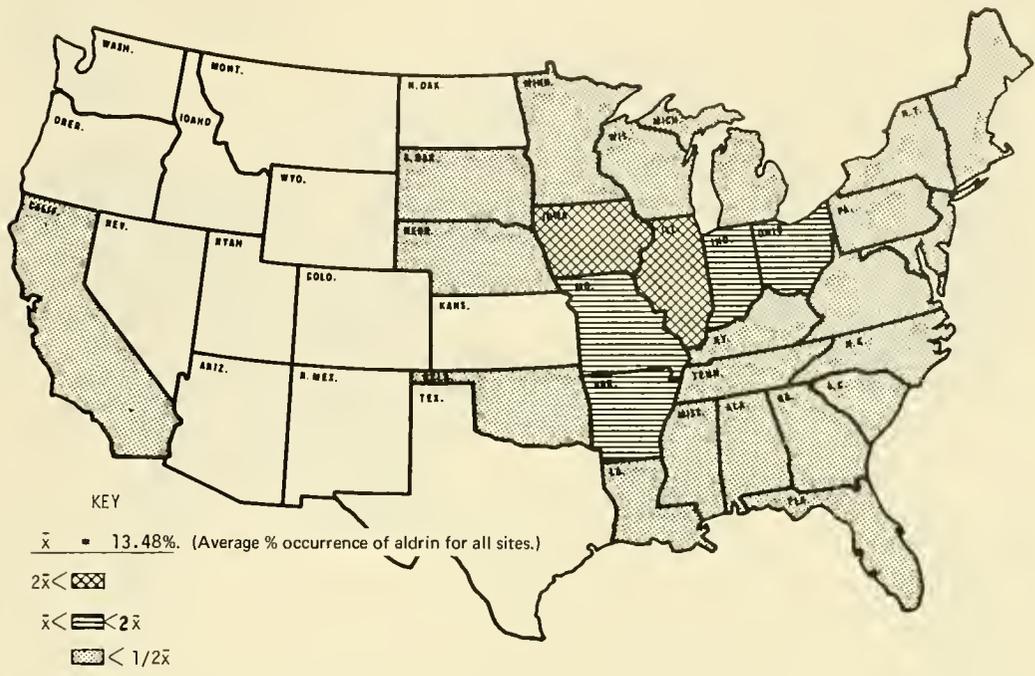


FIGURE 2. Aldrin residues, %, in cropland soil by State, FY-70

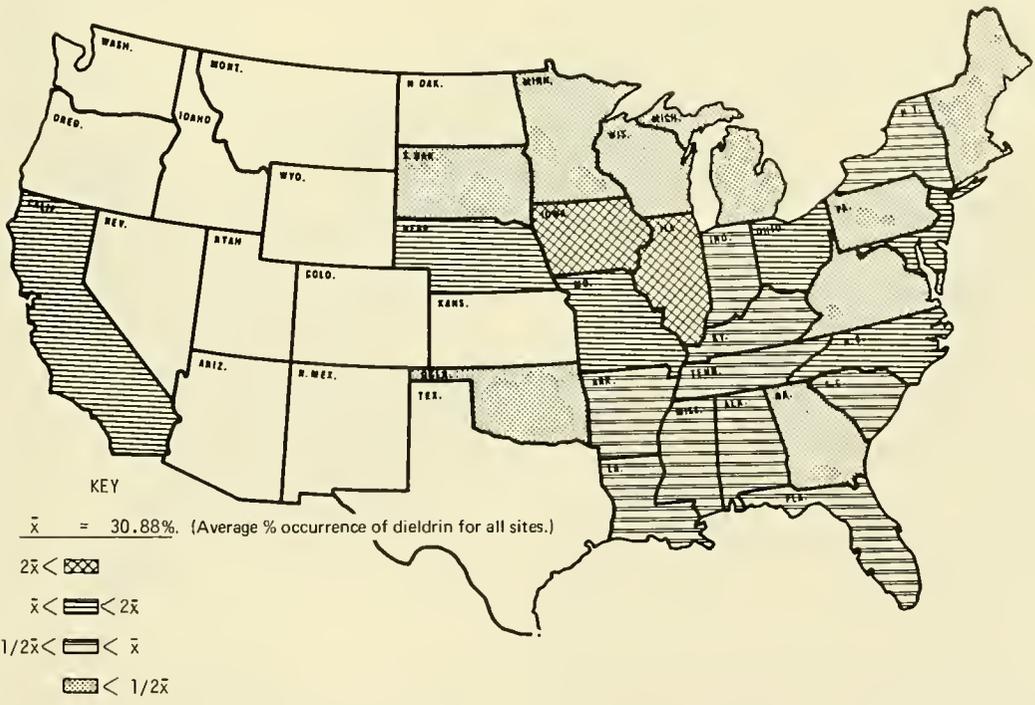


FIGURE 3. Dieldrin residues, %, in cropland soil by State, FY-70

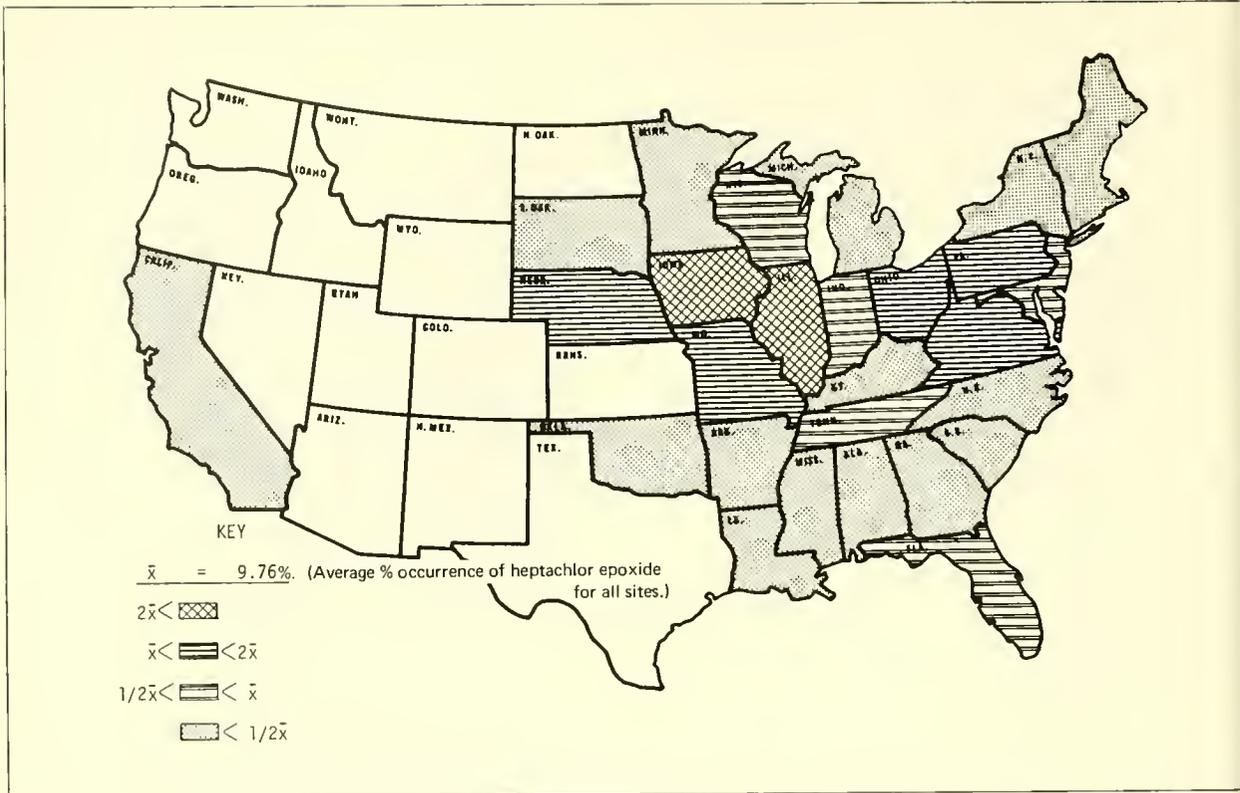


FIGURE 4. Heptachlor epoxide residues, %, in cropland soil by State, FY-70

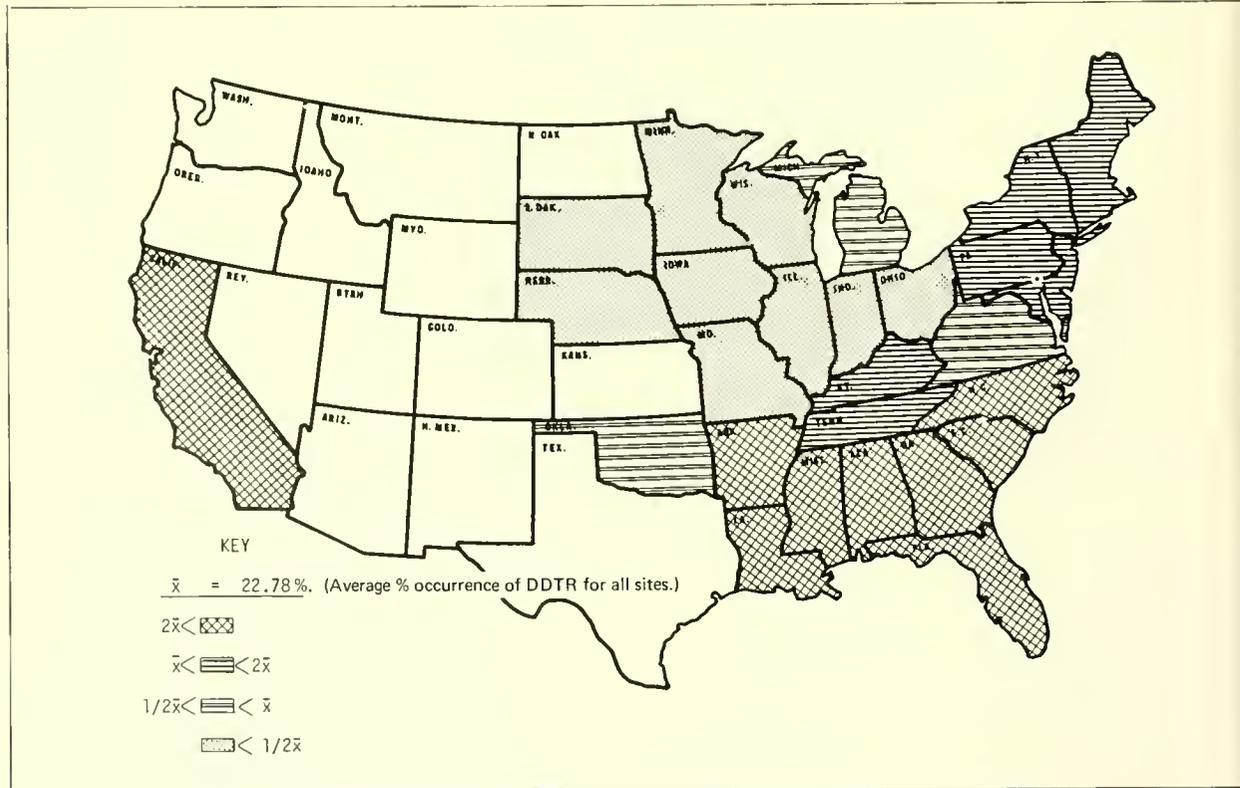


FIGURE 5. DDTR residues, %, in cropland soil by State, FY-70

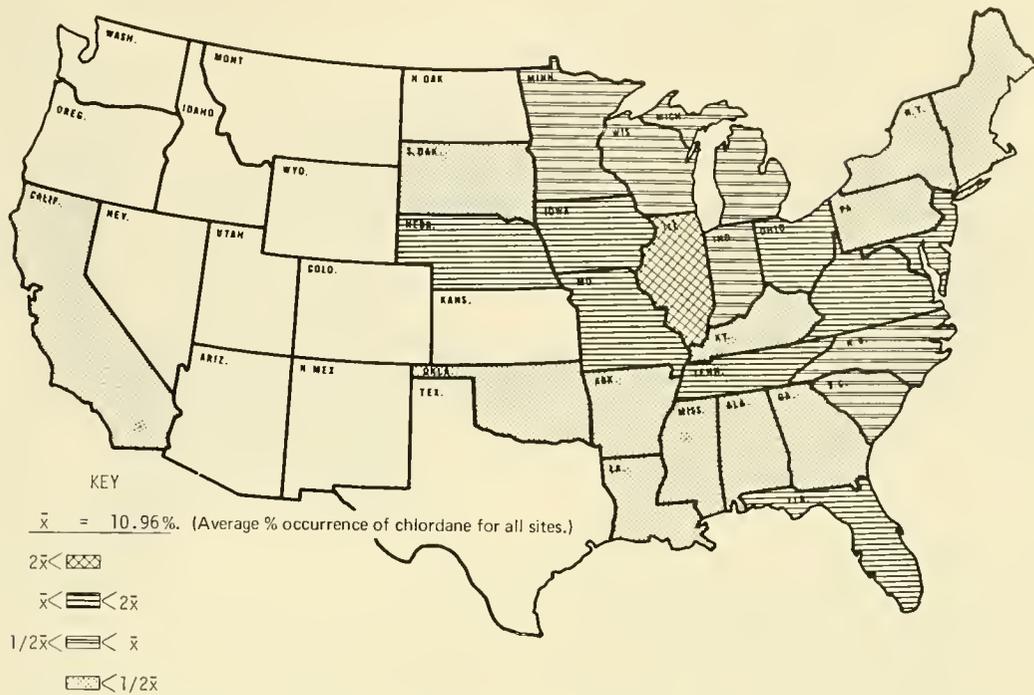


FIGURE 6. Chlordane residues, %, in cropland soil by State, FY-70

-4). DDTR detections were concentrated in Southeastern States and California (Fig. 5); Central States showed low incidence. Chlordane occurred most frequently in Illinois soil samples (Fig. 6).

Michigan, Minnesota, Oklahoma, and Wisconsin were below the all-sites average detection frequency for all five pesticides. Residue levels in South Dakota were less than half the comparable all-sites figures.

Table 6 lists the 50 percent estimates and 95 percent confidence interval of that estimate, offering a statistical comparison of pesticide residue levels between States. The given values were calculated using a slightly modified regression analysis method described by Daum (5). Residue values were ranked from lowest to highest and accumulated; percentages were then computed. Values were transformed to logarithms, percentages were transformed to probits, and the relationship between the logarithms and probits was calculated by regression analysis. Six different detectable residue levels were required for the calculation. When the upper limit of the 95 percent fiducial interval is less than 0.01 ppm, no value is shown.

BY CROPPING REGION

Data were grouped into cropping regions based upon a major land use map of the United States compiled by F. J. Marschner, U.S. Department of Agriculture, Bureau of Agricultural Economics, 1950. The land in

the United States was grouped by county into several major land use areas: corn, cotton, fruit, general farming, hay, small grain, and vegetables. In some cases, two areas overlapped: cotton and general farming, for example (Fig. 7). Field personnel determined at the time of sample collection whether land had been irrigated.

The percent occurrence and arithmetic means for soil residues by cropping region are presented in Tables 7 and 8. In the corn region, aldrin, chlordane, and dieldrin residues were widespread and the mean concentrations for these pesticides were also above the all-sites average. Cotton region soils had high DDTR, toxaphene, and trifluralin residues. A greater variety of pesticides was detected in the cotton and general farming region than in the cotton region, but residue values and percent occurrence of comparable pesticides were usually lower. Hay and general farming residues were lower and small-grain soils generally contained the lowest residue levels. The number of sites in irrigated land, vegetable and fruit, and vegetable regions was small; data appear to indicate widespread occurrence of DDT residues.

Table 9 lists the 50 percent estimate and 95 percent confidence interval of that estimate for pesticide residues in soil by cropping region. Using this table makes it possible to determine whether two residue values are significantly different with a risk of less than 5 percent.

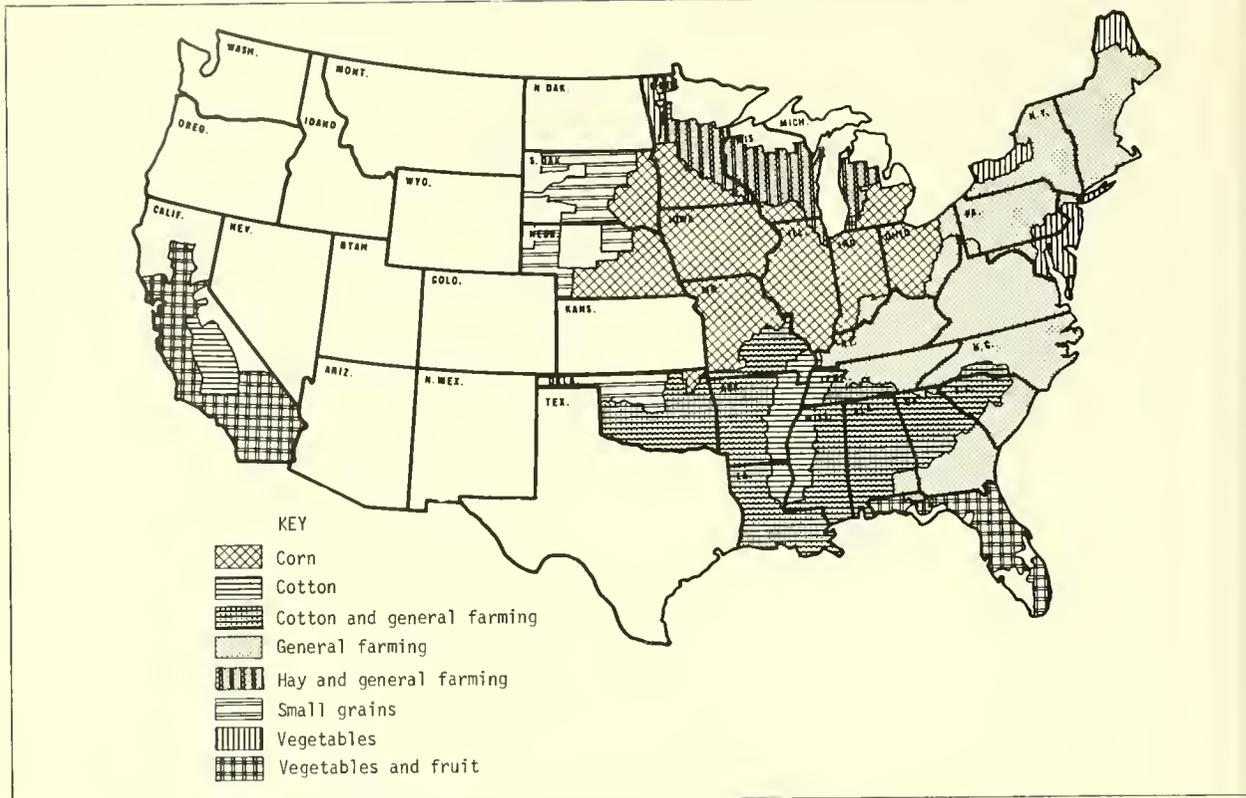


FIGURE 7. Cropping regions for States sampled, FY-70

When the confidence interval for DDTR for cotton is higher and does not overlap with the DDTR interval for cotton and general farming, it can be stated that the cotton region has higher DDTR residues in cropland soil than the cotton and general farming region with less than a 5 percent risk.

Table 9 indicates that DDTR residues were found principally in cotton, vegetable and fruit, and irrigated land regions; corn, hay, and vegetable regions were relatively free of this residue. Significantly high dieldrin residues were associated with corn and irrigated land regions.

BY CROP

Pesticide residues in soil have also been grouped according to crops grown on the soil (Table 10). The few minor discrepancies between the number of sites examined in Tables 3 and 10 are due to lost samples.

Soils under alfalfa and bur clover contained a number of low-level pesticide residues. Field corn soils showed detectable levels of dieldrin at 42 percent of the sites. Soil in cotton fields averaged over 2 ppm DDTR. Although very few pesticides were applied to grass hay or mixed hay sites, the occurrence of detectable residues of dieldrin and DDTR was surprisingly high. Dieldrin was the residue found most commonly

in soybean soils, but DDTR was the residue in highest concentration.

CHLORINATED HYDROCARBON AND ORGANO-PHOSPHATE PESTICIDE RESIDUES IN CROPS

As mentioned earlier, crop samples were collected only from crops which were ripe and/or ready for harvest. They were taken directly from the field and were collected whenever available. In total, 952 samples were collected from about 640 sites. All crop samples were analyzed for chlorinated hydrocarbon pesticides. In addition, samples were analyzed for organophosphates when use records indicated they had been applied. The organophosphate sample is thus biased and could be expected to yield higher residue values for a given crop than would have resulted had all samples been analyzed.

Alfalfa and bur clover samples contained DDTR 2 percent of the time (Table 11); chlordane and dieldrin were detected less frequently. Most of these samples were analyzed for organophosphate residues; no such residues were detected.

Field corn kernels were exceptionally free of both chlorinated hydrocarbon and organophosphate pesticide residues. However, pesticide residues in field corn stalks were detected considerably more often. DDTR, dieldrin

and chlordane occurred 20, 16, and 5 percent of the time, respectively; detected concentrations were low.

Cottonseeds were frequently contaminated with DDTR, toxaphene, DEF, and methyl parathion. Cotton stalks contained high concentrations of pesticides: DDTR was found in 91 percent of the stalk samples with an average concentration of 3.81 ppm; toxaphene occurred in 45 percent of the samples and averaged 6.96 ppm; dieldrin occurred frequently, but the residue levels were much lower. Of the 18 sites where organophosphates were applied to cotton, methyl parathion occurred 50 percent of the time. DEF, malathion, and ethyl parathion occurred 39, 22, and 17 percent of the time, respectively. Concentrations of both ethyl parathion and DEF were relatively high.

Grass hay contained a number of pesticides, but the frequency of any single pesticide was less than 11 percent. DDTR was the only pesticide with a significant level of occurrence, but even it had a low average-residue level: 0.07 ppm.

Mixed hay contained no detectable organophosphate residues, but frequently contained chlorinated hydrocarbons. DDTR was again the most prevalent pesticide, occurring 69 percent of the time. Chlordane and toxaphene were also found but, like DDTR, at low concentrations.

Soybeans showed traces of dieldrin in 39 percent of the samples, but no pesticide exceeded an average con-

centration of 0.03 ppm. Soybeans showed no organophosphate residues even though all 137 sites sampled had been treated with such pesticides.

Acknowledgments

It is not possible to list by name all persons who contributed to this study. However, authors are especially grateful to the staff at the Monitoring Laboratory, Mississippi Test Facility, Bay St. Louis, Miss., who processed and analyzed samples for chemical residues and contributed immeasurably to this study, and to inspectors from the Animal and Plant Health Inspection Service, USDA, who collected the samples. Finally, recognition is due Dr. Edwin Cox, Biometrical Services Staff, USDA, for sample allocation procedures, and to Dr. Richard Daum, Animal and Plant Health Inspection Service, for probit analyses.

Literature Cited

- (1) Bennett, I. L. 1967. Foreword. *Pestic. Monit. J.* 1(1).
- (2) Panel on Pesticide Monitoring. 1971. Criteria for defining pesticide levels to be considered an alert to potential problems. *Pestic. Monit. J.* 5(1):36.
- (3) Wiersma, G. B., H. Tai, and P. F. Sand. 1972. Pesticide residue levels in soil, FY 1969—National Soils Monitoring Program. *Pestic. Monit. J.* 6(3):194-201.
- (4) Wiersma, G. B., P. F. Sand, and E. L. Cox. 1971. A sampling design to determine pesticide residue levels in soils of the conterminous United States. *Pestic. Monit. J.* 5(1):63-66.
- (5) Daum, R. L. 1970. Revision of two computer programs for probit analysis. *Bull. Entomol. Soc. Am.* 16:10-15.

TABLE 1. Summary of pesticides applied to cropland, all sites,¹ FY-70

PESTICIDE	No. SITES USING PESTICIDE	PERCENT SITES USING PESTICIDE	ARITH. MEAN APPL. RATE (LB/A) ²	ARITH. MEAN (LB/A) ²
Aldrin	57	4.23	1.03	0.0434
Amiben	51	3.79	1.77	0.0669
Amitrole	1	0.07	2.11	0.0016
Atrazine	154	11.44	1.74	0.1987
Azinphosmethyl	15	1.11	4.19	0.0467
Azodrin (monocrotophos)	6	0.45	4.28	0.0191
Barban	1	0.07	0.20	0.0001
Benfenif	2	0.15	1.31	0.0019
Biflirin (dicrotophos)	8	0.59	0.31	0.0018
Borax	2	0.15	1.25	0.0019
Bordeaux mixtures	1	0.07	1.00	0.0007
Butoron	2	0.15	0.01	0.0000
Bux-ten (bux)	16	1.19	2.27	0.0269
Calcium arsenate	1	0.07	9.80	0.0073
Caplan	106	7.88	1.68	0.1323
Carbaryl	31	2.30	3.91	0.0900
Carbophenothion	3	0.22	0.92	0.0020
CEAA	1	0.07	0.60	0.0004
CEEA	1	0.07	2.00	0.0015
Ceresan L	3	0.22	0.04	0.0001
Ceresan M (granosan)	8	0.59	0.02	0.0001
Ceresan red	19	1.41	0.03	0.0004
Chevron RE-5353	1	0.07	0.70	0.0005
Chlordane	1	0.07	1.00	0.0007
Chlorobenzilate	3	0.22	0.95	0.0021
Chloroneb	5	0.37	0.01	0.0000
Chloroxuron	3	0.22	1.42	0.0032
CIPC (chloroprotham)	1	0.07	0.66	0.0005
Copper oxide	3	0.22	3.70	0.0082
Copper-8-quinolinolate	1	0.07	0.01	0.0000
Copper sulfate	9	0.67	56.65	0.3788
Cotoran (fluometuron)	15	1.11	0.68	0.0076
4-D	122	9.06	0.64	0.0578
DAC	3	0.22	3.50	0.0078
Dalapon	10	0.74	2.55	0.0189

Continued next page)

TABLE 1 (cont'd). Summary of pesticides applied to cropland, all sites,¹ FY-70

PESTICIDE	NO. SITES USING PESTICIDE	PERCENT SITES USING PESTICIDE	APPL. RATE ARITH. MEAN (LB/A) ²	ARITH. MEAN (LB/A) ²
2,4-DB	7	0.52	0.56	0.0029
DDT	37	3.75	5.20	0.1428
DEF	6	0.45	1.44	0.0064
Demeton	2	0.15	0.88	0.0013
Diazinon	11	0.82	1.95	0.0160
Dicamba	2	0.15	0.04	0.0001
Dichloropropane	1	0.07	26.00	0.0193
Dichloropropene	2	0.15	64.21	0.0954
Dichlorprop	1	0.07	0.50	0.0004
Dicofol	4	0.30	1.95	0.0058
Dieldrin	5	0.37	0.21	0.0008
Dimethoate	2	0.15	3.21	0.0048
Dinitrobutylphenol	6	0.45	2.84	0.0126
Dinitroresol	2	0.15	0.10	0.0002
Dinitrocyclohexylphenol	1	0.07	0.50	0.0004
Dioxathion	1	0.07	0.75	0.0006
Diphenamid	2	0.15	3.00	0.0045
Disulfoton	11	0.82	0.62	0.0050
Dithane M-45 (mancozeb)	1	0.07	1.50	0.0011
Diuron	8	0.59	0.47	0.0028
Dodine	3	0.22	5.23	0.0117
DSMA	6	0.45	2.02	0.0090
Endosulfan (I)	3	0.22	0.61	0.0014
Endothall	1	0.07	0.90	0.0007
Endrin	6	0.45	2.28	0.0102
EPN	2	0.15	1.10	0.0016
EPTC	5	0.37	22.10	0.0821
Ethion	8	0.59	2.13	0.0126
Ethylene dibromide	1	0.07	0.01	0.0000
Falone	1	0.07	2.00	0.0015
Fensulfothion	4	0.30	1.20	0.0036
Fenthion	1	0.07	0.09	0.0001
Ferbam	1	0.07	4.60	0.0034
Folex	7	0.52	1.30	0.0068
Furadan (carbofuran)	1	0.07	1.00	0.0007
Heptachlor	20	1.49	0.79	0.0118
Isopestox	1	0.07	0.01	0.0000
Lasso	13	0.97	1.01	0.0098
Lead arsenate	1	0.07	6.40	0.0048
Lindane	4	0.30	0.01	0.0000
Linuron	15	1.11	0.86	0.0096
Malathion	84	6.24	0.19	0.0117
Maleic hydrazide	3	0.22	1.80	0.0040
Maneb	2	0.15	1.00	0.0015
MCPA	10	0.74	0.66	0.0049
Methoxychlor	22	1.63	0.12	0.0020
Methyl demeton	2	0.15	1.13	0.0017
Methylmercury dicyandiamide	14	1.04	0.01	0.0001
Methyl trithion	2	0.15	7.75	0.0115
Mevinphos	2	0.15	0.10	0.0001
Mirex	1	0.07	0.01	0.0000
Monuron	2	0.15	0.31	0.0005
MSMA	13	0.97	1.79	0.0173
Nitralin	7	0.52	0.75	0.0039
Nitrate	7	0.52	51.71	0.2689
Norea	2	0.15	1.00	0.0015
NPA	6	0.45	2.02	0.0090
Paraquat	6	0.45	0.18	0.0008
Parathion, ethyl	20	1.49	3.41	0.0507
Parathion, methyl	44	3.27	4.16	0.1360
PCNB	3	0.22	0.01	0.0000
Phorate	19	1.41	3.17	0.0447
Picloram	1	0.07	1.00	0.0007
Prometryne	1	0.07	0.75	0.0006
Propanil	3	0.22	2.83	0.0063
Ramrod (propachlor)	45	3.34	1.47	0.0493
Silvex	5	0.37	0.64	0.0024
Simazine	5	0.37	2.66	0.0099
Sodium chlorate	5	0.37	6.40	0.0238
Strobane	1	0.07	3.00	0.0022
Sulfur	16	1.19	50.74	0.6032
Sutan	5	0.37	3.95	0.0147
2,4,5-T	1	0.07	2.00	0.0015
TCA	2	0.15	5.25	0.0078
TDE	6	0.45	2.38	0.0106
Terbacil	2	0.15	0.39	0.0006
Tetradifon	1	0.07	0.75	0.0006
Thiram	7	0.52	0.02	0.0001
Toxaphene	33	2.45	9.54	0.2339
Trifluralin	47	3.49	0.94	0.0330
Vernolate	7	0.52	2.90	0.0151

¹ 1,346 sites, 35 States.² To convert lb/a to kg/ha., multiply by 1.1208.

TABLE 2. Pesticides applied to cropland by State, FY-70

PESTICIDE	No. SITES USING PESTICIDE	PERCENT SITES USING PESTICIDE	ARITH. MEAN APPL. RATE (LB/A) ¹	ARITH. MEAN (LB/A) ¹
ALABAMA, 22 SITES				
Azinphosmethyl	1	4.55	4.00	0.1818
Azodrin	1	4.55	12.00	0.5455
Copper sulphate	1	4.55	8.00	0.3636
Cotoran	2	9.09	1.50	0.1364
DDT	6	27.27	11.08	3.0227
DEF	1	4.55	1.50	0.0682
DSMA	1	4.55	2.00	0.0909
Endothall	1	4.55	0.90	0.0409
Endrin	1	4.55	10.50	0.4773
Nitralin	2	9.09	1.00	0.0909
Parathion, ethyl	3	13.64	16.06	2.1900
Parathion, methyl	7	31.82	6.54	2.0823
Strobane	1	4.55	3.00	0.1364
Sulfur	1	4.55	72.00	3.2727
Toxaphene	3	13.64	48.31	6.5873
Trifluralin	3	13.64	2.03	0.2773
ARKANSAS, 47 SITES				
Aldrin	1	2.13	0.01	0.0002
Amiben	2	4.26	1.00	0.0428
Azodrin	1	2.13	3.75	0.0798
Captan	2	4.26	0.03	0.0015
Carbaryl	3	6.38	1.70	0.1085
Ceresan M	2	4.26	0.05	0.0023
Ceresan red	2	4.26	0.10	0.0043
Chloroneb	3	6.38	0.01	0.0009
Cotoran	2	4.26	0.77	0.0330
Dalapon	1	2.13	3.00	0.0638
2,4-DB	2	4.26	0.50	0.0213
DDT	2	4.26	6.25	0.2660
DEF	1	2.13	0.75	0.0160
Dinitrobutylphenol	1	2.13	10.00	0.2128
Dinitrocyclohexylphenol	1	2.13	0.50	0.0106
DSMA	1	2.13	1.00	0.0213
EPN	1	2.13	0.50	0.0106
Ethylene dibromide	1	2.13	0.01	0.0002
Folex	2	4.26	1.50	0.0638
Lasso	1	2.13	0.50	0.0106
Lnuron	1	2.13	1.50	0.0319
Methylmercury dicyandiamide	3	6.38	0.01	0.0006
Methyl trithion	1	2.13	5.50	0.1170
Monuron	1	2.13	0.25	0.0053
MSMA	3	6.38	3.33	0.2128
Nitralin	2	4.26	0.44	0.0187
Norea	1	2.13	1.00	0.0213
Paraquat	1	2.13	0.25	0.0053
Parathion, methyl	10	21.28	4.00	0.8511
Phorate	1	2.13	0.50	0.0106
Prometryne	1	2.13	0.75	0.1600
Propanil	1	2.13	2.50	0.0532
Toxaphene	2	4.26	1.75	0.0745
Trifluralin	9	19.15	0.68	0.1311
CALIFORNIA, 43 SITES				
Azinphosmethyl	3	6.98	0.92	0.0640
Azodrin	2	4.65	4.38	0.2035
Bidrin	1	2.33	0.75	0.0174
Bordeaux mixtures	1	2.33	1.00	0.0233
Carbaryl	1	2.33	1.25	0.0291
Carbophenothion	1	2.33	0.50	0.0116
Chlorobenzilate	1	2.33	1.00	0.0233
2,4-D	1	2.33	0.88	0.0205
DAC	1	2.33	4.00	0.0930
DDT	3	6.98	3.00	0.2093
DEF	1	2.33	3.00	0.0698
Diazinon	1	2.33	2.00	0.0465
Dicofol	2	4.65	0.88	0.0407
Dimethoate	1	2.33	0.33	0.0077
Dioxathion	1	2.33	0.75	0.0174
Disulfoton	1	2.33	1.00	0.0233
DSMA	1	2.33	2.00	0.0465
Endosulfan (1)	2	4.65	0.88	0.0407
Endrin	1	2.33	0.75	0.0174
Ethion	2	4.65	1.50	0.0698
Fenthion	1	2.33	0.09	0.0021
Malathion	2	4.65	2.02	0.0942
Methyl demeton	1	2.33	0.25	0.0058
Paraquat	2	4.65	0.18	0.0086
Parathion, ethyl	7	16.28	0.99	0.1616
Parathion, methyl	1	2.33	0.10	0.0023
Imazine	2	4.65	3.30	0.1535
Sodium chlorate	3	6.98	8.17	0.5698

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TABLE 2 (cont'd). Pesticides applied to cropland by State, FY-70

PESTICIDE	No. SITES USING PESTICIDE	PERCENT SITES USING PESTICIDE	ARITH. MEAN APPL. RATE (LB/A) ¹	ARITH. MEAN (LB/A) ¹
Sulfur	5	11.63	41.71	4.8502
Tetradifon	1	2.33	0.75	0.0174
Toxaphene	3	6.98	6.00	0.4186
Trifluralin	1	2.33	2.00	0.0465
FLORIDA, 18 SITES				
Aldrin	1	5.56	4.44	0.2467
Atrazine	1	5.56	0.50	0.0278
Carbaryl	1	5.56	5.00	0.2778
Carbophenothion	2	11.11	1.13	0.1250
Chlorobenzilate	2	11.11	0.92	0.1022
Copper oxide	2	11.11	4.65	0.5167
2,4-D	1	5.56	2.00	0.1111
Dalapon	1	5.56	2.00	0.1111
Dicofol	1	5.56	2.00	0.1111
Dimethoate	1	5.56	6.10	0.3389
Ethion	5	27.78	2.30	0.6389
Lead arsenate	1	5.56	6.40	0.3556
Parathion, ethyl	2	11.11	3.55	0.3944
Sulfur	4	22.22	60.65	13.4778
2,4,5-T	1	5.56	2.00	0.1111
Toxaphene	1	5.56	4.00	0.2222
GEORGIA, 30 SITES				
Atrazine	2	6.67	2.70	0.1800
Azodrin	1	3.33	0.60	0.0200
Benefin	2	6.67	1.31	0.0873
Bidrin	1	3.33	0.30	0.0100
Calcium arsenate	1	3.33	9.80	0.3267
Captan	8	26.67	0.05	0.0147
Carbaryl	5	16.67	4.45	0.7417
Ceresan red	4	13.33	0.01	0.0013
Copper sulfate	8	26.67	62.73	16.7283
DDT	7	23.33	3.96	0.9233
Dinitrobutylphenol	2	6.67	1.50	0.1000
Disulfoton	1	3.33	0.80	0.0267
Dithane M-45	1	3.33	1.50	0.0500
DSMA	1	3.33	0.50	0.0167
Endrin	1	3.33	0.33	0.0110
Falone	1	3.33	2.00	0.0667
Linuron	1	3.33	1.00	0.0333
Malathion	4	13.33	0.01	0.0013
Methoxychlor	4	13.33	0.03	0.0040
Methyl trithion	1	3.33	10.00	0.3333
Mirex	1	3.33	0.01	0.0003
Parathion, methyl	2	6.67	1.02	0.0683
Simazine	1	3.33	2.50	0.0833
Sulfur	3	10.00	20.00	2.0000
Toxaphene	7	23.33	4.63	1.0800
Trifluralin	1	3.33	1.50	0.0500
Vernolate	5	16.67	2.20	0.3667
ILLINOIS, 51 SITES ²				
Aldrin	9	17.65	0.92	0.1627
Amiben	5	9.80	2.60	0.2549
Atrazine	8	15.69	1.94	0.3049
Bux-ten (bux)	4	7.84	2.97	0.2333
Captan	23	45.10	0.03	0.0122
Carbaryl	1	1.96	2.00	0.0392
Ceresan red	2	3.92	0.01	0.0004
2,4-D	3	5.88	0.31	0.0182
DAC	1	1.96	1.50	0.0294
Dalapon	1	1.96	1.00	0.0196
Diazinon	2	3.92	0.50	0.0198
Dicamba	1	1.96	0.02	0.0004
Furadan	1	1.96	1.00	0.0196
Heptachlor	6	11.76	0.84	0.0984
Lasso	1	1.96	1.40	0.0275
Linuron	1	1.96	1.00	0.0196
Malathion	23	45.10	0.01	0.0045
Methoxychlor	5	9.80	0.01	0.0010
Phorate	1	1.96	0.05	0.0010
Ramrod	12	23.53	1.23	0.2904
Silvex	1	1.96	0.50	0.0098
Vernolate	1	1.96	1.30	0.0255
INDIANA, 77 SITES				
Aldrin	7	9.09	0.82	0.0742
Amiben	6	7.79	0.97	0.0756
Atrazine	13	16.88	1.37	0.2318
Captan	11	14.29	0.01	0.0016
Ceresan red	1	1.30	0.02	0.0003
2,4-D	9	11.69	0.66	0.0769

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TABLE 2 (cont'd). Pesticides applied to cropland by State, FY-70

PESTICIDE	No. SITES USING PESTICIDE	PERCENT SITES USING PESTICIDE	ARITH. MEAN APPL. RATE (LB/A) ¹	ARITH. MEAN (LB/A) ¹
Dinitrobutylphenol	1	1.30	2.00	0.0260
Heptachlor	2	2.60	0.76	0.0199
Lasso	5	6.49	1.40	0.0909
Linuron	2	2.60	1.05	0.0273
Malathion	6	7.79	0.01	0.0008
Methoxychlor	2	2.60	0.01	0.0003
Methylmercury dicyandiamide	1	1.30	0.01	0.0001
MSMA	1	1.30	4.00	0.0519
NPA	1	1.30	4.00	0.0519
Ramrod	4	5.19	2.06	0.1071
Trifluralin	1	1.30	1.00	0.0130
IOWA, 152 SITES				
Aldrin	15	9.87	0.83	0.0820
Amiben	14	9.21	0.84	0.0776
Atrazine	24	15.79	1.50	0.2367
Bux-ten (bux)	8	5.26	0.99	0.0520
Captan	2	1.32	0.01	0.0001
Carbaryl	1	0.66	1.60	0.0105
Chevron RE-5353	1	0.66	0.70	0.0046
CIPC	1	0.66	0.66	0.0043
2,4-D	17	11.18	0.60	0.0669
2,4-DB	2	1.32	0.88	0.0115
Diazinon	3	1.97	0.50	0.0099
Fensulfothion	2	1.32	1.38	0.0181
Heptachlor	5	3.29	0.61	0.0199
Lasso	3	1.97	0.91	0.0180
Lindane	1	0.66	0.02	0.0001
Linuron	1	0.66	0.60	0.0039
NPA	1	0.66	1.00	0.0066
Parathion, ethyl	1	0.66	0.02	0.0001
Phorate	7	4.61	0.85	0.0391
Ramrod	11	7.24	1.37	0.0991
Sutan	2	1.32	4.50	0.0592
Trifluralin	3	1.97	0.40	0.0079
KENTUCKY, 31 SITES				
Amiben	2	6.45	2.00	0.1290
Atrazine	2	6.45	1.75	0.1129
Chloroxuron	1	3.23	2.00	0.0645
2,4-D	2	6.45	0.88	0.0565
Dalapon	1	3.23	1.00	0.0323
LOUISIANA, 25 SITES				
Aldrin	3	12.00	0.10	0.0124
Azinphosmethyl	3	12.00	1.18	0.1420
Buturon	2	8.00	0.01	0.0008
Captan	1	4.00	0.02	0.0008
Ceresan L	2	8.00	0.01	0.0008
Cotoran	1	4.00	1.00	0.0400
2,4-D	4	16.00	0.88	0.1400
Dalapon	3	12.00	3.67	0.4400
2,4-DB	1	4.00	0.75	0.0300
DDT	2	8.00	2.50	0.2000
DEF	1	4.00	1.12	0.0448
Diuron	1	4.00	0.70	0.0280
DSMA	1	4.00	6.00	0.2400
Norea	1	4.00	1.00	0.0400
NPA	1	4.00	2.00	0.0800
Parathion, methyl	6	24.00	3.54	0.8500
Propanil	2	8.00	3.00	0.2400
Silvex	2	8.00	0.75	0.0600
TCA	2	8.00	5.25	0.4200
TDE	1	4.00	6.00	0.2400
Terbacil	2	8.00	0.39	0.0316
Toxaphene	3	12.00	6.33	0.7600
Trifluralin	4	16.00	0.81	0.1300
MICHIGAN, 34 SITES				
Atrazine	4	11.76	3.38	0.3971
Azinphosmethyl	3	8.82	3.75	0.3309
Captan	2	5.88	13.00	0.7647
Carbaryl	2	5.88	15.00	0.8824
CDEA	1	2.94	2.00	0.0588
Chlordane	1	2.94	1.00	0.0294
2,4-D	3	8.82	1.17	0.1029
Dodine	2	5.88	2.22	0.1309
EPTC	2	5.88	3.50	0.2059
Ethion	1	2.94	2.50	0.0735
Ferbam	1	2.94	4.60	0.1353
Malathion	1	2.94	3.75	0.1103
Simazine	1	2.94	2.00	0.0588
Sulfur	2	5.88	97.50	5.7353

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TABLE 2 (cont'd). Pesticides applied to cropland by State, FY-70

PESTICIDE	NO. SITES USING PESTICIDE	PERCENT SITES USING PESTICIDE	ARITH. MEAN APPL. RATE (LB/A) ¹	ARITH. MEAN (LB/A) ¹
MID-ATLANTIC STATES, ² 15 SITES				
Aldrin	1	6.67	1.20	0.0800
Atrazine	2	13.33	1.28	0.1707
Azinphosmethyl	1	6.67	0.05	0.0033
Captan	7	46.67	0.02	0.0107
2,4-D	3	20.00	0.77	0.1533
EPTC	1	6.67	100.00	6.6667
Heptachlor	1	6.67	0.04	0.0027
Lasso	1	6.67	0.20	0.0133
Linuron	1	6.67	0.15	0.0100
Malathion	4	26.67	0.01	0.0027
Maneb	1	6.67	2.00	0.1333
Methoxychlor	2	13.33	0.01	0.0013
Methyl demeton	1	6.67	2.00	0.1333
Phorate	1	6.67	20.00	1.3333
Simazine	1	6.67	2.20	0.1467
MINNESOTA, 119 SITES				
Amiben	4	3.36	2.00	0.0672
Atrazine	6	5.04	1.90	0.0958
Bux-ten (bux)	1	0.84	4.00	0.0336
Captan	2	1.68	0.01	0.0002
Carbaryl	2	1.68	1.45	0.0244
2,4-D	10	8.40	0.74	0.0626
Dalapon	1	0.84	1.00	0.0084
Isopestox	1	0.84	0.01	0.0001
Lasso	1	0.84	1.00	0.0084
Linuron	1	0.84	2.50	0.0210
Malathion	1	0.84	0.01	0.0001
MCPA	7	5.88	0.86	0.0504
Phorate	2	1.68	10.50	0.1765
Ramrod	7	5.88	1.94	0.1143
Silvex	1	0.84	0.40	0.0034
MISSISSIPPI, 31 SITES				
Azinphosmethyl	1	3.23	3.00	0.0968
Bidrin	6	19.35	0.23	0.0452
Captan	1	3.23	0.01	0.0003
Carbaryl	2	6.45	4.50	0.2903
Ceresan red	3	9.68	0.01	0.0010
Chloroneb	2	6.45	0.01	0.0006
Cotoran	8	25.81	0.38	0.0977
DDT	10	32.26	6.22	2.0081
DEF	2	6.45	1.13	0.0726
Dinitrobutylphenol	1	3.23	0.52	0.0168
Dinitrocresol	2	6.45	0.10	0.0068
Disulfoton	3	9.68	0.02	0.0016
Diuron	4	12.90	0.13	0.0171
DSMA	1	3.23	0.62	0.0200
Endrin	1	3.23	1.65	0.0532
EPN	1	3.23	1.70	0.0548
Folex	5	16.13	1.22	0.1968
Lasso	1	3.23	0.35	0.0113
Linuron	2	6.45	0.79	0.0510
Monuron	1	3.23	0.38	0.0123
MSMA	6	19.35	0.71	0.1384
Nitralin	2	6.45	0.88	0.0565
NPA	1	3.23	0.26	0.0084
Paraquat	3	9.68	0.16	0.0152
Parathion, methyl	15	48.39	4.82	2.3342
PCNB	1	3.23	0.01	0.0003
Sodium chlorate	1	3.23	3.00	0.0968
Toxaphene	7	22.58	11.86	2.6774
Trifluralin	13	41.94	0.98	0.4113
MISSOURI, 81 SITES				
Aldrin	10	12.35	1.00	0.1235
Amiben	5	6.17	1.35	0.0833
Atrazine	17	20.99	1.83	0.3840
Carbaryl	1	1.23	2.00	0.0247
2,4-D	9	11.11	0.58	0.0648
Diazinon	1	1.23	0.60	0.0074
Diuron	3	3.70	0.83	0.0309
Heptachlor	1	1.23	1.00	0.0123
Linuron	2	2.47	0.50	0.0123
Ramrod	3	3.70	1.52	0.0562
Sutan	1	1.23	4.00	0.0494
Trifluralin	5	6.17	0.85	0.0525
NEBRASKA, 106 SITES				
Aldrin	1	0.94	0.50	0.0047
Amiben	2	1.89	0.63	0.0118
Atrazine	16	15.09	1.28	0.1937

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TABLE 2 (cont'd). Pesticides applied to cropland by State, FY-70

PESTICIDE	NO. SITES USING PESTICIDE	PERCENT SITES USING PESTICIDE	ARITH. MEAN APPL. RATE (LB/A) ¹	ARITH. MEAN (LB/A) ¹
Bux-ten (bux)	2	1.89	1.22	0.0231
Captan	18	16.98	0.01	0.0017
Carbaryl	1	0.94	1.60	0.0151
Ceresan L	1	0.94	0.10	0.0009
2,4-D	9	8.49	0.60	0.0509
Dalapon	1	0.94	2.50	0.0236
Demeton	1	0.94	0.25	0.0024
Diazinon	1	0.94	0.22	0.0021
Dieldrin	1	0.94	0.01	0.0001
Disulfoton	3	2.83	1.14	0.0324
Endrin	2	1.89	0.22	0.0042
Fensulfothion	2	1.89	1.03	0.0195
Heptachlor	2	1.89	0.01	0.0002
Malathion	18	16.98	0.01	0.0017
Methoxychlor	2	1.89	0.01	0.0002
Methylmercury dicyandiamide	1	0.94	0.01	0.0001
Phorate	6	5.66	0.95	0.0540
Ramrod	4	3.77	1.09	0.0410
Thiram	3	2.83	0.01	0.0003
NEW ENGLAND, ⁴ 18 SITES				
No pesticides applied				
NEW YORK, 35 SITES				
Atrazine	5	14.29	2.00	0.2857
Azinphosmethyl	1	2.86	37.50	1.0714
Captan	5	14.29	30.01	4.2869
Carbaryl	3	8.57	8.33	0.7143
2,4-D	4	11.43	0.63	0.0726
Demeton	1	2.86	1.50	0.0429
Dichlorprop	1	2.86	0.50	0.0143
Dicofol	1	2.86	4.04	0.1154
Dieldrin	1	2.86	0.02	0.0006
Dodine	1	2.86	11.25	0.3214
EPTC	1	2.86	3.00	0.0857
Malathion	4	11.43	0.01	0.0011
Methoxychlor	3	8.57	0.01	0.0009
Methylmercury dicyandiamide	2	5.71	<0.01	0.0003
Nitrate	7	20.00	51.71	10.3429
Sutan	1	2.86	3.75	0.1071
Thiram	1	2.86	0.10	0.0029
NORTH CAROLINA, 31 SITES				
Amiben	1	3.23	2.00	0.0645
Atrazine	8	25.81	2.20	0.5677
Azodrin	1	3.23	0.60	0.0194
Captan	1	3.23	0.01	0.0003
Carbaryl	3	9.68	1.32	0.1274
Ceresan red	2	6.45	0.10	0.0065
Copper oxide	1	3.23	1.80	0.0581
Copper-8-quinolinolate	1	3.23	0.01	0.0003
2,4-D	3	9.68	0.83	0.0806
DDT	4	12.90	1.60	0.2065
Diazinon	2	6.45	3.58	0.2310
Dichloropropane	1	3.23	26.00	0.8387
Dichloropropene	2	6.45	64.21	4.1426
Dinitrobutylphenol	1	3.23	1.50	0.0484
Diphenamid	2	6.45	3.00	0.1935
Endosulfan (1)	1	3.23	0.08	0.0026
Lindane	1	3.23	0.01	0.0003
Malathion	1	3.23	2.50	0.0806
Maleic hydrazide	3	9.68	1.80	0.1742
MSMA	2	6.45	2.38	0.1532
Parathion, ethyl	2	6.45	0.60	0.0387
Sulfur	1	3.23	33.75	1.0887
TDE	4	12.90	1.33	0.1710
Thiram	1	3.23	0.01	0.0003
Toxaphene	1	3.23	2.00	0.0645
OHIO, 69 SITES				
Aldrin	6	8.70	1.67	0.1449
Amiben	8	11.59	1.55	0.1801
Atrazine	12	17.39	1.70	0.2955
Captan	1	1.45	0.01	0.0001
CDA A	1	1.45	0.60	0.0087
2,4-D	9	13.04	0.71	0.0920
Dicamba	1	1.45	0.06	0.0009
Dieldrin	1	1.45	1.00	0.0145
Heptachlor	2	2.90	2.56	0.0743
Malathion	2	2.90	0.50	0.0146
Parathion, ethyl	1	1.45	2.00	0.0290
Ramrod	3	4.35	1.40	0.0609
Vernolate	1	1.45	8.00	0.1159

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TABLE 2 (cont'd). Pesticides applied to cropland by State, FY-70

PESTICIDE	No. SITES USING PESTICIDE	PERCENT SITES USING PESTICIDE	ARITH. MEAN APPL. RATE (LB/A) ¹	ARITH. MEAN (LB/A) ¹
OKLAHOMA, 56 SITES				
Borax	2	3.57	1.25	0.0446
Ceresan M	4	7.14	0.01	0.0007
Ceresan red	3	5.36	0.01	0.0005
2,4-D	2	3.57	0.75	0.0268
Disulfoton	1	1.79	0.50	0.0089
Parathion, ethyl	2	3.57	0.75	0.0268
Parathion, methyl	2	3.57	0.50	0.0179
PCNB	1	1.79	0.01	0.0002
Picloram	1	1.79	1.00	0.0179
Toxaphene	1	1.79	2.00	0.0357
Trifluralin	2	3.57	0.88	0.0313
PENNSYLVANIA, 29 SITES				
Amitrole	1	3.45	2.11	0.0728
Atrazine	4	13.79	2.16	0.2983
Azinphosmethyl	1	3.45	0.25	0.0086
2,4-D	3	10.34	0.10	0.0100
Malathion	2	6.90	1.13	0.0776
Methoxychlor	2	6.90	1.13	0.0776
Parathion, ethyl	1	3.45	0.25	0.0086
Silvex	1	3.45	0.81	0.0279
SOUTH CAROLINA, 9 SITES				
Carbaryl	3	33.33	0.37	0.1222
2,4-D	1	11.11	0.50	0.0556
DDT	1	11.11	2.00	0.2222
Mevinphos	2	22.22	0.10	0.0222
Parathion, ethyl	1	11.11	1.00	0.1111
TDE	1	11.11	3.00	0.3333
Toxaphene	2	22.22	0.80	0.1778
Trifluralin	3	33.33	0.60	0.2000
SOUTH DAKOTA, 106 SITES				
Aldrin	2	1.89	0.25	0.0048
Atrazine	7	6.60	1.00	0.0658
Barban	1	0.94	0.20	0.0019
Bux-ten (bux)	1	0.94	10.00	0.0943
Captan	20	18.87	0.01	0.0020
Ceresan M	2	1.89	0.01	0.0002
2,4-D	26	24.53	0.48	0.1174
Dieldrin	2	1.89	0.01	0.0002
Heptachlor	1	0.94	0.06	0.0006
Lindane	1	0.94	0.01	0.0001
Malathion	15	14.15	0.11	0.0155
Maneb	1	0.94	0.01	0.0001
MCPA	2	1.89	0.17	0.0033
Methoxychlor	2	1.89	0.08	0.0015
Methylmercury dicyandiamide	7	6.60	0.01	0.0007
Thiram	2	1.89	0.01	0.0002
Toxaphene	1	0.94	2.00	0.0189
TENNESSEE, 23 SITES				
Atrazine	3	13.04	2.00	0.2609
Carbaryl	1	4.35	7.20	0.3130
Ceresan red	2	8.70	0.01	0.0009
Chloroxuron	2	8.70	1.13	0.0978
Cotoran	2	8.70	0.84	0.0730
2,4-D	1	4.35	1.50	0.0652
DAC	1	4.35	5.00	0.2174
Dalapon	1	4.35	4.00	0.1739
2,4-DB	2	8.70	0.19	0.0170
DDT	1	4.35	0.95	0.0413
Disulfoton	1	4.35	0.01	0.0004
EPTC	1	4.35	0.50	0.0217
Linuron	3	13.04	0.51	0.0670
MSMA	1	4.35	0.28	0.0122
Nitralin	1	4.35	0.60	0.0261
NPA	2	8.70	2.43	0.2113
Parathion, methyl	1	4.35	0.47	0.0204
PCNB	1	4.35	0.01	0.0004
Sodium chlorate	1	4.35	4.50	0.1957
Toxaphene	1	4.35	1.90	0.0826
Trifluralin	1	4.35	1.11	0.0483
VIRGINIA AND WEST VIRGINIA, 21 SITES				
Atrazine	3	14.29	1.33	0.1905
Azinphosmethyl	1	4.76	0.50	0.0238
Captan	2	9.52	0.09	0.0086
DDT	1	4.76	0.25	0.0119
Lindane	1	4.76	0.01	0.0005
Malathion	1	4.76	0.01	0.0005
Sutan	1	4.76	3.00	0.1429
Toxaphene	1	4.76	0.50	0.0238

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TABLE 2 (cont'd). *Pesticides applied to cropland by State, FY-70*

PESTICIDE	No. SITES USING PESTICIDE	PERCENT SITES USING PESTICIDE	ARITH. MEAN APPL. RATE (LB/A) ¹	ARITH. MEAN (LB/A) ¹
WISCONSIN, 67 SITES				
Aldrin	1	1.49	5.00	0.0746
Amiben	2	2.99	11.50	0.3433
Atrazine	17	25.37	2.12	0.5373
Carbaryl	1	1.49	1.25	0.0187
2,4-D	2	2.99	0.57	0.0172
Diazinon	1	1.49	9.00	0.1343
Disulfoton	1	1.49	1.00	0.0149
MCPA	1	1.49	0.25	0.0037
Phorate	1	1.49	7.00	0.1045
Ramrod	1	1.49	1.50	0.0224
Trifluralin	1	1.49	1.50	0.0224

¹ To convert lb/a to kg/ha., multiply by 1.1208.

² Use records were available for only 51 of the 150 sites in Illinois

³ Mid-Atlantic States include Maryland, Delaware, and New Jersey.

⁴ New England States include Maine, New Hampshire, Vermont, Massachusetts, Rhode Island, and Connecticut.

TABLE 3. *Pesticides applied to cropland by crop, FY-70*

PESTICIDE	No. SITES USING PESTICIDE	PERCENT SITES USING PESTICIDE	ARITH. MEAN APPL. RATE (LB/A) ¹	ARITH. MEAN (LB/A) ¹
ALFALFA AND BUR CLOVER, 114 SITES				
Azinphosmethyl	2	1.75	0.38	0.0066
Carbaryl	1	0.88	1.00	0.0088
Malathion	2	1.75	1.13	0.0197
Methoxychlor	2	1.75	1.13	0.0197
Parathion, ethyl	3	2.63	0.50	0.0132
FIELD CORN, 366 SITES				
Aldrin	51	13.93	1.00	0.1398
Amiben	3	0.82	1.47	0.0120
Amitrole	1	0.27	2.11	0.0058
Atrazine	146	39.89	1.75	0.7001
Bux-ten (bux)	16	4.37	2.27	0.0990
Captan	87	23.77	0.02	0.0052
Carbaryl	5	1.37	1.49	0.0204
CDA A	1	0.27	0.60	0.0016
Ceresan red	1	0.27	0.10	0.0003
Chevron RE-5353	1	0.27	0.70	0.0019
2,4-D	72	19.67	0.64	0.1266
Dalapon	2	0.55	2.50	0.0137
2,4-DB	1	0.27	1.00	0.0027
DDT	1	0.27	0.25	0.0007
Diazinon	9	2.46	2.15	0.0528
Dicamba	1	0.27	0.02	0.0001
Dichlorprop	1	0.27	0.50	0.0014
Disulfoton	4	1.09	1.11	0.0121
Fensulfothion	4	1.09	1.20	0.0132
Furadan	1	0.27	1.00	0.0027
Heptachlor	20	5.46	0.79	0.0433
Isopestox	1	0.27	0.01	0.0000
Lasso	3	0.82	0.92	0.0076
Lindane	3	0.82	0.01	0.0001
Linuron	4	1.09	0.90	0.0098
Malathion	71	19.40	0.01	0.0019
Maneb	1	0.27	0.01	0.0000
MCPA	1	0.27	1.00	0.0027
Methoxychlor	18	4.92	0.02	0.0011
MSMA	1	0.27	3.00	0.0082
Nitrate	4	1.09	49.88	0.5451
Parathion, ethyl	1	0.27	0.02	0.0001
Phorate	16	4.37	1.23	0.0539
Ramrod	40	10.93	1.49	0.1628
Silvex	2	0.55	0.45	0.0025
Simazine	1	0.27	2.20	0.0060
Sutan	5	1.37	3.95	0.0540
Thiram	2	0.55	0.01	0.0001
Toxaphene	1	0.27	0.50	0.0014

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TABLE 3 (cont'd). Pesticides applied to cropland by crop, FY-70

PESTICIDE	No. SITES USING PESTICIDE	PERCENT SITES USING PESTICIDE	ARITH. MEAN APPL. RATE (LB/A) ¹	ARITH. MEAN (LB/A) ¹
COTTON, 52 SITES				
Azinphosmethyl	1	1.92	3.00	0.0577
Azodrin	6	11.54	4.28	0.4942
Bidrin	8	15.38	0.31	0.0471
Calcium arsenate	1	1.92	9.80	0.1885
Captan	1	1.92	0.01	0.0002
Carbaryl	4	7.69	5.15	0.3962
Ceresan L	1	1.92	0.01	0.0002
Ceresan M	2	3.85	0.05	0.0021
Ceresan red	7	13.46	0.04	0.0048
Chlorobenzilate	1	1.92	1.00	0.0192
Chloroneb	5	9.62	0.01	0.0012
Cotoran	13	25.00	0.64	0.1608
DAC	1	1.92	4.00	0.0769
DDT	24	46.15	4.69	2.1625
DEF	6	11.54	1.44	0.1658
Dicofol	2	3.85	0.88	0.0337
Dimethoate	1	1.92	0.33	0.0063
Dinitroresol	2	3.85	0.10	0.0040
Disulfoton	4	7.69	0.01	0.0012
Diuron	8	15.38	0.47	0.0717
DSMA	6	11.54	2.02	0.2331
Endothall	1	1.92	0.90	0.0173
Endrin	3	5.77	4.16	0.2400
EPN	2	3.85	1.10	0.0423
Folex	7	13.46	1.30	0.1750
Linuron	2	3.85	0.79	0.0304
Malathion	1	1.92	2.50	0.0481
Methyl demeton	1	1.92	0.25	0.0048
Methylmercury dicyandiamide	1	1.92	0.01	0.0002
Methyl trithion	2	3.85	7.75	0.2981
Monuron	2	3.85	0.31	0.0121
MSMA	11	21.15	1.48	0.3138
Norea	1	1.92	1.00	0.0192
Nitralin	5	9.62	0.70	0.0669
Paraquat	6	11.54	0.18	0.0210
Parathion, ethyl	2	3.85	0.09	0.0035
Parathion, methyl	31	59.62	4.89	2.9129
PCNB	2	3.85	0.01	0.0004
Phorate	1	1.92	0.50	0.0096
Prometryne	1	1.92	0.75	0.0144
Sodium chlorate	4	7.69	6.88	0.5288
Strobane	1	1.92	3.00	0.0577
TDE	1	1.92	6.00	0.1154
Toxaphene	20	38.46	6.94	2.6696
Trifluralin	23	44.23	1.03	0.4550
GRASS/HAY, 30 SITES				
Atrazine	1	3.33	2.50	0.0833
Simazine	1	3.33	2.50	0.0833
MIXED HAY, 119 SITES				
Malathion	1	0.84	1.00	0.0084
Parathion, ethyl	1	0.84	2.00	0.0168
SOYBEANS, 257 SITES				
Amiben	47	18.29	1.48	0.2710
Azinphosmethyl	1	0.39	4.00	0.0156
Captan	3	1.17	0.03	0.0004
Carbaryl	5	1.95	1.36	0.0265
CDEA	1	0.39	2.00	0.0078
Ceresan red	1	0.39	0.10	0.0004
CIPC	1	0.39	0.66	0.0026
Chloroxuron	3	1.17	1.42	0.0165
Cotoran	1	0.39	0.90	0.0035
DAC	1	0.39	5.00	0.0195
Dalapon	2	0.78	4.50	0.0350
2,4-DB	5	1.95	0.43	0.0083
DDT	3	1.17	16.65	0.1944
Dinitrobutylphenol	3	1.17	4.17	0.0487
Dinitrocyclohexylphenol	1	0.39	0.50	0.0019
EPTC	1	0.39	0.50	0.0019
Lasso	9	3.50	1.10	0.0386
Linuron	9	3.50	0.87	0.0303
Methylmercury dicyandiamide	1	0.39	0.01	0.0000
Nitralin	2	0.78	0.88	0.0068
NPA	6	2.33	2.02	0.0472
Parathion, ethyl	1	0.39	48.00	0.1868
Parathion, methyl	10	3.89	3.05	0.1186
Ramrod	3	1.17	1.33	0.0156
Toxaphene	3	1.17	49.30	0.5755
Trifluralin	22	8.56	0.78	0.0670
Vernolate	2	0.78	4.65	0.0362

¹ To convert lb/a to kg/ha., multiply by 1.1208.

TABLE 4. Chlorinated hydrocarbon residues in cropland soil, all sites¹—FY-70

PESTICIDE	NO. TIMES PESTICIDE DETECTED	PERCENT OCCURRENCE	ARITH. MEAN CONC., PPM	GEOM. MEAN CONC., PPM	95% CONF. INTERVAL ABOUT GEOM. MEAN, PPM	RANGE OF DETECTED RESIDUES, PPM
Aldrin	203	13.48	0.02	0.0032	0.0027-0.0038	0.01- 4.25
Chlordane	165	10.96	0.08	0.0044	0.0036-0.0053	0.01- 13.34
DAC	1	0.07	<0.01	—	—	1.19
<i>o,p'</i> -DDE	43	2.86	<0.01	—	—	0.01- 0.51
<i>p,p'</i> -DDE	317	21.05	0.05	0.0062	0.0053-0.0071	0.01- 6.82
<i>o,p'</i> -DDT	211	14.01	0.04	0.0037	0.0031-0.0043	0.01- 11.70
<i>p,p'</i> -DDT	305	20.25	0.18	0.0085	0.0072-0.0098	0.01- 69.30
DDTR	343	22.78	0.30	0.0116	0.0099-0.0134	0.01-113.09
Dieldrin	465	30.88	0.04	0.0097	0.0086-0.0109	0.01- 1.85
Endosulfan (I)	1	0.07	<0.01	—	—	0.01
Endosulfan (II)	4	0.27	<0.01	—	—	0.02- 0.07
Endosulfan sulfate	5	0.33	<0.01	—	—	0.10- 0.29
Endrin	27	1.79	<0.01	—	—	0.01- 0.90
Heptachlor	98	6.51	0.01	—	—	0.01- 1.71
Heptachlor epoxide	147	9.76	0.01	0.0016	0.0013-0.0019	0.01- 0.34
Isodrin	34	2.26	<0.01	—	—	0.01- 0.18
Lindane	6	0.40	<0.01	—	—	0.01- 0.15
Nitralin	1	0.07	<0.01	—	—	2.47
Ramrod	1	0.07	<0.01	—	—	0.03
<i>o,p'</i> -TDE	37	2.46	0.01	—	—	0.01- 4.87
<i>p,p'</i> -TDE	217	14.41	0.03	0.0033	0.0028-0.0038	0.01- 20.40
Toxaphene	27	1.79	0.06	—	—	0.79- 8.75
Trifluralin	33	2.19	<0.01	—	—	0.01- 0.36

NOTE: All residues on dry-weight basis.

¹ 1,506 analyses, 35 States.

TABLE 5. Chlorinated hydrocarbon residues in cropland soil by State, FY-70

PESTICIDE	NO. TIMES PESTICIDE DETECTED	PERCENT OCCURRENCE	ARITH. MEAN CONC., PPM	RANGE OF DETECTED RESIDUES, PPM
ALABAMA, 21 SITES				
Chlordane	1	4.76	0.01	0.23
DAC	1	4.76	0.06	1.19
<i>o,p'</i> -DDE	2	9.52	<0.01	0.02-0.08
<i>p,p'</i> -DDE	17	80.95	0.13	0.02-0.49
<i>o,p'</i> -DDT	13	61.90	0.09	0.01-0.47
<i>p,p'</i> -DDT	16	76.19	0.50	0.03-3.08
DDTR	17	80.95	0.77	0.05-3.83
Dieldrin	4	19.05	<0.01	0.01-0.03
Endrin	2	9.52	0.01	0.05-0.16
Heptachlor epoxide	1	4.76	<0.01	0.03
Lindane	2	9.52	<0.01	0.01
<i>o,p'</i> -TDE	2	9.52	0.01	0.04-0.08
<i>p,p'</i> -TDE	12	57.14	0.04	0.01-0.20
Trifluralin	6	28.57	0.02	0.02-0.13
ARKANSAS, 47 SITES				
Aldrin	8	17.02	<0.01	0.01-0.05
<i>o,p'</i> -DDE	3	6.38	<0.01	0.01-0.03
<i>p,p'</i> -DDE	25	53.19	0.13	0.01-1.25
<i>o,p'</i> -DDT	15	31.91	0.06	0.01-0.62
<i>p,p'</i> -DDT	22	46.81	0.47	0.03-3.98
DDTR	25	53.19	0.69	0.02-5.30
Dieldrin	12	25.53	0.03	0.04-0.22
Endrin	3	6.38	<0.01	0.01-0.03
Lindane	1	2.13	<0.01	0.01
Nitralin	1	2.13	0.05	2.47
<i>o,p'</i> -TDE	2	4.26	0.01	0.09-0.21
<i>p,p'</i> -TDE	18	38.30	0.03	0.01-0.31
Trifluralin	2	4.26	0.01	0.01-0.36
CALIFORNIA, 65 SITES				
Aldrin	1	1.54	<0.01	0.17
Chlordane	2	3.08	<0.01	0.10-0.20
<i>o,p'</i> -DDE	14	21.54	0.01	0.01-0.38
<i>p,p'</i> -DDE	41	63.08	0.17	0.01-1.39
<i>o,p'</i> -DDT	32	49.23	0.08	0.01-0.62
<i>p,p'</i> -DDT	40	61.54	0.38	0.01-5.16
DDTR	46	70.77	0.74	0.01-7.75
Dieldrin	23	35.38	0.05	0.01-1.28
Endosulfan (I)	1	1.54	<0.01	0.01
Endosulfan (II)	2	3.08	<0.01	0.04-0.06
Endosulfan sulfate	2	3.08	0.01	0.17-0.29
Endrin	5	7.69	<0.01	0.02-0.10
Heptachlor epoxide	2	3.08	<0.01	0.01
<i>o,p'</i> -TDE	12	18.46	0.01	0.01-0.26
<i>p,p'</i> -TDE	34	52.31	0.08	0.01-1.20
Toxaphene	13	20.00	0.61	0.79-7.63

(Continued next page)

TABLE 5 (cont'd). Chlorinated hydrocarbon residues in cropland soil by State, FY-70

PESTICIDE	NO. TIMES PESTICIDE DETECTED	PERCENT OCCURRENCE	ARITH. MEAN CONC., PPM	RANGE OF DETECTED RESIDUES, PPM
FLORIDA, 17 SITES				
Aldrin	1	5.88	<0.01	0.06
Chlordane	2	11.76	0.17	0.10- 2.72
<i>p,p'</i> -DDE	7	41.18	0.35	0.01- 5.41
<i>o,p'</i> -DDT	5	29.41	0.25	0.01- 4.18
<i>p,p'</i> -DDT	9	52.94	1.24	0.02-20.26
DDTR	9	52.94	1.97	0.03-31.99
Dieldrin	5	29.41	0.21	0.05- 1.85
Endrin	1	5.88	0.05	0.90
Heptachlor	1	5.88	0.01	0.19
Heptachlor epoxide	1	5.88	0.01	0.09
<i>p,p'</i> -TDE	3	17.65	0.13	0.01- 2.14
Toxaphene	1	5.88	0.34	5.71
GEORGIA, 28 SITES				
<i>o,p'</i> -DDE	4	14.29	<0.01	0.01-0.02
<i>p,p'</i> -DDE	23	82.14	0.22	0.01-1.09
<i>o,p'</i> -DDT	19	67.86	0.13	0.02-0.84
<i>p,p'</i> -DDT	23	82.14	0.74	0.02-3.38
DDTR	24	85.71	1.21	0.03-5.11
Lindane	1	3.57	<0.01	0.07
<i>o,p'</i> -TDE	2	7.14	<0.01	0.02-0.09
<i>p,p'</i> -TDE	21	75.00	0.11	0.04-0.99
Toxaphene	3	10.71	0.17	1.21-2.27
Trifluralin	2	7.14	<0.01	0.02-0.03
ILLINOIS, 140 SITES				
Aldrin	73	52.14	0.08	0.01-1.38
Chlordane	48	34.29	0.25	0.05-3.76
<i>p,p'</i> -DDE	11	7.86	0.01	0.02-0.16
<i>o,p'</i> -DDT	2	1.43	<0.01	0.01-0.02
<i>p,p'</i> -DDT	13	9.29	0.01	0.02-0.20
DDTR	14	10.00	0.01	0.03-0.33
Dieldrin	96	68.57	0.15	0.02-0.92
Heptachlor	45	32.14	0.03	0.01-0.65
Heptachlor epoxide	46	32.86	0.02	0.01-0.34
Isodrin	20	14.29	<0.01	0.01-0.04
Lindane	1	0.71	<0.01	0.02
<i>p,p'</i> -TDE	5	3.57	<0.01	0.02-0.04
Trifluralin	1	0.71	<0.01	0.03
INDIANA, 78 SITES				
Aldrin	15	19.23	0.07	0.01-1.61
Chlordane	6	7.69	0.07	0.09-1.51
Dieldrin	17	21.79	0.04	0.02-0.58
Heptachlor	7	8.97	0.01	0.01-0.21
Heptachlor epoxide	5	6.41	<0.01	0.01-0.12
Isodrin	5	6.41	<0.01	0.01-0.18
Trifluralin	1	1.28	<0.01	0.06
IOWA, 150 SITES				
Aldrin	43	28.67	0.03	0.01-0.68
Chlordane	30	20.00	0.17	0.01-8.04
<i>p,p'</i> -DDE	10	6.67	<0.01	0.01-0.22
<i>o,p'</i> -DDT	6	4.00	<0.01	0.01-0.09
<i>p,p'</i> -DDT	14	9.33	0.01	0.02-0.43
DDTR	14	9.33	0.02	0.03-0.72
Dieldrin	95	63.33	0.07	0.01-0.56
Heptachlor	19	12.67	0.02	0.01-1.71
Heptachlor epoxide	33	22.00	0.01	0.01-0.28
Isodrin	1	0.67	<0.01	0.01
Lindane	1	0.67	<0.01	0.15
Ramrod	1	0.67	<0.01	0.03
<i>p,p'</i> -TDE	8	5.33	<0.01	0.01-0.05
KENTUCKY, 30 SITES				
Aldrin	1	3.33	<0.01	0.04
<i>o,p'</i> -DDE	1	3.33	<0.01	0.01
<i>p,p'</i> -DDE	8	26.67	0.01	0.01-0.15
<i>o,p'</i> -DDT	3	10.00	0.01	0.02-0.09
<i>p,p'</i> -DDT	6	20.00	0.02	0.02-0.31
DDTR	8	26.67	0.04	0.02-0.59
Dieldrin	8	26.67	0.01	0.01-0.06
<i>o,p'</i> -TDE	1	3.33	<0.01	0.03
<i>p,p'</i> -TDE	6	20.00	0.01	0.01-0.11
Toxaphene	1	3.33	0.03	0.89

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TABLE 5 (cont'd). Chlorinated hydrocarbon residues in cropland soil by State, FY-70

PESTICIDE	NO. TIMES PESTICIDE DETECTED	PERCENT OCCURRENCE	ARITH. MEAN CONC., PPM	RANGE OF DETECTED RESIDUES, PPM
LOUISIANA, 26 SITES				
Aldrin	1	3.85	<0.01	0.04
<i>o,p'</i> -DDE	2	7.69	<0.01	0.02-0.10
<i>p,p'</i> -DDE	12	46.15	0.20	0.02-1.98
<i>o,p'</i> -DDT	10	38.46	0.07	0.01-0.56
<i>p,p'</i> -DDT	12	46.15	0.40	0.06-3.21
DDTR	12	46.15	0.70	0.09-6.02
Dieldrin	8	30.77	0.02	0.02-0.08
Endrin	2	7.69	<0.01	0.02-0.03
Heptachlor	1	3.85	<0.01	0.01
<i>p,p'</i> -TDE	11	42.31	0.03	0.01-0.17
Toxaphene	1	3.85	0.20	5.32
Trifluralin	2	7.69	0.01	0.07-0.19
MICHIGAN, 54 SITES				
Chlordane	3	5.56	0.01	0.07- 0.51
<i>o,p'</i> -DDE	1	1.85	0.01	0.51
<i>p,p'</i> -DDE	7	12.96	0.06	0.01- 2.38
<i>o,p'</i> -DDT	5	9.26	0.16	0.04- 8.21
<i>p,p'</i> -DDT	6	11.11	0.26	0.03-12.03
DDTR	7	12.96	0.53	0.01-25.59
Dieldrin	7	12.96	0.01	0.01- 0.22
Endosulfan (II)	1	1.85	<0.01	0.02
Endosulfan sulfate	1	1.85	<0.01	0.10
Heptachlor	1	1.85	<0.01	0.04
Heptachlor epoxide	2	3.70	<0.01	0.01
<i>o,p'</i> -TDE	1	1.85	0.02	1.30
<i>p,p'</i> -TDE	5	9.26	0.03	0.02- 1.16
MID-ATLANTIC STATES, ¹ 19 SITES				
Aldrin	1	5.26	0.01	0.24
Chlordane	4	21.05	0.72	0.11-13.34
<i>p,p'</i> -DDE	3	15.79	0.02	0.01- 0.22
<i>o,p'</i> -DDT	2	10.53	<0.01	0.02- 0.03
<i>p,p'</i> -DDT	5	26.32	0.03	0.01- 0.38
DDTR	5	26.32	0.10	0.01- 1.46
Dieldrin	9	47.37	0.08	0.01- 0.74
Heptachlor epoxide	1	5.26	<0.01	0.03
<i>p,p'</i> -TDE	3	15.79	0.05	0.02- 0.86
MINNESOTA, 120 SITES				
Aldrin	6	5.00	0.05	0.03-4.25
Chlordane	8	6.67	0.02	0.03-0.94
<i>o,p'</i> -DDE	1	0.83	<0.01	0.01
<i>p,p'</i> -DDE	12	10.00	0.01	0.01-0.25
<i>o,p'</i> -DDT	9	7.50	<0.01	0.01-0.25
<i>p,p'</i> -DDT	13	10.83	0.02	0.02-0.74
DDTR	13	10.83	0.03	0.02-1.29
Dieldrin	17	14.17	0.02	0.01-0.92
Endrin	2	1.67	<0.01	0.01-0.02
Heptachlor	3	2.50	<0.01	0.01-0.05
Heptachlor epoxide	5	4.17	<0.01	0.01-0.09
Isodrin	2	1.67	<0.01	0.01-0.05
<i>p,p'</i> -TDE	4	3.33	<0.01	0.01-0.08
MISSISSIPPI, 29 SITES				
Chlordane	1	3.45	<0.01	0.08
<i>o,p'</i> -DDE	8	27.59	0.01	0.02-0.05
<i>p,p'</i> -DDE	27	93.10	0.28	0.01-1.71
<i>o,p'</i> -DDT	22	75.86	0.19	0.02-0.74
<i>p,p'</i> -DDT	27	93.10	1.29	0.01-6.61
DDTR	27	93.10	1.85	0.03-9.81
Dieldrin	6	20.69	0.02	0.01-0.18
Endrin	3	10.34	0.01	0.02-0.11
Heptachlor epoxide	1	3.45	<0.01	0.03
<i>p,p'</i> -TDE	18	62.07	0.08	0.01-0.71
Toxaphene	5	17.24	0.73	2.79-8.75
Trifluralin	5	17.24	0.03	0.03-0.27
MISSOURI, 81 SITES				
Aldrin	20	24.69	0.04	0.01-0.49
Chlordane	9	11.11	0.16	0.07-5.62
<i>p,p'</i> -DDE	6	7.41	<0.01	0.01-0.10
<i>o,p'</i> -DDT	2	2.47	<0.01	0.03-0.04
<i>p,p'</i> -DDT	6	7.41	0.01	0.03-0.26
DDTR	6	7.41	0.01	0.04-0.43
Dieldrin	28	34.57	0.06	0.01-0.53
Endrin	1	1.23	<0.01	0.02
Heptachlor	8	9.88	0.03	0.02-0.94
Heptachlor Epoxide	8	9.88	0.01	0.01-0.31
Isodrin	1	1.23	<0.01	0.01
<i>p,p'</i> -TDE	3	3.70	<0.01	0.02-0.04
Trifluralin	5	6.17	<0.01	0.02-0.09

(Continued next page)

TABLE 5 (cont'd). Chlorinated hydrocarbon residues in cropland soil by State, FY-70

PESTICIDE	NO. TIMES PESTICIDE DETECTED	PERCENT OCCURRENCE	ARITH. MEAN CONC., PPM	RANGE OF DETECTED RESIDUES, PPM
NEBRASKA, 106 SITES				
Aldrin	4	3.77	<0.01	0.01
Chlordane	16	15.09	0.01	0.02-0.14
<i>o,p'</i> -DDE	1	0.94	<0.01	0.01
<i>p,p'</i> -DDE	10	9.43	<0.01	0.01-0.19
<i>o,p'</i> -DDT	5	4.72	<0.01	0.01-0.06
<i>p,p'</i> -DDT	7	6.60	0.01	0.03-0.28
DDTR	10	9.43	0.01	0.01-0.59
Dieldrin	48	45.28	0.03	0.01-0.17
Endrin	4	3.77	<0.01	0.01-0.03
Heptachlor epoxide	18	16.98	<0.01	0.01-0.02
<i>p,p'</i> -TDE	3	2.83	<0.01	0.01-0.05
NEW ENGLAND STATES, ² 20 SITES				
Chlordane	1	5.00	0.01	0.19
<i>o,p'</i> -DDE	1	5.00	<0.01	0.03
<i>p,p'</i> -DDE	5	25.00	0.07	0.01-0.68
<i>o,p'</i> -DDT	5	25.00	0.07	0.01-0.86
<i>p,p'</i> -DDT	5	25.00	0.45	0.02-4.65
DDTR	5	25.00	0.65	0.04-6.65
Dieldrin	2	10.00	0.03	0.32-0.33
Endosulfan (II)	1	5.00	<0.01	0.07
Endosulfan sulfate	1	5.00	0.01	0.23
<i>p,p'</i> -TDE	4	20.00	0.05	0.14-0.43
NEW YORK, 38 SITES				
Chlordane	1	2.63	0.01	0.28
<i>p,p'</i> -DDE	13	34.21	0.21	0.01- 6.82
<i>o,p'</i> -DDT	6	15.79	0.31	0.01- 11.70
<i>p,p'</i> -DDT	12	31.58	1.87	0.01- 69.30
DDTR	15	39.47	3.06	0.01-113.09
Dieldrin	10	26.32	0.01	0.01- 0.10
Heptachlor epoxide	1	2.63	<0.01	0.06
<i>o,p'</i> -TDE	1	2.63	0.13	4.87
<i>p,p'</i> -TDE	6	15.79	0.54	0.01- 20.40
NORTH CAROLINA, 30 SITES				
Aldrin	1	3.33	<0.01	0.02
Chlordane	3	10.00	0.01	0.03-0.32
<i>o,p'</i> -DDE	1	3.33	<0.01	0.02
<i>p,p'</i> -DDE	21	70.00	0.07	0.01-0.44
<i>o,p'</i> -DDT	16	53.33	0.06	0.02-0.43
<i>p,p'</i> -DDT	20	66.67	0.31	0.02-2.93
DDTR	22	73.33	0.53	0.03-4.12
Dieldrin	10	33.33	0.03	0.01-0.29
Endrin	2	6.67	<0.01	0.01-0.03
Heptachlor epoxide	1	3.33	<0.01	0.01
<i>o,p'</i> -TDE	8	26.67	0.01	0.01-0.12
<i>p,p'</i> -TDE	18	60.00	0.07	0.01-0.42
Trifluralin	1	3.33	<0.01	0.07
OHIO, 69 SITES				
Aldrin	17	24.64	0.04	0.01-1.84
Chlordane	15	21.74	0.08	0.05-1.44
<i>p,p'</i> -DDE	6	8.70	<0.01	0.01-0.10
<i>o,p'</i> -DDT	1	1.45	<0.01	0.09
<i>p,p'</i> -DDT	3	4.35	<0.01	0.01-0.28
DDTR	7	10.14	0.02	0.02-0.43
Dieldrin	26	37.68	0.05	0.01-0.77
Endrin	1	1.45	<0.01	0.02
Heptachlor	6	8.70	0.01	0.01-0.27
Heptachlor epoxide	9	13.04	<0.01	0.01-0.05
Isodrin	2	2.90	<0.01	0.01-0.09
<i>o,p'</i> -TDE	4	5.80	<0.01	0.02-0.09
<i>p,p'</i> -TDE	6	8.70	0.01	0.01-0.23
Trifluralin	2	2.90	<0.01	0.04-0.06
OKLAHOMA, 65 SITES				
<i>p,p'</i> -DDE	12	18.46	0.03	0.01-0.89
<i>o,p'</i> -DDT	7	10.77	0.01	0.02-0.20
<i>p,p'</i> -DDT	9	13.85	0.03	0.02-0.57
DDTR	12	18.46	0.07	0.01-1.71
Dieldrin	1	1.54	<0.01	0.07
Endrin	1	1.54	<0.01	0.06
<i>p,p'</i> -TDE	6	9.23	<0.01	0.01-0.08
Toxaphene	1	1.54	0.02	1.60

(Continued next page)

TABLE 5 (cont'd). Chlorinated hydrocarbon residues in cropland soil by State, FY-70

PESTICIDE	NO. TIMES PESTICIDE DETECTED	PERCENT OCCURRENCE	ARITH. MEAN CONC., PPM	RANGE OF DETECTED RESIDUES, PPM
PENNSYLVANIA, 32 SITES				
Chlordane	1	3.13	<0.01	0.02
<i>o,p'</i> -DDE	1	3.13	<0.01	0.01
<i>p,p'</i> -DDE	9	28.13	0.05	0.01-0.74
<i>o,p'</i> -DDT	4	12.50	0.01	0.01-0.08
<i>p,p'</i> -DDT	9	28.13	0.04	0.02-0.42
DDTR	9	28.13	0.09	0.04-1.26
Dieldrin	2	6.25	0.01	0.02-0.25
Heptachlor epoxide	2	6.25	<0.01	0.01
<i>p,p'</i> -TDE	4	12.50	<0.01	0.01-0.05
SOUTH CAROLINA, 17 SITES				
Aldrin	1	5.88	<0.01	0.01
Chlordane	1	5.88	0.05	0.92
<i>o,p'</i> -DDE	2	11.76	<0.01	0.02
<i>p,p'</i> -DDE	13	76.47	0.23	0.04-0.77
<i>o,p'</i> -DDT	12	70.59	0.15	0.01-0.59
<i>p,p'</i> -DDT	13	76.47	0.63	0.05-2.98
DDTR	13	76.47	1.10	0.12-4.04
Dieldrin	3	17.65	0.06	0.01-0.98
Endosulfan sulfate	1	5.88	0.01	0.10
<i>o,p'</i> -TDE	1	5.88	0.01	0.09
<i>p,p'</i> -TDE	11	64.71	0.07	0.02-0.61
Toxaphene	2	11.76	0.34	2.44-3.34
Trifluralin	3	17.65	0.01	0.02-0.11
SOUTH DAKOTA, 106 SITES				
Aldrin	6	5.66	0.01	0.01-0.22
Chlordane	1	0.94	<0.01	0.03
<i>p,p'</i> -DDE	1	0.94	<0.01	0.02
<i>o,p'</i> -DDT	2	1.89	<0.01	0.01-0.02
<i>p,p'</i> -DDT	3	2.83	<0.01	0.03-0.04
DDTR	3	2.83	<0.01	0.05
Dieldrin	12	11.32	0.01	0.01-0.46
Isodrin	1	0.94	<0.01	0.01
TENNESSEE, 25 SITES				
Chlordane	3	12.00	0.05	0.09-0.77
<i>o,p'</i> -DDE	1	4.00	<0.01	0.02
<i>p,p'</i> -DDE	7	28.00	0.02	0.01-0.31
<i>o,p'</i> -DDT	4	16.00	0.01	0.01-0.14
<i>p,p'</i> -DDT	5	20.00	0.04	0.01-0.65
DDTR	8	32.00	0.08	0.01-1.44
Dieldrin	6	24.00	0.01	0.01-0.06
Heptachlor	2	8.00	<0.01	0.01
Heptachlor epoxide	2	8.00	<0.01	0.01-0.11
<i>o,p'</i> -TDE	1	4.00	<0.01	0.08
<i>p,p'</i> -TDE	4	16.00	0.01	0.02-0.24
Trifluralin	1	4.00	<0.01	0.01
VIRGINIA AND WEST VIRGINIA, 26 SITES				
Chlordane	3	11.54	0.02	0.04-0.37
<i>p,p'</i> -DDE	4	15.38	0.01	0.04-0.08
<i>o,p'</i> -DDT	2	7.69	<0.01	0.01-0.03
<i>p,p'</i> -DDT	3	11.54	0.01	0.01-0.14
DDTR	5	19.23	0.02	0.01-0.23
Dieldrin	3	11.54	<0.01	0.02
Heptachlor epoxide	3	11.54	0.01	0.03-0.13
<i>o,p'</i> -TDE	1	3.85	<0.01	0.01
<i>p,p'</i> -TDE	3	11.54	<0.01	0.01-0.06
WISCONSIN, 67 SITES				
Aldrin	4	5.97	0.04	0.02-1.40
Chlordane	6	8.96	0.05	0.06-1.46
<i>p,p'</i> -DDE	7	10.45	0.01	0.01-0.34
<i>o,p'</i> -DDT	2	2.99	0.01	0.13-0.35
<i>p,p'</i> -DDT	4	5.97	0.02	0.02-1.11
DDTR	7	10.45	0.04	0.01-1.91
Dieldrin	7	10.45	0.02	0.01-0.34
Heptachlor	5	7.46	<0.01	0.01-0.03
Heptachlor epoxide	6	8.96	<0.01	0.01-0.06
Isodrin	2	2.99	<0.01	0.02-0.03
<i>o,p'</i> -TDE	1	1.49	<0.01	0.01
<i>p,p'</i> -TDE	1	1.49	<0.01	0.10
Trifluralin	2	2.99	<0.01	0.01-0.05

NOTE: All residues on dry-weight basis.

¹ Mid-Atlantic States include Maryland, Delaware, and New Jersey.

² New England States include Maine, New Hampshire, Vermont, Massachusetts, Rhode Island, and Connecticut.

TABLE 6. Chlorinated hydrocarbon residues in cropland soil by State, FY-70
(50% estimate and 95% confidence interval of median)

PESTICIDE	UPPER LIMIT, ¹ PPM	RESIDUE LEVEL, PPM	LOWER LIMIT, PPM	PESTICIDE	UPPER LIMIT, ¹ PPM	RESIDUE LEVEL, PPM	LOWER LIMIT, PPM
ALABAMA				LOUISIANA			
<i>p,p'</i> -DDE	0.07	0.06	0.05	<i>p,p'</i> -DDE	0.01	0.01	0.00
<i>o,p'</i> -DDT	0.03	0.02	0.01	<i>o,p'</i> -DDT	0.01	0.00	0.00
<i>p,p'</i> -DDT	0.13	0.11	0.09	<i>p,p'</i> -DDT	0.05	0.03	0.01
DDTR	0.28	0.24	0.20	DDTR	0.08	0.04	0.02
<i>p,p'</i> -TDE	0.02	0.02	0.01	<i>p,p'</i> -TDE	0.01	0.01	0.00
ARKANSAS				MISSISSIPPI			
<i>p,p'</i> -DDE	0.01	0.01	0.01	<i>p,p'</i> -EDE	0.12	0.10	0.08
<i>p,p'</i> -DDT	0.03	0.02	0.01	<i>o,p'</i> -DDT	0.10	0.08	0.07
DDTR	0.04	0.03	0.03	<i>p,p'</i> -DDT	0.53	0.37	0.25
Dieldrin	0.02	0.01	0.01	DDTR	0.80	0.57	0.38
<i>p,p'</i> -TDE	0.01	0.01	0.00	<i>p,p'</i> -TDE	0.04	0.03	0.01
CALIFORNIA				MISSOURI			
<i>p,p'</i> -DDE	0.05	0.04	0.03	<i>p,p'</i> -DDT	0.01	0.00	0.00
<i>o,p'</i> -DDT	0.02	0.02	0.01	Dieldrin	0.01	0.01	0.00
<i>p,p'</i> -DDT	0.07	0.06	0.05	NEBRASKA			
DDTR	0.16	0.13	0.11	Chlordane	0.01	0.00	0.00
Dieldrin	0.01	0.00	0.00	<i>p,p'</i> -DDT	0.01	0.00	0.00
<i>p,p'</i> -TDE	0.02	0.02	0.01	Dieldrin	0.01	0.01	0.00
Toxaphene	0.34	0.20	0.08	NORTH CAROLINA			
FLORIDA				<i>p,p'</i> -DDE	0.03	0.02	0.02
<i>p,p'</i> -DDE	0.01	0.00	0.00	<i>o,p'</i> -DDT	0.02	0.01	0.01
<i>p,p'</i> -DDT	0.02	0.01	0.01	<i>p,p'</i> -DDT	0.06	0.05	0.04
DDTR	0.03	0.02	0.01	DDTR	0.14	0.12	0.09
GEORGIA				Dieldrin	0.01	0.00	0.00
<i>p,p'</i> -DDE	0.11	0.09	0.07	<i>o,p'</i> -TDE	0.01	0.00	0.00
<i>o,p'</i> -DDT	0.05	0.04	0.04	<i>p,p'</i> -TDE	0.03	0.02	0.02
<i>p,p'</i> -DDT	0.37	0.29	0.21	OHIO			
DDTR	0.62	0.46	0.32	Chlordane	0.01	0.00	0.00
<i>p,p'</i> -TDE	0.03	0.03	0.02	PENNSYLVANIA			
ILLINOIS				<i>p,p'</i> -DDT	0.01	0.00	0.00
Aldrin	0.01	0.01	0.01	DDTR	0.02	0.01	0.01
Chlordane	0.04	0.03	0.02	SOUTH CAROLINA			
<i>p,p'</i> -DDT	0.01	0.00	0.00	<i>p,p'</i> -DDE	0.15	0.11	0.07
Dieldrin	0.07	0.06	0.06	<i>o,p'</i> -DDT	0.06	0.04	0.02
INDIANA				<i>p,p'</i> -DDT	0.24	0.17	0.10
Chlordane	0.01	0.00	0.00	DDTR	0.60	0.40	0.20
Dieldrin	0.01	0.00	0.00	<i>p,p'</i> -TDE	0.03	0.02	0.02
IOWA				WISCONSIN			
Dieldrin	0.02	0.02	0.02	Chlordane	0.01	0.00	0.00
KENTUCKY							
DDTR	0.01	0.00	0.00				

NOTE: All residues on dry-weight basis.

¹ Values not shown where upper limit is less than 0.01 ppm.

TABLE 7. Chlorinated hydrocarbon residues in cropland soil by cropping region, FY-70
(% sites showing detectable residues)

PESTICIDE	CORN	COTTON	COTTON & GEN. FARMING	GEN. FARMING	HAY & GEN. FARMING	IRRIGATED LAND	SMALL GRAINS	VEG.	VEG. & FRUIT
	NUMBER OF SITES ANALYZED								
	713	101	117	147	184	39	105	72	42
PERCENT OF SITES SHOWING DETECTABLE RESIDUES									
Aldrin	25.39	7.92	2.56	2.04	1.09	5.13	0.95	1.39	4.76
Chlordane	18.51	ND	3.42	6.12	4.35	7.69	0.95	6.94	9.52
DAC	ND	ND	0.85	ND	ND	ND	ND	ND	ND
<i>o,p'</i> -DDE	0.14	12.87	5.98	4.08	2.17	28.21	ND	ND	4.76
<i>p,p'</i> -DDE	6.87	58.42	48.72	41.50	15.22	56.41	2.86	27.78	47.62
<i>o,p'</i> -DDT	3.09	41.58	33.33	30.61	7.07	46.15	1.90	20.83	33.33
<i>p,p'</i> -DDT	7.57	55.45	44.44	37.41	12.50	48.72	1.90	30.56	52.38
DDTR	8.42	59.41	48.72	44.22	15.22	58.97	2.86	33.33	59.52
Dieldrin	45.44	23.76	14.53	17.69	9.78	56.41	4.76	23.61	30.95
Endosulfan I	ND	ND	ND	ND	ND	ND	ND	ND	2.38
Endosulfan II	ND	ND	ND	ND	1.09	2.56	ND	ND	2.38
Endosulfan sulfate	ND	ND	0.85	ND	1.63	2.56	ND	ND	2.38
Endrin	0.42	5.94	4.27	1.36	ND	10.26	3.81	1.39	4.76
Heptachlor	12.76	ND	0.85	0.68	1.63	2.56	ND	ND	2.38
Heptachlor epoxide	17.11	ND	1.71	4.08	4.35	12.82	0.95	1.39	4.76
Isodrin	4.63	ND	ND	ND	0.54	ND	ND	ND	ND
Lindane	0.28	0.99	1.71	0.68	ND	ND	ND	ND	ND
Nitralin	ND	0.99	ND	ND	ND	ND	ND	ND	ND
Ramrod	0.14	ND	ND	ND	ND	ND	ND	ND	ND
<i>o,p'</i> -TDE	0.56	2.97	1.71	9.52	1.09	25.64	ND	1.39	2.38
<i>p,p'</i> -TDE	3.79	41.58	32.48	36.05	5.98	41.03	0.95	18.06	35.71
Toxaphene	ND	8.91	3.42	3.40	ND	20.51	ND	ND	2.38
Trifluralin	0.70	13.86	5.13	4.08	1.09	ND	ND	ND	ND

NOTE: ND = not detected.

TABLE 8. Chlorinated hydrocarbon residues in cropland soil by cropping region, FY-70
(Arithmetic mean conc.)

PESTICIDE	CORN	COTTON	COTTON & GEN. FARMING	GEN. FARMING	HAY & GEN. FARMING	IRRIGATED LAND	SMALL GRAINS	VEG.	VEG. & FRUIT
	NUMBER OF SITES ANALYZED								
	713	101	117	147	184	39	105	72	42
ARITHMETIC MEAN CONC., ppm									
Aldrin	0.05	<0.01	<0.01	<0.01	0.01	<0.01	<0.01	<0.01	0.01
Chlordane	0.13	ND	0.01	0.02	0.02	0.01	<0.01	0.19	0.07
DAC	ND	ND	0.01	ND	ND	ND	ND	ND	ND
<i>o,p'</i> -DDE	<0.01	<0.01	<0.01	<0.01	<0.01	0.01	ND	ND	0.01
<i>p,p'</i> -DDE	<0.01	0.13	0.15	0.06	0.03	0.16	<0.01	0.13	0.21
<i>o,p'</i> -DDT	<0.01	0.08	0.06	0.05	0.05	0.07	<0.01	0.18	0.13
<i>p,p'</i> -DDT	0.01	0.52	0.35	0.25	0.11	0.31	<0.01	1.06	0.69
DDTR	0.01	0.78	0.59	0.40	0.22	0.64	0.01	1.74	1.11
Dieldrin	0.07	0.04	0.02	0.01	0.01	0.05	<0.01	0.02	0.10
Endosulfan I	ND	ND	ND	ND	ND	ND	ND	ND	<0.01
Endosulfan II	ND	ND	ND	ND	<0.01	<0.01	ND	ND	<0.01
Endosulfan sulfate	ND	ND	<0.01	ND	<0.01	<0.01	ND	ND	0.01
Endrin	<0.01	<0.01	<0.01	<0.01	ND	0.01	<0.01	<0.01	0.02
Heptachlor	0.01	ND	<0.01	<0.01	<0.01	<0.01	<0.01	ND	<0.01
Heptachlor epoxide	0.01	ND	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
Isodrin	<0.01	ND	ND	ND	<0.01	ND	ND	ND	ND
Lindane	<0.01	<0.01	<0.01	<0.01	ND	ND	ND	ND	ND
Nitralin	ND	0.02	ND	ND	ND	ND	ND	ND	ND
Ramrod	<0.01	ND	ND	ND	ND	ND	ND	ND	ND
<i>o,p'</i> -TDE	<0.01	<0.01	<0.01	0.01	0.01	0.02	ND	0.07	<0.01
<i>p,p'</i> -TDE	<0.01	0.04	0.03	0.04	0.01	0.07	<0.01	0.30	0.08
Toxaphene	ND	0.32	0.09	0.07	ND	0.68	ND	ND	0.14
Trifluralin	<0.01	0.02	<0.01	<0.01	<0.01	ND	ND	ND	ND

NOTE: ND = not detected.

TABLE 9. Chlorinated hydrocarbon residues in cropland soil by cropping region, FY-70
(50% estimate and 95% confidence interval for selected pesticides, ppm)

PESTICIDE	PARAMETER	CORN	COTTON	COTTON & GEN. FARMING	GEN. FARMING	HAY & GEN. FARMING	IRRIGATED LAND	VEG.	VEG. & FRUIT
Chlordane	Upper Limit	0.002	NC	NC	0.001	0.000	NC	NC	NC
	Residue Level	0.001	NC	NC	0.000	0.000	NC	NC	NC
	Lower Limit	0.001	NC	NC	0.000	0.000	NC	NC	NC
<i>p,p'</i> -DDE	Upper Limit	0.000	0.018	0.010	0.009	0.000	0.039	0.002	0.013
	Residue Level	0.000	0.016	0.008	0.007	0.000	0.024	0.001	0.009
	Lower Limit	0.000	0.013	0.006	0.005	0.000	0.011	0.000	0.005
<i>o,p'</i> -DDT	Upper Limit	NC	0.010	0.006	0.005	0.000	0.038	0.000	0.002
	Residue Level	NC	0.008	0.003	0.004	0.000	0.029	0.000	0.002
	Lower Limit	NC	0.005	0.002	0.003	0.000	0.018	0.000	0.001
<i>p,p'</i> -DDT	Upper Limit	0.000	0.054	0.013	0.013	0.000	0.077	0.001	0.019
	Residue Level	0.000	0.046	0.010	0.009	0.000	0.054	0.001	0.015
	Lower Limit	0.000	0.038	0.007	0.006	0.000	0.033	0.000	0.011
DDTR	Upper Limit	0.000	0.085	0.023	0.022	0.000	0.079	0.002	0.047
	Residue Level	0.000	0.071	0.017	0.016	0.000	0.040	0.002	0.037
	Lower Limit	0.000	0.058	0.012	0.011	0.000	0.014	0.001	0.028
Dieldrin	Upper Limit	0.011	0.003	0.002	0.002	0.000	0.027	0.001	0.003
	Residue Level	0.009	0.002	0.001	0.001	0.000	0.018	0.000	0.002
	Lower Limit	0.007	0.001	0.000	0.000	0.000	0.008	0.000	0.001
<i>p,p'</i> -TDE	Upper Limit	0.000	0.009	0.004	0.008	0.000	0.017	0.000	0.006
	Residue Level	0.000	0.008	0.003	0.006	0.000	0.014	0.000	0.005
	Lower Limit	0.000	0.006	0.002	0.005	0.000	0.010	0.000	0.003
Toxaphene	Upper Limit	NC	0.149	NC	NC	NC	0.336	NC	NC
	Residue Level	NC	0.036	NC	NC	NC	0.171	NC	NC
	Lower Limit	NC	0.001	NC	NC	NC	0.041	NC	NC

NOTE: NC = not calculated, less than 6 different values.
All residues on dry-weight basis.

TABLE 10. Chlorinated hydrocarbon residues in cropland soil by crop, FY-70

PESTICIDE	NO. TIMES PESTICIDE DETECTED	PERCENT OCCURRENCE	ARITH. MEAN CONC., PPM	RANGE OF DETECTED RESIDUES, PPM
ALFALFA AND BUR CLOVER, 114 SITES				
Aldrin	8	7.02	0.01	0.01-0.38
Chlordane	10	8.77	0.04	0.03-1.46
<i>o,p'</i> -DDE	4	3.51	<0.01	0.01-0.03
<i>p,p'</i> -DDE	13	11.40	0.02	0.01-0.74
<i>o,p'</i> -DDT	10	8.77	0.01	0.02-0.14
<i>p,p'</i> -DDT	17	14.91	0.02	0.01-0.42
DDTR	17	14.91	0.06	0.02-1.26
Dieldrin	28	24.56	0.03	0.01-0.51
Endrin	3	2.63	<0.01	0.03-0.07
Heptachlor	4	3.51	<0.01	0.01-0.12
Heptachlor epoxide	9	7.89	<0.01	0.01-0.07
<i>o,p'</i> -TDE	4	3.51	<0.01	0.01-0.08
<i>p,p'</i> -TDE	12	10.53	<0.01	0.01-0.10
Toxaphene	4	3.51	0.08	0.79-4.35
Trifluralin	1	0.88	<0.01	0.02
FIELD CORN, 363 SITES				
Aldrin	75	20.66	0.06	0.01-4.25
Chlordane	64	17.63	0.15	0.02-8.04
<i>o,p'</i> -DDE	3	0.83	<0.01	0.01-0.02
<i>p,p'</i> -DDE	66	18.18	0.02	0.01-1.09
<i>o,p'</i> -DDT	34	9.37	0.01	0.01-0.84
<i>p,p'</i> -DDT	63	17.36	0.04	0.01-2.98
DDTR	73	20.11	0.07	0.01-4.94
Dieldrin	152	41.87	0.06	0.01-0.92
Endrin	4	1.10	<0.01	0.01-0.03
Heptachlor	40	11.02	0.02	0.01-1.71
Heptachlor epoxide	62	17.08	0.01	0.01-0.31
Isodrin	11	3.03	<0.01	0.01-0.18
Lindane	2	0.55	<0.01	0.07-0.15
Ramrod	1	0.28	<0.01	0.03
<i>o,p'</i> -TDE	6	1.65	<0.01	0.02-0.09
<i>p,p'</i> -TDE	40	11.02	0.01	0.01-0.99
Toxaphene	1	0.28	0.01	2.27
Trifluralin	2	0.55	<0.01	0.04-0.10

(Continued next page)

TABLE 10 (cont'd). Chlorinated hydrocarbon residues in cropland soil by crop, FY-70

PESTICIDE	NO. TIMES PESTICIDE DETECTED	PERCENT OCCURRENCE	ARTH. MIAN CONC., PPM	RANGE OF DETECTED RESIDUES, PPM
COTTON, 49 SITES				
Chlordane	1	2.04	<0.01	0.23
DAC	1	2.04	0.02	1.19
<i>o,p'</i> -DDE	15	30.61	0.01	0.02-0.10
<i>p,p'</i> -DDE	40	81.63	0.38	0.01-1.98
<i>o,p'</i> -DDT	37	75.51	0.22	0.01-0.74
<i>p,p'</i> -DDT	38	77.55	1.37	0.04-6.61
DDTR	40	81.63	2.07	0.01-9.81
Dieldrin	9	18.37	0.02	0.01-0.18
Endrin	7	14.29	0.01	0.01-0.16
Heptachlor epoxide	1	2.04	<0.01	0.03
Lindane	2	4.08	<0.01	0.01
Nitralin	1	2.04	0.05	2.47
<i>o,p'</i> -TDE	7	14.29	0.01	0.02-0.12
<i>p,p'</i> -TDE	32	65.31	0.08	0.01-0.71
Toxaphene	7	14.29	0.55	1.04-7.63
Trifluralin	11	22.45	0.02	0.02-0.24
GRASS AND HAY, 29 SITES				
Aldrin	1	3.45	<0.01	0.04
Chlordane	1	3.45	0.01	0.27
<i>p,p'</i> -DDE	6	20.69	0.01	0.01-0.21
<i>o,p'</i> -DDT	2	6.90	0.01	0.07-0.09
<i>p,p'</i> -DDT	4	13.79	0.02	0.01-0.31
DDTR	6	20.69	0.04	0.02-0.59
Dieldrin	4	13.79	<0.01	0.01-0.06
Heptachlor	1	3.45	<0.01	0.05
Heptachlor epoxide	1	3.45	<0.01	0.09
<i>p,p'</i> -TDE	4	13.79	<0.01	0.01-0.04
Toxaphene	1	3.45	0.03	0.89
MIXED HAY, 118 SITES				
Aldrin	4	3.39	<0.01	0.01-0.04
Chlordane	7	5.93	0.02	0.02-1.23
<i>o,p'</i> -DDE	2	1.69	<0.01	0.01-0.02
<i>p,p'</i> -DDE	13	11.02	0.01	0.01-0.34
<i>o,p'</i> -DDT	7	5.93	<0.01	0.01-0.25
<i>p,p'</i> -DDT	11	9.32	0.02	0.01-1.35
DDTR	14	11.86	0.04	0.01-2.08
Dieldrin	16	13.56	0.01	0.01-0.37
Heptachlor	2	1.69	<0.01	0.09-0.44
Heptachlor epoxide	5	4.24	<0.01	0.01-0.16
<i>o,p'</i> -TDE	3	2.54	<0.01	0.01-0.08
<i>p,p'</i> -TDE	6	5.08	0.01	0.02-0.24
SOYBEANS, 254 SITES				
Aldrin	37	14.57	0.01	0.01-1.22
Chlordane	19	7.48	0.04	0.01-1.44
<i>o,p'</i> -DDE	7	2.76	<0.01	0.01-0.03
<i>p,p'</i> -DDE	58	22.83	0.03	0.01-1.25
<i>o,p'</i> -DDT	37	14.57	0.02	0.01-0.51
<i>p,p'</i> -DDT	56	22.05	0.11	0.01-3.43
DDTR	59	23.23	0.17	0.01-3.83
Dieldrin	79	31.10	0.03	0.01-0.56
Endrin	2	0.79	<0.01	0.01-0.03
Heptachlor	14	5.51	<0.01	0.01-0.27
Heptachlor epoxide	17	6.69	<0.01	0.01-0.10
Isodrin	2	0.79	<0.01	0.01
Lindane	1	0.39	<0.01	0.02
Nitralin	1	0.39	0.01	2.47
<i>o,p'</i> -TDE	4	1.57	<0.01	0.02-0.21
<i>p,p'</i> -TDE	40	15.75	0.01	0.01-0.31
Toxaphene	3	1.18	0.07	2.79-8.75
Trifluralin	15	5.91	0.01	0.01-0.36

NOTE: All residues on dry-weight basis.

TABLE 11. Chlorinated hydrocarbon and organophosphate residues in crops, all sites, FY-70

PESTICIDE	NO. TIMES PESTICIDE DETECTED	PERCENT OCCURRENCE	ARITH. MEAN CONC., PPM	RANGE OF DETECTED RESIDUES, PPM
ALFALFA AND/OR BUR CLOVER				
CHLORINATED HYDROCARBONS, 39 SITES				
Chlordane	3	7.69	0.01	0.03-0.19
<i>p,p'</i> -DDE	3	7.69	<0.01	0.01-0.02
<i>o,p'</i> -DDT	5	12.82	<0.01	0.01-0.08
<i>p,p'</i> -DDT	11	28.21	0.01	0.01-0.18
DDTR	11	28.21	0.02	0.01-0.34
Dieldrin	3	7.69	<0.01	0.01-0.02
<i>p,p'</i> -TDE	3	7.69	<0.01	0.01-0.14
ORGANOPHOSPHATES, 37 SITES: 0 DETECTIONS				
FIELD CORN: KERNELS				
CHLORINATED HYDROCARBONS, 276 SITES				
Dieldrin	1	0.36	<0.01	0.01
Endrin	1	0.36	<0.01	0.03
ORGANOPHOSPHATES, 240 SITES				
Ethion	1	0.42	<0.01	0.13
COTTON: STALKS AND GREEN BOLLS				
CHLORINATED HYDROCARBONS, 33 SITES				
<i>o,p'</i> -DDE	3	9.09	<0.01	0.02- 0.04
<i>p,p'</i> -DDE	29	87.88	0.31	0.01- 4.37
<i>o,p'</i> -DDT	29	87.88	0.37	0.01- 2.36
<i>p,p'</i> -DDT	29	87.88	2.95	0.03-27.03
DDTR	30	90.91	3.81	0.02-34.63
Dieldrin	7	21.21	<0.01	0.01- 0.05
Endrin	1	3.03	<0.01	0.05
<i>p,p'</i> -TDE	25	75.76	0.17	0.01- 0.87
Toxaphene	15	45.45	6.96	0.68-55.80
ORGANOPHOSPHATES, 18 SITES				
DEF	7	38.89	1.54	0.04-14.28
Diazinon	1	5.56	<0.01	0.06
Folex	1	5.56	0.09	1.55
Malathion	4	22.22	0.16	0.08- 2.17
Parathion, ethyl	3	16.67	0.01	0.02- 0.07
Parathion, methyl	9	50.00	0.58	0.13- 6.20
GRASS HAY				
CHLORINATED HYDROCARBONS, 48 SITES				
Chlordane	1	2.08	<0.01	0.16
<i>p,p'</i> -DDE	5	10.42	<0.01	0.01-0.07
<i>o,p'</i> -DDT	3	6.25	0.01	0.05-0.19
<i>p,p'</i> -DDT	5	10.42	0.06	0.02-2.31
DDTR	5	10.42	0.07	0.03-2.60
Dieldrin	1	2.08	<0.01	0.02
<i>p,p'</i> -TDE	1	2.08	<0.01	0.03
Toxaphene	1	2.08	<0.01	0.05
ORGANOPHOSPHATES, 47 SITES				
DEF	1	2.13	<0.01	0.01
Disulfoton	3	6.38	<0.01	0.01
Malathion	1	2.13	<0.01	0.03
Parathion, ethyl	1	2.13	<0.01	0.01
FIELD CORN: STALKS				
CHLORINATED HYDROCARBONS, 270 SITES				
Chlordane	14	5.19	0.01	0.01-0.52
<i>o,p'</i> -DDE	2	0.74	<0.01	0.01
<i>p,p'</i> -DDE	33	12.22	<0.01	0.01-0.36
<i>o,p'</i> -DDT	33	12.22	0.01	0.01-0.28
<i>p,p'</i> -DDT	53	19.63	0.03	0.01-2.20
DDTR	54	20.00	0.04	0.01-2.88
Dieldrin	42	15.56	<0.01	0.01-0.09
Heptachlor	1	0.37	<0.01	0.06
Heptachlor epoxide	5	1.85	<0.01	0.01-0.12
<i>p,p'</i> -TDE	29	10.74	<0.01	0.01-0.30
Toxaphene	12	4.44	0.02	0.09-1.35
ORGANOPHOSPHATES, 228 SITES				
Malathion	1	0.44	<0.01	0.04

(Continued next page)

TABLE 11 (cont'd). Chlorinated hydrocarbon and organophosphate residues in crops, all sites, FY-70

PESTICIDE	NO. TIMES PESTICIDE DETECTED	PERCENT OCCURRENCE	ARITH. MEAN CONC., PPM	RANGE OF DETECTED RESIDUES, PPM
COTTON: SEEDS				
CHLORINATED HYDROCARBONS, 39 SITES				
<i>p,p'</i> -DDE	13	33.33	2.57	0.01-100.01
<i>o,p'</i> -DDT	14	35.90	0.01	0.01- 0.18
<i>p,p'</i> -DDT	20	51.28	0.07	0.01- 1.02
DDTR	20	51.28	2.65	0.01-100.05
Dieldrin	2	5.13	<0.01	0.01
<i>p,p'</i> -TDE	8	20.51	<0.01	0.01- 0.02
Toxaphene	12	30.77	0.15	0.05- 1.85
ORGANOPHOSPHATES, 37 SITES				
DEF	17	45.95	0.11	0.02-1.10
Parathion, ethyl	3	8.11	<0.01	0.01-0.03
Parathion, methyl	7	18.92	0.01	0.01-0.08
MIXED HAY				
CHLORINATED HYDROCARBONS, 29 SITES				
Aldrin	1	3.45	<0.01	0.07
Chlordane	5	17.24	0.07	0.05-1.19
<i>p,p'</i> -DDE	11	37.93	0.01	0.01-0.19
<i>o,p'</i> -DDT	11	37.93	0.01	0.01-0.04
<i>p,p'</i> -DDT	20	68.97	0.02	0.01-0.13
DDTR	20	68.97	0.04	0.01-0.36
Dieldrin	19	65.52	0.01	0.01-0.11
Endrin	1	3.45	<0.01	0.12
Heptachlor	1	3.45	<0.01	0.02
<i>p,p'</i> -TDE	6	20.69	<0.01	0.01-0.02
Toxaphene	4	13.79	0.01	0.05-0.13
ORGANOPHOSPHATES, 29 SITES: 0 DETECTIONS				
SOYBEANS: BEANS				
CHLORINATED HYDROCARBONS, 178 SITES				
Chlordane	3	1.69	<0.01	0.01-0.10
Dieldrin	69	38.76	0.01	0.01-0.09
Endrin	15	8.43	<0.01	0.01-0.14
Heptachlor	2	1.12	<0.01	0.01
Heptachlor epoxide	12	6.74	<0.01	0.01-0.05
Ramrod	1	0.56	<0.01	0.24
Toxaphene	19	10.67	0.02	0.08-0.41
Trifluralin	8	4.49	<0.01	0.01-0.09
ORGANOPHOSPHATES, 137 SITES: 0 DETECTIONS				

NOTE: Samples were examined for organophosphates only when use records indicated they had been applied.
All residues on dry-weight basis.

DDT Moratorium in Arizona—Agricultural Residues after 4 Years¹

G. W. Ware, B. J. Estes, and W. P. Cahill

ABSTRACT

The moratorium on agricultural use of DDT in Arizona that began in January 1969 has proved very effective during the 4 years of its enforcement. Residues on green alfalfa have declined significantly during this period to a probable inherent level of 0.03 ppm, wet weight. Soil residues of DDTR have changed almost imperceptibly; this suggests a soil half-life greater than 20 years. These soil residues are mostly DDE; the little remaining DDT is being converted gradually to DDE, the slowly degraded metabolite of DDT.

This paper retracts a statement made in an earlier study which implied violation of the DDT moratorium in the Yuma mesa and valley in Yuma County. Authors have concluded that the consistently high residues in the Yuma area resulted from climatological conditions not found in other sampling areas, rather than from any violation of the moratorium.

Introduction

The current moratorium on agricultural use of DDT in Arizona that began in January 1969 has completed its fourth year (1,2). This is the third report on the status of DDT residues and DDTR, related degradation products, following 18 years of unrestricted use and 4 years of restricted use in Arizona under the guidance of the Arizona Board of Pesticide Control.

Analytical Methods

Soil and alfalfa samples were collected precisely as described in previous reports (1,2) from the three major irrigated areas in Arizona: Salt River Valley, which

surrounds Phoenix; Pinal County; and the Yuma mesa and valley in Yuma County. Desert soil samples adjacent to these areas were also collected but only from the top 0.25 inch. Authors had hoped to demonstrate that airborne contaminated dust was a prime source of forage contamination. This theory was disproved. Additionally, an earlier study (3) was continued to provide reference standards and residue continuity retrospectively through 1967 (Table 1). The sampling sites are located on a 60-mile Maricopa County east-west transect along Baseline Road.

Alfalfa and soil samples were carried through the extraction and cleanup procedures formerly delineated by the authors (1-3).

Analysis was performed by electron-capture/gas-liquid chromatography (EC/GLC). Recovery standards and analytical reagent blanks were carried through the extraction and cleanup procedures for each day's analysis. Recoveries were consistently above 90 percent; however, corrections were not applied to the data presented. The minimum sensitivity of the method was arbitrarily set at 0.02 ng for *p,p'*- and *o,p'*-DDT, DDE, and DDD. Standard curves extended from 0.03 to 0.10 ng. The relative sensitivities were 0.001 ppm for alfalfa and 0.003 ppm for soil. Results are based on a minimum sample size and 6 μ l extract injected into the chromatograph.

Analytical EC/GLC confirmatory tests were conducted on a random basis using a double-length GLC column at a temperature slightly higher than that used in previous studies, as well as *p*-value determinations using acetonitrile and hexane (4). Because of low levels of DDTR and interfering peaks of toxaphene which drifted from nearby cottonfields, all alfalfa extracts were dehydrohalogenated after cleanup on florisil and measured only as *o,p'*- and *p,p'*-DDE as described by Cahill et al. (5).

¹ Contribution to Regional Project W-45, "Residues of Pesticides and Related Chemicals in the Agricultural Environment—Their Nature, Distribution, Persistence, and Toxicological Implications." University of Arizona Agricultural Experiment Station Journal Series No. 2139. Department of Entomology, University of Arizona, Tucson, Ariz. 85721.

TABLE 1. *DDTR residues (ppm) in green alfalfa, 1967-72, Maricopa County, Ariz.*

SAMPLE	1967 AUG.	1968 SEPT.	1969 SEPT.	1970 SEPT.	1971 SEPT.	1972 SEPT.
2	—	0.220	0.038	0.050	0.020	0.023*
3	0.283	—	0.027	0.030	—	0.025*
4	0.170	0.120	0.038	0.037	0.031	0.022
5	—	0.060	0.020	0.024	0.011	0.029*
6	0.277	—	0.035	0.022	—	0.008*
8	0.794	—	—	0.027	0.038	0.013*
9	—	0.076	0.034	0.042	0.020	0.029*
10	0.350	0.092	0.054	0.162	0.027	0.031
11	0.453	0.580	0.064	0.047	0.085	0.056
12	0.299	0.077	0.025	0.038	—	0.023*
13	0.606	—	—	0.021	0.027	—
Means ¹	0.404 ^c	0.175 ^b	0.037 ^a	0.045 ^a	0.032 ^a	0.026 ^a

NOTE: — = no samples analyzed; * = substitute adjacent fields.
¹ Means with same letter are not significantly different at the 0.05 level.

TABLE 2. *DDTR residues (ppm) in green alfalfa during 1969-71 DDT moratorium, Maricopa County, Ariz.*

SAMPLE	1969 JAN.	1969 SEPT.	1970 SEPT.	1971 SEPT.	1972 SEPT.
1	0.087	0.042	0.057	—	—
2	0.303	0.062	0.050	0.025	0.039*
3	0.102	0.078	0.093	0.038	—
4	0.107	0.047	0.076	0.037	0.046*
5	0.049	0.030	0.025	0.007	0.011
6	0.113	0.064	0.060	0.051	0.045*
7	0.082	0.034	0.023	—	0.055
8	0.125	0.056	—	—	—
9	0.085	0.044	0.101	—	—
10	—	—	0.080	0.059	—
Mean ¹	0.117 ^b	0.051 ^a	0.063 ^a	0.036 ^a	0.039 ^a

NOTE: — = no samples analyzed; * = substitute adjacent fields.
¹ Means with same letter are not significantly different at the 0.05 level.

TABLE 3. *DDTR residues (ppm) in green alfalfa during 1969-71 DDT moratorium, Pinal County, Ariz.*

SAMPLE	1969 JAN.	1969 SEPT.	1970 SEPT.	1971 SEPT.	1972 SEPT.
1	0.047	0.042	0.034	0.055	0.041*
2	0.047	0.031	0.059	0.036	—
3	0.142	0.187	—	—	—
4	0.231	0.076	0.071	0.072	0.025
5	0.092	0.130	0.045	—	0.025*
6	0.038	0.058	0.045	—	—
7	0.079	0.118	0.059	0.038	0.044
8	0.068	0.071	0.031	0.034	0.018
9	0.054	0.068	0.057	0.060	—
Means ¹	0.088 ^b	0.086 ^b	0.050 ^a	0.049 ^a	0.031 ^a

NOTE: — = no samples analyzed; * = substitute adjacent fields.
¹ Means with same letter are not significantly different at the 0.05 level.

TABLE 4. *DDTR residues (ppm) in green alfalfa during 1969-71 DDT moratorium, Yuma County, Ariz.*

SAMPLE	1969 JAN.	1969 SEPT.	1970 SEPT.	1971 SEPT.	1972 JAN.	1972 SEPT.
1	0.047	0.373	—	0.120	0.025	0.032
2	0.039	0.098	—	—	0.010*	0.017*
3	0.049	0.256	0.084	0.270	0.073*	0.040*
4	0.057	0.093	—	—	0.055*	0.075*
5	0.057	0.545	0.063	0.340	0.047*	0.290*
6	0.044	0.317	—	—	0.035*	0.300*
7	0.059	0.241	—	—	0.026*	0.190*
8	0.036	0.045	0.034	0.031	0.039*	—
9	0.021	0.056	—	—	0.015*	—
10	0.046	0.074	0.051	0.050	0.028	0.045
Mean ¹	0.046 ^a	0.210 ^b	0.058 ^a	0.162 ^b	0.035 ^a	0.123 ^b

NOTE: — = no samples analyzed; * = substitute adjacent fields.
¹ Means with same letter are not significantly different at the 0.05 level.

TABLE 5. *DDTR residues (ppm) in soils during 1969-72 moratorium, Maricopa County, Ariz.*

FIELD No.	1969 JAN.				1970 SEPT.				1972 SEPT.			
	DDE	<i>o,p'</i> - DDT	<i>p,p'</i> - DDT	TOTAL ¹	DDE	<i>o,p'</i> - DDT	<i>p,p'</i> - DDT	TOTAL	DDE	<i>o,p'</i> - DDT	<i>p,p'</i> - DDT	TOTAL
1	0.35	0.04	0.12	0.54	0.32	0.04	0.11	0.47	0.40	0.04	0.11	0.55
2	0.48	0.17	0.78	1.54	0.79	0.20	0.96	1.95	0.98	0.18	0.47	1.63
3	0.33	0.07	0.16	0.59	1.35	0.13	0.32	1.80	1.24	0.13	0.32	1.69
4	0.49	0.05	0.17	0.74	0.56	0.06	0.22	0.84	0.58	0.05	0.23	0.86
5	0.29	0.05	0.09	0.44	0.15	0.02	0.05	0.22	0.17	0.01	0.05	0.23
6	2.10	0.43	1.10	3.93	2.57	0.39	1.18	4.14	2.58	0.28	0.96	3.82
7	0.84	0.11	0.23	1.22	0.84	0.13	0.23	1.20	0.92	0.09	0.29	1.30
8	2.22	0.38	1.29	4.00	2.50	0.47	1.61	4.58	2.37	0.27	1.21	3.85
9	1.18	0.21	0.91	2.41	1.24	0.24	0.82	2.30	1.12	0.17	0.77	2.06
10	—	—	—	(0.24)	0.48	0.06	0.14	0.68	0.31	0.04	0.07	0.42
Means ²	0.92	0.17	0.54	1.57 ^a	1.08	0.17	0.56	1.82 ^{ab}	1.07	0.13	0.45	1.64 ^a
Desert Sample												
1	0.08	<0.01	0.03	0.13	0.48	0.04	0.09	0.61	0.43	0.07	0.09	0.59
2	0.24	0.02	0.06	0.35	0.41	0.05	0.10	0.56	0.28	0.03	0.58	0.89
3	0.44	0.04	0.15	0.67	0.28	0.02	0.07	0.37	0.18	0.02	0.04	0.24
4	—	—	—	(2.39)	1.44	0.09	0.38	1.91	0.54	0.08	0.06	0.68
Means ²	—	—	—	0.89 ^a	0.65	0.05	0.16	0.86 ^a	0.36	0.05	0.19	0.60 ^a

NOTE: — = no samples analyzed.
¹ Figures in parentheses are missing values calculated by randomized blocks missing value formula.
² Means with same letter are not significantly different at the 0.05 level.

TABLE 6. DDTR residues (ppm) in soils during 1969-72 moratorium, Pinal County, Ariz.

FIELD NO.	1969 JAN.				1970 SEPT.				1972 SEPT.			
	DDE	<i>o,p'</i> - DDT	<i>p,p'</i> - DDT	TOTAL	DDE	<i>o,p'</i> - DDT	<i>p,p'</i> - DDT	TOTAL ¹	DDE	<i>o,p'</i> - DDT	<i>p,p'</i> - DDT	TOTAL
1	0.64	0.48	2.43	3.77	0.61	0.35	2.82	3.78	0.74	0.34	2.64	3.72
2	0.27	0.15	1.03	1.52	0.35	0.11	1.00	1.46	0.41	0.13	0.96	1.50
3	1.05	0.32	1.38	2.75	1.32	0.23	1.03	2.58	1.16	0.16	0.80	2.12
4	0.99	0.27	1.04	2.30	1.23	0.24	0.68	2.15	1.40	0.18	0.74	2.32
5	0.16	0.02	0.21	0.41	—	—	—	(0.38)	0.25	0.02	0.16	0.43
6	0.06	0.01	0.07	0.14	—	—	—	(0.06)	0.07	0.01	0.04	0.12
7	1.09	0.28	1.37	2.74	1.41	0.31	1.30	3.02	1.63	0.20	0.80	2.63
8	0.09	<0.01	0.04	0.14	0.06	0.01	0.02	0.09	0.08	0.01	0.02	0.11
9	0.67	0.09	0.29	1.06	0.79	0.08	0.20	1.07	0.74	0.03	0.06	0.83
10	0.66	0.14	0.36	1.16	1.14	0.12	0.27	1.53	1.19	0.15	0.39	1.73
Means ²	0.57	0.18	0.82	1.60 ^a	0.72	0.15	0.76	1.61 ^a	0.69	0.12	0.66	1.55 ^a
Desert Sample												
1	0.09	<0.01	0.06	0.16	0.18	0.01	0.03	0.22	0.17	0.02	0.12	0.31
2	0.18	0.01	0.11	0.32	0.38	0.03	0.06	0.47	0.21	0.02	0.21	0.44
3	0.05	0.03	0.10	0.21	0.12	0.02	0.05	0.19	0.06	0.01	0.02	0.09
4	0.09	0.03	0.10	0.25	1.18	0.06	0.16	1.40	0.77	0.07	0.09	0.93
Means ²	0.10	0.02	0.09	0.24 ^a	0.47	0.03	0.08	0.57 ^a	0.30	0.03	0.11	0.44 ^a

NOTE: — = no samples analyzed.

¹ Figures in parentheses are missing values calculated by randomized blocks missing value formula.² Means with same letter are not significantly different at the 0.05 level.

TABLE 7. DDTR residues (ppm) in soils during 1969-72 moratorium, Yuma County, Ariz.

FIELD NO.	1969 JAN.				1970 SEPT.				1972 SEPT.			
	DDE	<i>o,p'</i> - DDT	<i>p,p'</i> - DDT	TOTAL	DDE	<i>o,p'</i> - DDT	<i>p,p'</i> - DDT	TOTAL	DDE	<i>o,p'</i> - DDT	<i>p,p'</i> - DDT	TOTAL
1	0.10	<0.01	0.07	0.17	0.11	0.02	0.06	0.19	0.12	0.02	0.03	0.17
2	0.24	0.05	0.25	0.54	0.35	0.10	0.25	0.70	0.20	0.03	0.07	0.30
3	0.72	0.16	0.72	1.60	0.66	0.18	0.52	1.36	0.79	0.16	0.49	1.44
4	0.59	0.11	0.47	1.17	0.78	0.17	0.49	1.44	0.98	0.15	0.46	1.59
5	0.48	0.05	0.30	0.83	0.44	0.12	0.31	0.87	0.75	0.12	0.34	1.21
6	0.29	0.16	0.74	1.19	0.40	0.14	0.56	1.10	0.48	0.10	0.43	1.01
7	1.29	0.07	0.37	1.73	1.09	0.11	0.35	1.55	1.11	0.09	0.60	1.80
8	0.06	0.01	0.01	0.08	0.00	0.00	0.00	0.04	0.05	<0.01	<0.01	0.07
9	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	<0.01	<0.01	<0.01	0.03
10	0.26	0.02	0.03	0.31	0.22	0.02	0.03	0.27	0.17	0.01	0.02	0.20
Means ¹	0.40	0.06	0.30	0.76 ^a	0.41	0.09	0.26	0.75 ^a	0.47	0.07	0.25	0.78 ^a
Desert Sample												
1	0.27	0.02	0.07	0.36	0.22	0.03	0.09	0.34	0.24	0.06	0.09	0.39
2	0.03	0.01	0.02	0.06	0.08	0.01	0.04	0.13	0.02	0.01	0.02	0.05
3	0.02	0.01	0.03	0.06	0.02	0.00	0.03	0.05	0.02	0.01	0.02	0.05
4	0.00	0.00	0.01	0.01	0.00	0.00	0.01	0.01	0.79	0.07	0.15	1.04
Means ¹	0.08	0.01	0.03	0.12 ^a	0.08	0.01	0.04	0.14 ^a	0.27	0.04	0.08	0.38 ^b

¹ Means with same letter are not significantly different at the 0.05 level.

Results and Discussion

Residues observed in alfalfa and soil samplings during the past 4 years are presented in Tables 1-7 as DDTR. The Student-Newman Keul's test was used to analyze differences among residue means for the various sampling dates. Comparisons were made on least-squares means in the soil samples (Tables 5-7) due to inadequate samples. Residues on alfalfa from all four areas shown in Tables 1-4 appear to have leveled off at about 0.03 ppm except in Yuma County (Table 4), where September residues from 1969 through 1972 were about threefold higher than were September residues from

other areas. Sampling in January 1972 indicated that residues in Yuma had declined to the levels of the other areas. High September values for Yuma have occurred consistently in 1969, 1970, and 1971. This condition requires the retraction of a statement in the last report (2) indicating violations of the DDT moratorium in the Yuma area. These phenomenally high residues are apparently the result of climatological conditions not found in the other sampling areas.

Residue levels in alfalfa soils did not appear to decline from the last sampling period. September 1970 (Tables 5-7). Because any decline has been imperceptible, the

time required for these residues to reach one-half their present level is now estimated to be greater than 20 years, with desert soils changing the least.

DDTR residues now found in Arizona alfalfa and soil are primarily DDE. DDT residues are slowly becoming DDE and then declining negligibly. As suggested from past studies, future problems arising from DDT will be attributable to DDE, the very slowly degraded metabolite of DDT.

LITERATURE CITED

- (1) *Ware, G. W., Betty Estes, C. D. Jahn, and W. P. Cahill. 1970. DDT moratorium in Arizona—agricul-*

tural residues after 1 year. *Pestic. Monit. J.* 4(1):21-24.

- (2) *Ware, G. W., Betty Estes, and W. P. Cahill. 1971. DDT moratorium in Arizona—agricultural residues after 2 years. Pestic. Monit. J.* 5(3):276-280.
- (3) *Ware, G. W., Betty Estes, and W. P. Cahill. 1968. Pesticides in soil—an ecological study of DDT residues in Arizona soils and alfalfa. Pestic. Monit. J.* 2(3): 129-132.
- (4) *Bowman, M. C., and Morton Beroza. 1965. Extraction p-values of pesticides and related compounds in six binary solvent systems. J. Assoc. Off. Agric. Chem.* 48(5):943-952.
- (5) *Cahill, W. P., Betty Estes, and G. W. Ware. 1970. Determination of DDT in the presence of toxaphene residues. Bull. Environ. Contam. Toxicol.* 5(3):260-262.

RESIDUES IN FISH, WILDLIFE, AND ESTUARIES

Mercury Residues in the Common Pigeon (Columba livia) from the Jackson, Mississippi, Area—1972

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ABSTRACT

Total mercury in the common pigeon (*Columba livia*) from the Jackson, Miss., area was measured by atomic absorption spectrophotometry. Pigeons captured in 1972 from downtown Jackson were killed on the day of capture to determine mercury levels in wild birds in urban environments; others were caged and analyzed for mercury residues weekly or biweekly for 9 weeks. Data are presented to show possible pathways by which organisms eliminate this element. Median concentration of mercury in brains of newly captured pigeons was 22 ppb. Claws showed 14 to 85 ppb mercury. Possible sources of mercury contamination in these birds are treated grains, contaminated weed seeds, and naturally occurring mercurials.

Introduction

Even at trace levels, certain contaminants may have effects on the ecosystem as great or greater than those of the more common pollutants (1). Mercurials have been used for many years in agriculture, industry, and medicine, and have caused much concern about their effects on the biosphere. In his review of mercury uses in Canada, Fimreite emphasized that mercury contamination has been investigated in Scandinavian countries where it has produced greater wildlife problems than have DDT and other organochlorine pesticides used prevalently in Scandinavia (2). The seriousness of water pollution by mercury in industrial effluents was accentuated by the occurrence of Minamata disease in Japan (3) and, as a consequence of the potential human health hazard, considerable emphasis has been placed upon the danger of mercurials in the aquatic environment in the United States and Canada. After reviewing sources and uses of mercury, Summer, Saha, and Lee stated that elevated levels of the element may be expected in

fish from waters receiving mercury containing industrial and/or municipal wastes (4).

In particular, fish have been used to study the extent and effects of this type of pollution. A number of States have banned the sale of commercial fish or warned against public consumption of fish from contaminated waters (5). Fimreite, Fyfe, and Keith (6) demonstrated widespread contamination among seed-eating birds in areas of Canada where mercury-containing fungicides are used in seed treatment. A decline in seed-eating bird populations was traced to the use of mercurials as fungicides in Sweden (7). Findings of elevated levels of mercury in various game birds have prompted several States and the Canadian provinces of Alberta and Saskatchewan to monitor mercurial concentrations in their wildlife (2,6,8,9).

In Mississippi, Knight and Herring reported concentrations of total mercury from less than 0.05 to 0.74 ppm in muscles of largemouth bass from Ross Barnett Reservoir (10). However, there is a lack of data on the extent of trace metal contamination in ecosystems of Mississippi. Organisms which accumulate trace metals can act as indicators of pollution levels in their environments. In view of the paucity of local data on trace elements, a study was initiated to evaluate possible indicator organisms and to measure mercury and lead in the Jackson, Miss., area. This paper reports the preliminary results of monitoring total mercury in the common pigeon (*Columba livia*).

Analytical Methods

Wild pigeons were chosen as test animals because of their abundance and adaptation to urban environments. Approximately 100 pigeons were captured in an abandoned hotel in downtown Jackson on October 10, 1972. Researchers killed 25 of the birds that day and placed the remainder in outside, off-the-ground cages

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for analysis on a weekly schedule. Birds were fed a commercial pigeon scratch and corn which contained no detectable amounts of mercury residues. This control diet assured authors that any mercury detected in pigeons during the 9 weeks of analyses originated from their urban eating patterns before capture rather than from their control diets.

The flameless atomic absorption method described by Hatch and Ott (11) was used to measure total mercury in all birds: those killed at time of capture and those killed during the next 9 weeks. A 1- to 3-g sample of tissue was digested with concentrated nitric and sulfuric acids in a 125-ml flask at 50°C to destroy the organic matter. After dissolution, samples were cooled to room temperature and 6 percent potassium permanganate was added until a faint color persisted. To eliminate excess oxidants, 30 ml of reductant containing hydroxylamine sulfate was added; stannous sulfate was used to reduce mercury compounds to the elemental state. The flask was then placed in the absorption system and removed after maximum absorption was reached. Mercury vapor was vented to the hood. Standards obtained from Beckman Instruments, Inc., Fullerton, Calif., were run in the same manner. Foaming of samples was abated with Dow Corning Antifoam A. For these analyses, a Beckman atomic absorption spectrophotometer system equipped with a 10-inch potentiometric recorder was used.

Recovery rates were determined by adding mercury as HgCl to the various tissues. Data are corrected for recovery rates. The minimum detectable amount of mercury was 5 ppb. Accuracy has been given as 0.1 ppb (11) and 0.01 ng (8).

Results and Discussion

No heart tissue sample contained more than 5 ppb total mercury. The median mercury concentration in blood of birds killed on the day of capture was 7 ppb. Brain tissues of these first pigeons had a median residue level of 22 ppb; those caged for 1 week had only 6 ppb mercury in their brains. Subsequent samples of these tissues revealed no more than 5 ppb mercury (Table 1). Tejning determined that domestic fowls fed methylmercury-dicyandiamide-treated grain excreted about 11 percent of the mercury (12). After cessation of experimental feeding, he observed that this loss gradually decreased and finally stopped altogether. Our data indicate that mercury was removed with feces in quantities of about 11 to 13 ppb for the birds. In captivity, however, residues in excreta decreased to levels less than 5 ppb after 5 weeks.

Feathers used in the study included mature and immature contour and down feathers from the tail region. Pigeons that had been in captivity for 1 week showed somewhat higher concentrations of mercury in the

plumage than did those of subsequent analyses (Table 1). Mercury concentrations in feathers appear to show no consistent decline after the first week. Some variation in residue concentrations may be expected in natural populations of pigeons. Although analyses were not extended through a complete molting cycle, large concentrations of total mercury in plumage seem to indicate that feathers are a pathway through which the metal is concentrated and eventually lost through molting. This corroborates Tejning's work on pheasants and domestic fowls which showed that most of the mercury in blood and organs is not excreted, but is transported to the plumage (12). Claws also contained sizable amounts of mercury (14-85 ppb), but no pathways were established with the limited data available although the residue level patterns in similar claws and feathers may suggest some correlation.

Crops of pigeons killed on the day of capture contained corn, soybeans, Johnson grass seeds, and miscellaneous weed seeds. Other pigeons from the test birds' population were observed feeding along the right-of-way of a main-line railroad and in the yards of several grain storage facilities. Their drinking water was, for the most part, obtained from Town Creek, a generally sluggish stream receiving industrial waste and runoff that flows within 200 yards of the hotel. Mercury was undetectable in water samples from the creek. Pigeons drinking here have also been observed eating materials from bottom sediments near the shore of the creek. Crop contents of birds from the initial kill showed from less than 5 ppb to 7 ppb mercury. Authors suggest that possible contamination sources are treated grains, contaminated weed seeds, and naturally occurring mercurials. No apparently hazardous sources of mercury contamination were found to be available to these pigeons.

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LITERATURE CITED

- (1) Lucas, H. F., Jr., D. N. Edington, and P. J. Colby. 1970. Concentrations of trace elements in Great Lakes fishes. *J. Fish. Res. Bd. Can.* 27(4):677-684.
- (2) Fimreite, N. 1970. Mercury uses in Canada and their possible hazards as sources of mercury contamination. *Environ. Pollut.* 1(2):119-131.
- (3) Kurland, L. T., S. M. Faro, and N. Sjedeler. 1960. Minamata disease. *World Neurol.* 1(5):360-395.
- (4) Summer, A. K., J. G. Saha, and Y. W. Lee. 1972. Mercury residues in fish from Saskatchewan waters with and without known sources of pollution—1970. *Pestic. Monit. J.* 6(2):122-125.
- (5) Harriss, R. C. 1971. Ecological implications of mercury pollution in aquatic systems. *Biol. Conser.* 3(4):279-283.
- (6) Fimreite, N., R. W. Fyfe, and J. A. Keith. 1970.

Mercury contamination of Canadian prairie seed eaters and their avian predators. *Can. Field Nat.* 84(3):269-276.

- (7) *Johnels, A. G., and T. Westermark.* 1969. Mercury contamination of the environment in Sweden. pp. 221-241, in M. W. Miller and G. Berg (Eds.) *Chemical Fallout*. Charles Thomas Publishers, Springfield, Ill.
- (8) *Adley, F. E., and D. W. Brown.* 1972. Mercury concentrations in game birds, State of Washington—1970 and 1971. *Pestic. Monit. J.* 6(2):91-93.
- (9) *Benson, W. B., D. W. Brock, F. Shields III, E. R. Norberg, and J. Cline.* 1971. An analysis of mercury residues in Idaho pheasants. *J. Idaho Acad. Sci. Spec. Res. Issue.* 2:17-26.

- (10) *Knight, L. A., Jr., and J. Herring.* 1972. Total mercury in largemouth bass (*Micropterus salmoides*) in Ross Barnett Reservoir, Mississippi—1970 and 1971. *Pestic. Monit. J.* 6(2):103-106.
- (11) *Hatch, R., and W. L. Ott.* 1968. Determination of submicrogram quantities of mercury by atomic absorption spectrophotometry. *Anal. Chem.* 40(14):2085-2087.
- (12) *Tejning, S.* 1967. Mercury in pheasants (*Phasianus colchicus* L.) deriving from seed grain dressed with methyl and ethyl mercury compounds. *Oikos.* 18(1):334-344.

TABLE 1. Residues of total mercury (ppb wet weight) in tissues and feces of pigeons from Jackson, Miss.—1972

	0	1	2	Weeks in Captivity		5	6	7	9
				3	4				
Brain									
Range	9-230	5-10	—	—	—	—	—	—	—
Median	22	6	ND	ND	ND	ND	ND	ND	ND
No. birds	9	3	3	3	3	3	3	3	3
Feathers									
Range	8-30	22-70	16-20	20-51	22-40	25-26	<5-26	21-33	14-21
Median	19	49	17	22	27	26	13	30	18
No. birds	10	3	3	3	3	3	3	3	3
Skin									
Range	5-44	20-49	6-16	<5-5	<5-7	5-6	—	<5-13	<5-6
Median	29	35	10	5	6	5	ND	11	ND
No. birds	7	3	3	3	3	3	3	3	2
Scales									
Range	—	14-15	6-10	<5-11	8-18	5-10	—	11-19	<5-58
Median	ND	15	8	5	10	5	ND	11	8
No. birds	9	3	3	3	3	3	3	3	3
Liver									
Range	—	<5-9	—	—	<5-5	5-10	—	—	—
Median	ND	6	ND	ND	ND	5	ND	ND	ND
No. birds	9	3	3	3	3	3	3	3	3
Breast									
Range	<5-51	—	—	<5-5	6-9	—	—	—	—
Median	20	ND	ND	5	9	ND	ND	ND	ND
No. birds	7	3	3	3	3	3	3	3	3
Bones									
Range	<5-6	—	—	—	8-16	10-17	—	—	—
Median	ND	ND	ND	ND	8	15	ND	ND	ND
No. birds	9	3	3	3	3	2	3	3	3
Blood									
Range	5-12	—	—	—	—	—	—	—	—
Median	7	ND	ND	ND	ND	ND	ND	ND	ND
No. birds	10	3	2	2	2	2	1	2	3
Heart									
Range	—	—	—	—	—	—	—	—	—
Median	ND	ND	ND	ND	ND	ND	ND	ND	ND
No. birds	8	3	3	3	3	3	3	3	3
Claws¹	29	59	34	55	14	51	23	47	85
No. birds	20	3	3	3	3	3	3	3	3
Oil Glands¹	10	29	NS	39	84	—	50	8	13
No. birds	20	3	NS	3	3	3	3	3	3
Feces¹	11	13	11	9	7	NS	—	—	—
No. birds	20	3	3	3	3	NS	3	3	3

NOTE: — = concentrations of mercury less than 5 ppb.
 ND = not determined.
 NS = no sample.

¹ Tissues or feces combined for analysis.

Distribution of PCB and p,p'-DDE Residues in Atlantic Herring (*Clupea harengus harengus*) and Yellow Perch (*Perca flavescens*) in Eastern Canada—1972¹

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ABSTRACT

In two localities of Eastern Canada in 1972, Atlantic herring (*Clupea harengus harengus*) and yellow perch (*Perca flavescens*) were analyzed for residues of polychlorinated biphenyls (PCB's), p,p'-DDE, p,p'-DDD, and p,p'-DDT, and for lipid and body weight. From each locality, 24 herring and 25 perch were analyzed: all were males between 2 and 4 years old, and all were analyzed individually. Data were statistically evaluated. In most cases PCB, p,p'-DDE, and lipid were better approximated by lognormal distribution; weight was better approximated by normal distribution. All determined parameters were highly variable. One objective of the study was to weigh the possibility of using the two species under observation to detect temporal trends in levels of environmental contamination by PCB's and p,p'-DDE. The study concludes, however, that it is probably impossible to detect a significant change of PCB levels in fish of equal age in 2 consecutive years by using samples of this size.

Introduction

This paper describes levels and distribution of polychlorinated biphenyls (PCB's), p,p'-DDE, wet body weight, and lipid in Atlantic herring (*Clupea harengus harengus*) and yellow perch (*Perca flavescens*). An objective of this study was to evaluate the possibility of using these species to detect temporal trends in levels of environmental contamination by PCB's and p,p'-DDE.

Species originated in waters of Eastern Canada: Gulf of St. Lawrence, Bay of Fundy, and New Brunswick Rivers.

Forest-based industries, mining, and smelting operations are the typical industrial activities in the Gulf of St. Lawrence area. In the past, DDT was used for forest spraying in New Brunswick, Quebec, and Newfoundland; other pesticides are still used for agricultural purposes on Prince Edward Island. The St. Lawrence River runoff may be a source of chlorinated hydrocarbons. Little industrial or agricultural activity takes place in southern Nova Scotia. Surface circulation in the Gulf of Maine—Bay of Fundy area (1) may bring chlorinated hydrocarbons from the south into the area.

Occurrence and movement patterns of four major stocks of Atlantic herring (2) are illustrated in Figure 1. Levels of PCB's and chlorinated hydrocarbon pesticides in two weight groups of the Banquereau stock and in one weight group of the Gulf of Maine stock have been reported (3). Pooled samples were analyzed in the earlier study; there was no information available on statistical distribution of the residues with which to compare results of the current study. The concentration of PCB's and chlorinated hydrocarbon pesticides in herring oils obtained by commercial processes from the Gulf of St. Lawrence herring stock between 1967 and 1970 was determined by Addison et al. (4). Yellow perch from New Brunswick, Canada, has not been analyzed previously.

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Materials and Methods

SAMPLING

Samples of herring were obtained from commercial fisheries. Sex, age, and wet body weight were determined; male fish were frozen (-14°C) until analysis. Herring sample B (Gulf of St. Lawrence stock) was taken May 25, 1972; herring sample T (Nova Scotia stock) was

TABLE 1. Residues of PCB's in muscle of Atlantic herring and yellow perch—Eastern Canada, 1972

SAMPLE ¹	RESIDUES, $\mu\text{g/g}$ WET WEIGHT					
	MEAN		STANDARD DEVIATION		CHI SQUARE PROBABILITY, %	
	N	L	N	L	N	L
Herring B	0.31	0.25	0.18	0.27	2	50
Herring T	0.64	0.44	0.49	0.43	5	2
Perch 2	0.089	0.078	0.031	0.18	50	70
Perch 3	0.13	0.12	0.046	0.22	20	80

NOTE: N = data as such; L = logarithmically transformed data. Mean is antilog form; standard deviation is in log form.

¹ Herring samples represented 24 individual fish; perch represented 25.

TABLE 2. Residues of p,p'-DDE in muscle of Atlantic herring and yellow perch—Eastern Canada, 1972

SAMPLE ^{1,2}	RESIDUES, $\mu\text{g/g}$ WET WEIGHT					
	MEAN		STANDARD DEVIATION		CHI SQUARE PROBABILITY, %	
	N	L	N	L	N	L
Herring B	0.070	0.059	0.048	0.29	10	20
Herring T	0.11	0.085	0.071	0.43	2	70
Perch 3	0.11	0.089	0.040	0.22	1	70

NOTE: N = data as such; L = logarithmically transformed data. Mean is antilog form; standard deviation is in log form.

¹ Herring samples represented 24 individual fish; perch represented 25

² DDE not detectable in perch sample 2.

TABLE 3. Residues of p,p'-DDD and p,p'-DDT in muscle of Atlantic herring—Eastern Canada, 1972

SAMPLE ²	RESIDUES, $\mu\text{g/g}$ WET WEIGHT ¹			
	MEAN		STANDARD DEVIATION	
	p,p'-DDD	p,p'-DDT	p,p'-DDD	p,p'-DDT
Herring B	0.042	0.021	0.31	0.27
Herring T	0.049	0.041	0.37	0.44

¹ Logarithmically transformed data. Mean is in antilog; standard deviation is in log form.

² Herring samples represented 24 individual fish; perch represented 25.

TABLE 4. Hexane-extractable lipid in muscle of Atlantic herring and yellow perch—Eastern Canada, 1972

SAMPLE ¹	LIPID, % WET WEIGHT					
	MEAN		STANDARD DEVIATION		CHI SQUARE PROBABILITY, %	
	N	L	N	L	N	L
Herring B	2.70	1.98	1.93	0.42	2	30
Herring T	12.7	11.7	6.26	0.38	50	5
Perch 2	0.32	0.29	0.17	0.21	20	30
Perch 3	0.54	0.51	0.20	0.17	1	20

NOTE: N = data as such; L = logarithmically transformed data. Mean is in antilog form; standard deviation is in log form.

¹ Herring samples represented 24 individual fish; perch represented 25.

taken August 18, 1972 (Tables 1-7). The former fish are spring spawners and the latter are fall spawners; both samples were taken just before spawning. Herring in these samples were 4 years old.

TABLE 5. Body weight of Atlantic herring and yellow perch—Eastern Canada, 1972

SAMPLE ¹	ARITHMETIC MEAN ²	STANDARD DEVIATION	CHI SQUARE PROBABILITY, %
Herring B	188	15	50
Herring T ³	194	0.066	30
Perch 2	9.3	2.34	80

NOTE: Weights not available for perch sample 3.

¹ Herring samples represented 24 individual fish; perch represented 25.

² Grams, wet weight.

³ Logarithmically transformed data. Mean is in antilog form, standard deviation is in log form.

TABLE 6. Decrease of PCB and p,p'-DDE residues in muscle of Atlantic herring and yellow perch—Eastern Canada

SAMPLE ¹	NEW MEAN IN % OF PRESENT MEAN			
	PCB		p,p'-DDE	
	DISTRIBUTION		DISTRIBUTION	
	N	L	N	L
Herring B	72	76	81	73
Herring T	62	64	73	62
Perch 2	83	82	ND	ND
Perch 3	85	79	82	79

NOTE: N = normal; L = lognormal; ND = no residues detected. Data are statistically significant at 5% probability.

Herring samples represented 24 individual fish; perch represented 25.

Yellow perch were obtained by seining from the shore with a 3-ft-by-15-ft chain-weighted net with floats and a mesh size of $\frac{1}{2}$ inch; Figure 1 indicates sampling stations. Sex, age, and wet body weight were determined and, like the herring, male perch were frozen (-14°C) until analysis. Perch sample 2 was obtained May 2 and 5, 1972; perch sample 3 was obtained May 25, 1972. Analysis was performed on two- and three-year-old fish from stations 2 and 3, respectively. Station 2 (Grand Falls, St. Croix River) is in a rather sparsely populated area with little agricultural or industrial activity. A pulp mill and two towns with a total population of about 12,000 are located downstream. Station 3 (Grand Point, Grand Lake) is on the St. John River, where pulp mills, potato and food processing plants, and a system of dams are located. The station is about 30 miles downstream from the city of Fredericton (population 25,000), and 40 miles upstream from the city of Saint John (population 100,000).

ANALYSIS

Sample analysis similar to that described in a 1972 study (5) utilized the white lateral muscle between the dorsal fin and the lateral line. The sample (5.5-6.0 g for herring, 1.5-2.0 g for perch) was ground with anhydrous sodium sulfate (Fisher Scientific S-421, 30 g) in a mor-

TABLE 7. Residue levels of PCB's and p,p'-DDE ($\mu\text{g/g}$ wet weight), hexane-extractable lipid (% wet weight), and body weight (g, wet weight), in Atlantic herring and yellow perch—Eastern Canada, 1972

PCB	p,p'-DDE	LIPID	WEIGHT	PCB	p,p'-DDE	LIPID	WEIGHT
Herring B ¹				Herring T ¹			
0.51	0.18	1.74	202.8	1.02	0.16	13.7	186.7
0.21	0.04	2.15	191.3	0.60*	0.11*	10.1*	210.9
0.18	0.04	1.53	183.2	0.50*	0.09*	9.38*	
0.44	0.10	4.75	180.2	Perch 2 ²			
0.15*	0.04*	0.34*	171.7	0.11	TR	0.13	11.51
0.13*	0.04*	0.32*		0.12	TR	0.59	6.92
0.22	0.06	2.65	182.1	0.08	TR	0.14	6.98
0.17	0.04	0.81	191.0	0.07	0.01	0.16	10.10
0.11	0.03	0.42	177.1	0.09	TR	0.41	7.32
0.28	0.06	5.24	196.8	0.16	TR	0.19	6.65
0.16*	0.05*	0.96*	177.1	0.08	0.01	0.25	7.38
0.15*	0.04*	0.95*		0.07	TR	0.26	9.34
0.24	0.06	3.27	178.9	0.06	TR	0.28	10.10
0.51	0.06	1.46	198.4	0.22	TR	0.44	7.91
0.55	0.14	4.76	178.7	0.12	TR	0.31	8.73
0.70	0.19	3.52	192.5	0.05	TR	0.28	10.40
0.10*	0.02*	0.88*	189.1	0.04	TR	0.29	13.41
0.12*	0.03*	1.02*		0.09	TR	0.50	5.65
0.40	0.09	1.64	192.5	0.07	TR	0.34	9.32
0.26	0.06	4.30	200.3	0.06	TR	0.76	9.49
0.41	0.07	12.94	146.4	0.05	0.01	0.32	13.16
0.10	0.03	0.43	164.5	0.06	TR	0.30	9.74
0.12*	0.03*	1.32*	196.7	0.08	TR	0.29	10.91
0.12*	0.03*	1.64*		0.07	TR	0.19	8.27
0.56	0.16	5.68	210.8	0.05	TR	0.23	13.04
0.42	0.11	4.88	215.1	0.09	0.01	0.14	8.95
0.46	0.15	4.91	186.2	0.10	0.01	0.34	8.04
0.09*	0.03*	0.48*	208.3	0.05	TR	0.29	12.15
0.12*	0.02*	0.64*		0.12	TR	0.74	5.72
Herring T ¹				Perch 3 ³			
0.08	0.02	6.28	131.5	0.09	0.13	1.42	
0.19	0.03	6.71	145.0	0.14	0.10	0.87	
0.20	0.04	6.95	218.7	0.04	0.06	0.39	
0.10	0.02	5.00	177.2	0.05	0.05	0.67	
0.65*	0.16*	16.7*	212.3	0.16	0.10	0.47	
0.61*	0.14*	16.0*		0.06	0.08	0.69	
0.12	0.03	7.87	201.8	0.11	0.14	0.33	
0.13	0.03	9.07	213.2	0.18	0.17	0.35	
0.15	0.04	3.39	187.2	0.27	0.19	0.70	
2.28*	0.32*	26.9*	233.4	0.11	0.07	0.57	
2.17*	0.32*	24.3*		0.14	0.04	0.56	
0.03	0.01	0.69	176.1	0.29	0.13	0.91	
0.56	0.11	11.5	202.1	0.26	0.24	0.47	
1.58	0.40	22.4	224.5	0.14	0.10	0.40	
1.29	0.29	19.6	229.4	0.10	0.06	0.35	
0.48*	0.09*	16.1*	163.2	0.12	0.09	0.88	
0.53*	0.09*	15.8*		0.22	0.15	0.44	
0.61	0.11	20.1	197.7	0.07	0.05	0.37	
0.62	0.11	17.1	175.0	0.09	0.10	0.34	
0.44	0.09	15.4	163.0	0.13	0.14	0.44	
1.07	0.20	15.8	202.0	0.10	0.09	0.31	
0.57*	0.07*	16.5*	181.4	0.07	0.08	0.37	
0.55*	0.07*	16.1*		0.13	0.03	0.41	
1.62	0.29	12.1	216.8	0.11	0.07	0.48	
0.88	0.16	18.2	244.6	0.19	0.06	0.50	
1.04	0.18	12.9	210.1				

NOTE: * = duplicate analyses of a single specimen. TR = trace: <0.01.

¹ Herring samples represented 24 individual fish.

² Perch samples represented 25 individual fish.

³ Weights not available for perch sample 3.

tar to yield a free-flowing powder and extracted with pesticide-grade hexane (Fisher Scientific H-300) in a Soxhlet extractor for 1 hour. The volume of the extract was adjusted to 100 ml in a volumetric flask with pesticide-grade hexane. An aliquot of the extract (10-20 ml) was dried in a rotatory evaporator in vacuum at room temperature to determine hexane-extractable lipids. An aliquot, not exceeding 100 mg of lipids, was applied in 1.5 ml pesticide-grade hexane to a 45-by-0.7-cm glass column with a glass wool plug, containing

2 g alumina, Fisher Scientific A-540, activated at 800°C for 4 hours and deactivated by the addition of 5 percent distilled water. The solvent was washed into the column with another 1.5 ml pesticide-grade hexane and the column was percolated with the same solvent to collect 20 ml effluent.

After the effluent had been concentrated almost to dryness on a rotatory evaporator, it was applied in 1.5 ml 0.5 percent v/v pesticide-grade benzene (Fisher Scientific B-426) in pesticide-grade hexane to a column

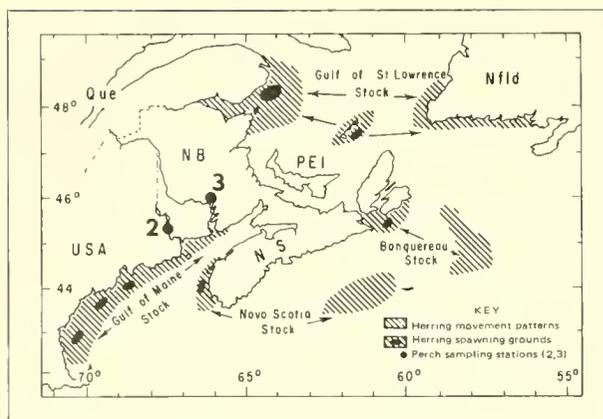


FIGURE 1. Atlantic herring stock structure and yellow perch sampling stations—Eastern Canada, 1972

filled with silica. The column was the same as that described above, and contained 2 g Mallinckrodt Silica-100-200 mesh. The solvent was washed with pesticide-grade hexane, dried in a rotatory evaporator at 36°C in vacuum, activated overnight at 130°C, and deactivated by the addition of 3 percent distilled water. The applied aliquot was washed into the column with another 1.5 ml of the solvent. The column was percolated with the same solvent to collect 15 ml effluent. This fraction contained PCB's and *p,p'*-DDE.

The column was percolated further with 10 percent diethyl ether (Fisher Scientific E-134) in hexane and 10 ml effluent was collected. This fraction contained *p,p'*-DDD and *p,p'*-DDT. Fractions were evaporated just to dryness on a rotatory evaporator in vacuum at room temperature. The residue was dissolved in pesticide-grade hexane (0.2-0.4 ml) and analyzed by gas chromatography. The gas chromatograph, a Packard A7901, was operated at 200°C. It had a glass column (6 ft by 4 mm), containing 4 percent SE-30 on acid-washed Chromosorb W, 60-80 mesh. Carrier gas was nitrogen at a flow rate of 60 ml/min. Injector and detector (³H, 150 mc) were kept at 210°C. A solution of Aroclor 1254 (2.232 µg/ml) and a solution containing *p,p'*-DDE, *p,p'*-DDD, and *p,p'*-DDT (0.182, 0.235, and 0.247 µg/ml, respectively) were used daily to calibrate the detector. Heights of five of the six major peaks of Aroclor 1254 were used for quantitation. Peak heights were also used to quantitate the other compounds. Minimum detectable levels of PCB's, *p,p'*-DDE, *p,p'*-DDD, and *p,p'*-DDT were 0.01, 0.003, 0.002, and 0.002 µg/g wet weight, respectively.

All glassware was washed with a laboratory detergent in tap water and rinsed with distilled water, acetone, and pesticide-grade hexane. Sodium sulfate was washed with pesticide-grade hexane and dried in a rotatory evaporator at 36°C in vacuum. Extraction thimbles and glass wool were pre-extracted with pesticide-grade hexane in a Soxhlet extractor. In preparing the 0.5 percent

v/v benzene in pesticide-grade hexane, an allowance was made for benzene already present in hexane. The concentration of benzene in each batch of pesticide-grade hexane was determined from the absorbance at 253 nm against spectrograde hexane (Fisher Scientific H-334).

In each sample, 24 herring and 25 perch were analyzed individually. Five fish from each sample were analyzed in duplicate, including duplicate extraction. Results of duplicate analyses usually agreed within 10 percent and arithmetic means of duplicate analyses were used in further evaluation of data.

DATA EVALUATION

Arithmetic means and standard deviations (Tables 1-6) were calculated from the data (Table 7) and from their decadic logarithms. To determine whether distribution of data can be approximated by a normal or a lognormal distribution, data were divided into classes; enough classes were chosen to assure that the original mean and standard deviation would not alter appreciably. Frequencies expected for normal and lognormal distribution were calculated from the means and standard deviations and compared with observed frequencies, testing the goodness of fit by the chi square test (6). Higher chi square probabilities (Tables 1,2,4,5) indicate better fit of the theoretical to the observed distribution.

Results and Discussion

PCB'S

In all samples PCB's resembled and were quantitated as Aroclor 1254. Data are summarized in Table 1. As can be seen from the chi square probability, in three out of four cases lognormal distribution would be preferred to normal. PCB distribution in the herring sample T could not be adequately characterized by either distribution. The PCB level reported previously (3) for the Banquereau stock of similar weight group (arithmetic mean 0.54) falls between the levels observed in the Nova Scotia and Gulf of St. Lawrence stocks. This may indicate that the level of PCB's in herring of equal size decreases in the northerly direction.

CHLORINATED HYDROCARBON PESTICIDES

Levels of *p,p'*-DDE are presented in Table 2. DDE was not detectable in perch sample 2. In all cases, the distribution is better described as lognormal. Levels of *p,p'*-DDD and *p,p'*-DDT in herring are summarized in Table 3. Because of the low levels found, no detailed statistical evaluation of the data was made and it was assumed that, as in the case of *p,p'*-DDE, the distribution is lognormal. No measurable residues of *p,p'*-DDD and *p,p'*-DDT were found in perch sample 2. Perch sample 3 contained very low levels of these compounds

(0.005-0.02 µg/g) in six fish analyzed individually. Statistical evaluation was not carried out.

LIPID AND BODY WEIGHT

In three out of four cases the distribution of lipid was best described as lognormal (Table 4). Herring sample T may be described by a normal distribution. This was the only sample taken at the end of the feeding season and it is possible that there is a relation between the feeding activity and the distribution of lipid. The weight of the fish was normally distributed (Table 5), with the exception of herring sample T, where the data may be described by a lognormal distribution. Weights were not available for perch sample 3.

TRENDS OF PCB AND *p,p'*-DDE LEVELS

Knowing the trends of the environmental levels of persistent pollutants enables one to assess the effectiveness of regulatory actions such as the Canadian ban on DDT and restriction of PCB's. As stated earlier, one objective of this study was to weigh the possibility of using Atlantic herring and yellow perch to detect such trends. Authors' findings now render that possibility obscure. Analytical data indicate that even after elimination of possible sex and age (or size) variations, the variability between individual fish still remains very high and a large number of fish have to be analyzed to detect statistically significant differences. Table 6 calculates differences for the 5 percent probability level, using the observed standard deviations and assuming that 25 individual fish are analyzed in each sample.

It is very likely that no significant difference in PCB levels can be detected in 2 consecutive years when using samples of this size. Concentration of PCB's in fish is determined by the rate of PCB uptake and excretion and by the growth of fish. The rate of excretion is very slow. In related studies fish did not metabolize chlorobiphenyl isomers (7) and excreted very little, if any, Aroclor 1254 ingested in a laboratory experiment (8). If, in a hypothetical case, the uptake of PCB's were completely eliminated, concentration of PCB's in fish would depend only on the rate of growth. The relative weight increase of the investigated stocks of herring between the age of 3 and 4 years is approximately 46 percent and the level of PCB's in 3-year-old fish is about 86 percent of that in 4-year-old fish (9). The concentration of PCB's in 4-year-old herring in 1974 would therefore be 59 percent of the level in herring of the same age in 1973. This hypothetical level is quite close to the minimum detectable difference in Table 6. The

uptake of PCB's cannot be completely eliminated due to the presence of PCB's in the environment; the difference will be smaller than estimated above. It may be more pertinent and less costly to analyze a large number of individual fish only every 4-5 years to determine trends of PCB levels.

Insufficient data on the excretion rate of *p,p'*-DDE by fish do not allow prediction of trends of *p,p'*-DDE levels. It is possible that *p,p'*-DDE residues disappear from fish faster than PCB residues. The average level of *p,p'*-DDE in the Banquereau herring in 1971 was 0.24 µg/g (3) and the levels of *p,p'*-DDE in herring oils in 1968-70 were comparable to those of PCB's (4). Levels of *p,p'*-DDE reported in this paper are much lower.

Acknowledgments

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LITERATURE CITED

- (1) *Bumpus, D. F., and M. Lauzier. 1965.* Surface circulation on the continental shelf off Eastern North America between Newfoundland and Florida. Serial Atlas of the Marine Environment Folio 7. American Geographical Society.
- (2) *Iles, T. D., and S. N. Tibbo. 1970.* Recent events in Canadian Atlantic herring fisheries. ICNAF Redbook, Pt. III; 134-147.
- (3) *Zitko, V. 1971.* Polychlorinated biphenyls and organochlorine pesticides in some freshwater and marine fishes. *Bull. Environ. Contam. Toxicol.* 6:464-470.
- (4) *Addison, R. F., M. E. Zinck, and R. G. Ackman. 1972.* Residues of organochlorine pesticides and polychlorinated biphenyls in some commercially produced Canadian marine oils. *J. Fish. Res. Board Can.* 29(4): 349-355.
- (5) *Zitko, V. 1972.* Problems in the determination of polychlorinated biphenyls. *Intern. J. Environ. Anal. Chem.* 1:221-231.
- (6) *Sokal, R. R., and F. J. Rohlf. 1969.* Biometry. The principles and practice of statistics in biological research, pp. 550-572. W. H. Freeman and Company, San Francisco, Calif.
- (7) *Hutzinger, O., D. M. Nash, S. Safe, A. S. W. DeFreitas, R. J. Norstrom, D. J. Wildish, and V. Zitko. 1972.* Polychlorinated biphenyls: Metabolic behavior of pure isomers in pigeons, rats, and brook trout. *Science* 178:312-314.
- (8) *Zitko, V., and O. Hutzinger. 1973.* Sources, levels, and toxicological significance of PCB's in hatchery-reared Atlantic salmon, in PCB's—still prevalent—still persistent. C. G. Gustafson, ed., Marcel Dekker, Inc., New York, N.Y., in press.
- (9) *Monaghan, C. F., and V. Zitko. 1973.* Unpublished data.

RESIDUES IN FOOD AND FEED

Pesticide Residues in Total Diet Samples (VII)

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ABSTRACT

Pesticide residue levels detected in ready-to-eat foods remained at relatively low levels during the seventh year of the Total Diet Study in its present form. Samples were collected from 30 markets in 27 different cities. Populations of cities ranged from less than 50,000 to 1,000,000 or more. Averages and ranges of pesticides commonly found are reported for the period June 1970-April 1971 by region and food class. Pesticides found infrequently are also reported for this period by region and food class. Results of recovery studies with various classes of pesticides are also presented. After October 1970, analyses of bromides, amitrole, and dithiocarbamates were discontinued; mercury and orthophenylphenol were added. Residue levels in three major fatty food groups are now reported on a whole-product basis, rather than on a fat basis. Data for June and August were adjusted accordingly.

Introduction

The Total Diet Program (1) has been used since 1964 by the Food and Drug Administration (FDA), U.S. Department of Health, Education, and Welfare, as a way to monitor pesticide residues in foods. This program measures the amount of pesticide chemicals in food samples collected in retail outlets and prepared for consumption. Although the program was designed to measure pesticide residues in foods, some chemicals determined and reported here may not have been used as pesticides; this includes such materials as polychlorinated biphenyls (PCB's), cadmium, and mercury. Increased awareness of the potential hazards presented by these chemicals necessitates their inclusion in this program.

Amounts and types of residues found from June 1964 through April 1970 have been described in earlier reports (2-7). The present report covers the period June 1970 through April 1971. Tabular data included are comparable to those of previous years.

Analytical Methods

No significant changes were made in sampling and compositing procedures described in the initial issue of *Pesticides Monitoring Journal* (1). Samples were collected in 30 different grocery markets in 27 different cities representing five regions of the United States: Baltimore, Boston, Kansas City, Los Angeles, and Minneapolis. Population of the cities ranged from less than 50,000 to 1,000,000 or more; the average sampling site was in the 250,000 to 500,000 range.

Beginning with the October 1970 sample, significant changes were made regarding analysis. At that time, all Total Diet analyses were centralized at the FDA Kansas City district. Analyses for bromides, amitrole, and dithiocarbamates were discontinued, and PCB's, mercury, and orthophenylphenol (*o*-phenylphenol) were added. Analyses for residues of organochlorines, some parent organophosphorus pesticides, chlorophenoxy acid herbicides, carbaryl, arsenic, and cadmium were continued as in previous programs.

Procedural changes were made in analyses of fatty food groups for chlorinated and organophosphorus residues. These food groups were Group I: Dairy Products; Group II: Meat, Fish, and Poultry; and Group X: Oils, Fats, and Shortening. Prior to October 1970, all organochlorine and organophosphorus residues found in these three groups were reported on a fat basis. After this date, residues were calculated on a whole-product basis. Results reported here from June and August samples have been converted to the whole-product basis using

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an average fat content of 10.5 percent for Group I, 20 percent for Group II, and 85.5 percent for Group X.

Methods used for most analyses are described in the FDA Pesticide Analytical Manual, Vol. I and II (8). Other analytical methodology was used for certain residues: colorimetry for arsenic (9); flameless atomic absorption spectroscopy for mercury (10), and atomic absorption or polarography for cadmium (11). Carbaryl and *o*-phenylphenol were extracted by the method of Porter et al. (12) and quantified by thin-layer chromatography (TLC) (13).

Quantitative values reported for organochlorine and organophosphorus compounds were obtained by gas-liquid chromatography (GLC) using the electron capture, the thermionic or the flame photometric detection system. Confirmation was made by TLC and/or GLC with halogen-specific microcoulometric detection. For additional confirmation of residues, identity techniques such as *p*-values, alternative GLC column packings, alkaline hydrolysis, and mass spectrometry were used.

The methodology permits the quantitation of heptachlor epoxide, an organochlorine, at about 0.003 parts per million (ppm), and of parathion, an organophosphate, at about 0.01 ppm. The limit of quantitation for both classes varies with the individual compound being determined. In some cases, finite residue levels are reported below the approximate limits of quantitation. The quantitative reliability of these extremely low levels is not known because the authors have no recovery information about dietary composites below 0.003 ppm for organochlorine compounds or 0.01 ppm for organophosphorus compounds. As a general rule residue determinations below 0.005 ppm are subject to a high degree of variability. Those residues detected and qualitatively confirmed at too low a level to be quantified are reported as trace (T).

Approximate limits of quantitation for other analyses were chlorophenoxy acid herbicides and pentachlorophenol (PCP): 0.02 ppm; carbaryl: 0.05 ppm; arsenic: 0.1 ppm; cadmium: 0.01 ppm; amitrole (June and August samples only): 0.05 ppm; bromides (June and August samples only): 0.5 ppm. Individual fruits and vegetables were examined for dithiocarbamate residues (June and August samples only). Beginning in October 1970, each composite was examined for PCB's with a limit of quantitation of about 0.05 ppm; for *o*-phenylphenol, with a limit of 0.1 ppm; and for mercury, with a limit of 0.02 ppm.

Results

A total of 1,081 residues of 33 different chemicals were found in samples in the current reporting period. In the previous reporting period, 1,446 occurrences of 31 different chemicals were found. This apparently large decrease is deceptive; almost one-half the decrease oc-

curred in reported bromide residues because bromide analyses were discontinued in October 1970. As in previous years, a total of 360 composites were examined for all residues: there were 12 composites from each of the 30 markets. The program calls for carbaryl and *o*-phenylphenol analyses on only the nonfatty composites (1,3-6,9-11,13), of which there were 270. Program changes also resulted in analyses of only 240 composites for mercury and 120 composites for bromides. The 33 different residues found are listed in decreasing order of frequency in Table 1.

The most common residues, maximum levels of those residues, and residues reported less frequently are discussed below for each of the 12 food composites. Tables 2a and 2b report findings in more detail according to food class and region. None of the reported findings have been corrected for recoveries obtained in recovery experiments. Table 3 summarizes studies.

DAIRY PRODUCTS

Of the 30 composites examined, 28 contained residues. Organochlorine pesticide residues were the most common, appearing in 27 composites. The most common organochlorines and their maximum concentrations were DDT, 0.005 ppm; DDE, 0.028 ppm; dieldrin, 0.007 ppm; heptachlor epoxide, 0.001 ppm; and BHC, 0.001 ppm. Also found were hexachlorobenzene (HCB), lindane, TDE, methoxychlor, and PCP. Bromides were found in 7 of 10 composites examined at levels of 1.0 ppm to 5.5 ppm. Cadmium was found in 4 of 30 composites at 0.01 to 0.06 ppm.

MEAT, FISH, AND POULTRY

Residues of 9 organochlorine compounds were found in varying combinations in all 30 composites examined. Most common organochlorine residues and their maximum concentrations were DDE: 0.048 ppm; DDT: 0.033 ppm; TDE: 0.010 ppm; and dieldrin: 0.015 ppm. Heptachlor epoxide, lindane, BHC, bromides, and HCB were also found, although less frequently. PCB's were found in 14 of the 30 composites; the highest PCB residue was 0.15 ppm. Arsenic was found in 9 composites: 0.1-0.3 ppm; and cadmium was found in 17 composites: 0.01-0.04 ppm.

GRAIN AND CFREAL PRODUCTS

Organophosphorus residues were the most common found in this commodity class. Malathion was found in 28 of 30 composites (maximum level 0.170 ppm); diazinon was found in 12 of 30 composites (maximum level 0.015 ppm). Varying combinations of 8 organochlorine compounds were found in 20 of 30 composites. The most common organochlorines and their maximum levels found were DDE: 0.001 ppm; DDT: 0.009 ppm; and dieldrin: 0.012 ppm. PCB's were found in 4 composites; 0.36 ppm was the highest level reported.

Cadmium was found in 27 of 30 composites at 0.01-0.07 ppm. Other residues found were TDE, ronnel, *o*-phenylphenol, and methoxychlor.

POTATOES

Residues of 8 organochlorine compounds were detected in 15 of the 30 composites. The most common of

TABLE 1. Insecticide residues found in food composites, June 1970-April 1971¹

CHEMICAL FOUND	NO. OF COMPOSITES WITH RESIDUES	NO. OF POSITIVE COMPOSITES WITH RESIDUES REPORTED AS TRACE ²	RANGES OF PPM REPORTINGS
CADMIUM	213	0	0.01-0.20
DDE 1,1-dichloro-2,2-bis (<i>p</i> -chlorophenyl) ethylene (isomers other than <i>p,p'</i> also included in reportings)	133	55	T-0.028
DDT 1,1,1-trichloro-2,2-bis (<i>p</i> -chlorophenyl) ethane (isomers other than <i>p,p'</i> also included in reportings)	118	51	T-0.037
DIELDRIN Not less than 85% of 1,2,3,4,10,10-hexachloro-6,7-epoxy-1,4,4a,5,6,7,8,8a-octahydro-1,4- <i>endo-exo</i> -5,8-dimethanonaphthalene	110	23	T-0.015
TDE 1,1-dichloro-2,2-bis (<i>p</i> -chlorophenyl) ethane (isomers other than <i>p,p'</i> also included in reportings)	90	42	T-0.087
BROMIDES ¹	81	0	0.5-51
MALATHION diethylmercaptosuccinate, <i>S</i> -ester with <i>o,o</i> -dimethyl phosphorodithioate	49	2	T-0.170
BHC 1,2,3,4,5,6-hexachlorocyclohexane, mixed isomers except gamma	42	19	T-0.009
HEPTACHLOR EPOXIDE 1,4,5,6,7,8,8-heptachloro-2,3-epoxy-3a,4,7,7a-tetrahydro-4,7-methanoindan	36	23	T-0.011
LINDANE 1,2,3,4,5,6-hexachlorocyclohexane, 99% or more gamma isomer	28	8	T-0.023
ENDOSULFAN 6,7,8,9,10,10-hexachloro-1,5,5a,6,9,9a-hexahydro-6,9-methano-2,4,3-benzodioxathiepin 3-oxide (reportings include isomers I,II, and the Sulfate)	24	8	T-0.063
CARBARYL ¹ 1-naphthyl methyl carbamate	20	15	T-0.5
PCB'S (polychlorinated biphenyls) Calculated as Aroclor® with varied chlorine content—54% and 60% reported this period	18	13	T-0.36
DIAZINON <i>o,o</i> -diethyl <i>o</i> -(2-isopropyl-6-methyl-4-pyrimidinyl) phosphorothioate	15	10	T-0.015
ETHION <i>o,o,o',o'</i> -tetraethyl <i>S,S'</i> -methylene bisphosphorodithioate	15	3	T-0.099
ARSENIC (As ₂ O ₃)	13	0	0.1-0.3
DICOFOL (KELTHANE®) 4,4'-dichloro- <i>a</i> -(trichloromethyl) benzhydrol	13	2	T-0.066
PARATHION <i>o,o</i> -diethyl <i>o-p</i> -nitrophenyl phosphorothioate	11	4	T-0.012
ORTHOPHENYLPHENOL ¹ 2-hydroxydiphenyl	10	7	T-0.25
MERCURY ¹	10	3	T-0.05
HCB hexachlorobenzene	6	3	T-0.001
PERTHANE 1,1-dichloro-2,2-bis (<i>p</i> -ethyl phenyl) ethane	5	2	T-0.022
METHOXYCHLOR 1,1,1-trichloro-2,2-bis (<i>p</i> -methoxyphenyl) ethane	4	2	T-0.008
METHYL PARATHION <i>o,o</i> -dimethyl <i>o-p</i> -nitrophenyl phosphorothioate	3	2	T-0.011
2,4-D 2,4-dichlorophenoxyacetic acid	3	0	0.01-0.02
PENTACHLOROPHENOL	2	1	T-0.011
BOTRAN® 2,6-dichloro-4-nitroaniline	2	0	0.003-0.006
ENDRIN 1,2,3,4,10,10-hexachloro-6,7-epoxy-1,4,4a,5,6,7,8,8a-octahydro-1,4- <i>endo-endo</i> -5,8-dimethanonaphthalene	2	1	T-0.007
TOXAPHENE chlorinated camphene containing 67-69% chlorine	1	1	T
DCPA (DACTHAL®) 2,3,5,6-tetrachloroterephthalic acid dimethyl ester	1	1	T
CIPC isopropyl <i>n</i> -(3-chlorophenyl) carbamate	1	0	0.14
PHOSALONE S[(6-chloro-2-oxo-3-benzoxazolonyl)] methyl <i>o,o</i> -diethyl phosphorodithioate	1	0	0.278
RONNEL <i>o,o</i> -dimethyl <i>o</i> -2,4,5-trichlorophenyl phosphorothioate	1	0	0.007

¹ Total of 360 composites examined for each compound except as follows: mercury—240 composites; bromides—120 composites; carbaryl and orthophenylphenol—270 composites.

² Pesticide chemicals capable of being detected by the specific analytical methodology may be confirmed qualitatively but are not quantifiable when they are present at concentrations below the limit of quantitation. Limit of quantitation varies with residue and food class.

these were dieldrin, DDE, and DDT with maximum values of 0.006 ppm, 0.018 ppm, and 0.020 ppm, respectively. Also detected were Botran (dichloran), TDE, BHC, endrin, carbaryl, endosulfan, CIPC (chlorpropham), bromides, and arsenic. Cadmium was found in 28 of 30 composites at 0.02-0.09 ppm.

LEAFY VEGETABLES

Residues of 9 organochlorine compounds were found in varying combinations in 23 of 30 composites. Organophosphorus residues were found in 10 of 30 composites. The most common residues and their maximum levels were DDT: 0.026 ppm; endosulfan: 0.063 ppm; parathion: 0.012 ppm; DDE: 0.016 ppm; and dieldrin: 0.005 ppm. Cadmium (0.01-0.20 ppm) was found in 28 of 30 composites examined. Other residues found were methyl parathion, carbaryl, diazinon, 2,4-D, bromides, HCB, TDE, Dacthal (DCPA), and malathion.

LEGUME VEGETABLES

Residues of 5 organochlorine compounds were found in 7 of 30 composites. DDE and DDT were most common, with maximum values of 0.005 ppm and 0.031 ppm, respectively. Other residues found were TDE, carbaryl, BHC, dieldrin, parathion, cadmium, and bromides.

ROOT VEGETABLES

Of 30 composites, 11 were found to contain 6 different organochlorine residues in varying combinations. The most common residues found and maximum levels detected were DDE: 0.006 ppm; and DDT: 0.008 ppm. Cadmium was discovered in 24 of 30 composites at 0.01-0.06 ppm. Other residues were dieldrin, TDE, *o*-phenylphenol, lindane, toxaphene, carbaryl, and bromides.

GARDEN FRUITS

Residues of 8 organochlorine compounds were found in varying combinations in 28 of 30 composites. The most common of these and the maximum levels were TDE: 0.087 ppm; DDT: 0.037 ppm; dieldrin: 0.010 ppm; and BHC: 0.009 ppm. Cadmium was found in 26 of 30 composites at 0.01-0.05 ppm. Other residues detected were parathion, *o*-phenylphenol, DDE, carbaryl, endosulfan, bromides, lindane, and Kelthane (dicofol).

FRUITS

Residues of 9 organochlorine compounds were found in 19 of 30 composites. The most common of these and the maximum levels found were DDE: 0.002 ppm; Kelthane: 0.066 ppm; and DDT: 0.003 ppm. Residues of 5 organophosphorus compounds were found in varying combinations in 20 of 30 composites. The most common and the highest levels found were ethion: 0.099

ppm; and malathion: 0.089 ppm. Other residues found included TDE, *o*-phenylphenol, carbaryl, perthane, endosulfan, phosalone, lindane, diazinon, dieldrin, Botran, arsenic, cadmium, and bromides.

OILS, FATS, AND SHORTENING

Residues of 4 organochlorine compounds were found in varying combinations in 24 of 30 composites. The residues and their maximum levels were dieldrin: 0.006 ppm; DDE: 0.008 ppm; TDE: 0.013 ppm; and DDT: 0.012 ppm. Malathion was found in 12 composites; maximum level was 0.097 ppm. Cadmium appeared in 27 of 30 composites at levels of 0.01 to 0.04 ppm. Bromides were detected in 5 composites at a maximum of 12.0 ppm.

SUGARS AND ADJUNCTS

Residues of 7 organochlorine compounds were found in varying combinations in 15 of 30 composites. The most common organochlorines and their maximum levels were lindane: 0.004 ppm; DDT: 0.017 ppm; and DDE: 0.002 ppm. Heptachlor epoxide, BHC, PCP, diazinon, malathion, arsenic, and bromides were also detected. Cadmium (0.01-0.03 ppm) was found in 14 of 30 composites.

BEVERAGES

Of all food composites studied, beverages had the lowest amounts of pesticides; only 9 of 30 composites contained any residues. DDT, TDE, and lindane each appeared in 1 composite, cadmium appeared in 3 composites, and bromides appeared in 5. All residues were at or near trace levels.

Discussion

Organochlorine residues were found in 221 of 360 composites, or 61.4 percent of those examined. Corresponding percentages from previous years were 74.2 percent in 1969-70, 64.7 percent in 1968-69, and 65.6 percent in 1967-68. Organophosphorus compounds in the current reporting period were found in 77 composites or 21.4 percent. The three previous reporting periods showed 74, 59, and 26 composites, respectively, which had organophosphorus residues.

Carbaryl was found in 20 composites during this reporting period; 15 of these findings were at trace levels. This is in contrast to the June 1969-April 1970 period (4), which showed no carbaryl, and to the June 1968-April 1969 period (3), which showed only three positive composites. However, it should be noted that during the two previous periods the fruit and vegetable composites were examined both before and after processing. Foods were processed in the usual manner: peeling, stripping outer leaves, cooking when appropriate, etc. This dual analysis was conducted only during the two previous reporting periods, serving as an indicator of

residue loss through preparation of foods for table-ready consumption. Carbaryl loss through such processing was not presented in earlier reports because of its low frequency and level of occurrence. However, carbaryl did occur as indicated in the following paragraph. Findings are presented as parts per million in both the unprocessed composite and in the diet-prepared composite; ND signifies no residues detected, TR signifies trace residues detected.

June 1969-April 1970	Unprocessed	Diet-prepared
Group VI, Legume Vegetables, 30 composites examined	0.13 ppm	ND
Group VII, Root Vegetables, 30 composites examined	0.14 ppm	ND
June 1968-April 1969		
Group VI, Legume Vegetables, 25 composites examined	0.5 ppm	TR
	TR	TR
Group IX, Fruits, 25 composites examined	0.4 ppm	ND
	0.2 ppm	ND
	0.3 ppm	0.3 ppm

It appears that normal preparation of foods for human consumption generally renders carbaryl residues below detection levels, or very near that point. Accordingly, it is difficult to define the significance of the apparent increase in incidence during this reporting period because the majority of findings were at trace levels.

Analysis for *o*-phenylphenol was included this reporting period because it is detectable simultaneously with the carbaryl; *o*-phenylphenol was found in 10 composites.

Arsenic residues were found in 13 composites at concentrations from 0.1 ppm to 0.3 ppm. Of these arsenic findings, nine were in Group II: Meat, Fish, and Poultry.

Cadmium was found in 213 of 360 composites: maximum level was 0.20 ppm.

No amitrole or dithiocarbamate residues were found during this reporting period. Chlorophenoxy acid herbicides (2,4-D) were found in three leafy vegetable composites, PCP, which is detected by the chlorophenoxy acid methodology, was reported in two composites. Previous reportings showed chlorophenoxy acid herbicides in four composites in 1969-70, and four in 1968-69.

Mercury residues were found in 10 of 240 composites. All mercury residues were found in Group II: Meat, Fish, and Poultry. Analyses of individual commodities

within Group II have shown that the principal source of mercury in the diet is seafood.

Recovery studies were conducted for all classes of chemicals sought throughout the entire year. Table 3 lists recovery data for this reporting period for 14 of the more commonly found organochlorine residues and data for representative compounds in the other chemical classes. Each recovery experiment consisted of a single determination for the unfortified food composite and a single determination for the fortified sample. Since these were performed simultaneously, the fortification level was occasionally below the level present in the sample. In other cases, not enough recoveries were run to permit statistical evaluation. These recovery data are not reported.

At very low fortification levels recoveries may range from 0 to 200 percent. As the fortification level is raised, however, the recovery improves. Based on recovery data, it is apparent that individual, low-level residues reported may vary from the so-called true value but the overall findings are useful in appraising the national residue picture.

LITERATURE CITED

- (1) Duggan, R. E., and F. J. McFarland. 1967. Assessments include raw food and feed commodities, market basket items prepared for consumption, meat samples taken at slaughter. *Pestic. Monit. J.* 1(1):1-5.
- (2) Corneliussen, P. E. 1969. Pesticide residues in total diet samples (IV). *Pestic. Monit. J.* 2(4):140-152.
- (3) Corneliussen, P. E. 1970. Pesticide residues in total diet samples (V). *Pestic. Monit. J.* 4(3):89-105.
- (4) Corneliussen, P. E. 1972. Pesticide residues in total diet samples (VI). *Pestic. Monit. J.* 5(4):313-330.
- (5) Duggan, R. E., H. C. Barry, and L. Y. Johnson. 1966. Pesticide residues in total diet samples. *Science* 151:101-105.
- (6) Duggan, R. E., H. C. Barry, and L. Y. Johnson. 1967. Pesticide residues in total diet samples (II). *Pestic. Monit. J.* 1(2):2-12.
- (7) Martin, R. J., and R. E. Duggan. 1968. Pesticide residues in total diet samples (III). *Pestic. Monit. J.* 1(4):11-20.
- (8) Barry, H. C., J. G. Hundley, and L. Y. Johnson. 1963. (Revised 1970.) *Pesticide Analytical Manual, Vol. I and II*, Food and Drug Administration, U.S. Department of Health, Education, and Welfare.
- (9) Hundley, H. K., and J. C. Underwood. 1970. Private communication. Also: *Official Methods of Analysis*, 11th ed., Association of Official Analytical Chemists, Washington, D.C., sec. 25.016.
- (10) Munns, R. K., and D. C. Holland. 1971. *J. Ass. Offic. Anal. Chem.* 54(1):202-205.
- (11) Okrasinski, J. Private communication: Determination of cadmium in total diet samples.
- (12) Porter, M. L., R. J. Gajan, and J. A. Burke. 1969. Acetonitrile extraction and determination of carbaryl in fruits and vegetables. *J. Ass. Offic. Anal. Chem.* 52(1):177-181.
- (13) Finocchiaro, J. M., and W. R. Benson. 1965. Thin layer chromatographic determination of carbaryl (Sevin) in some foods. *J. Ass. Offic. Anal. Chem.* 48(4):736-738.

TABLE 2A. Levels of pesticide residues commonly found—by food class and region, June 1970-April 1971

CHEMICAL	BALTIMORE	BOSTON	KANSAS CITY	LOS ANGELES	MINNEAPOLIS
I. DAIRY PRODUCTS ¹ RESIDUES, PPM					
DDT					
Average	T	0.001	0.001	T	T
Positive Composites					
Number	1	3	3	3	1
Range	0.001	T-0.005	T-0.003	T-0.002	0.001
DDE					
Average	T	T	T	0.019	T
Positive Composites					
Number	4	5	3	6	2
Range	T-0.001	T-0.002	T-0.001	0.010-0.028	0.001
DIELDRIN					
Average	T	0.002	0.003	0.001	0.003
Positive Composites					
Number	3	5	5	6	5
Range	T-0.002	0.001-0.003	T-0.007	T-0.002	0.001-0.005
BHC					
Average	T	T	T	T	T
Positive Composites					
Number	1	4	4	2	3
Range	T	T-0.001	T-0.001	T	T-0.001
HEPTACHLOR EPOXIDE					
Average	T	T	T	T	T
Positive Composites					
Number	2	5	3	2	3
Range	T	T	T-0.001	T-0.001	T-0.002
II. MEAT, FISH, AND POULTRY ¹ RESIDUES, PPM					
TDE					
Average	0.003	0.003	0.004	T	0.001
Positive Composites					
Number	3	5	4	3	5
Range	T-0.009	T-0.010	T-0.019	T	T-0.002
DDT					
Average	0.005	0.009	0.013	0.005	0.004
Positive Composites					
Number	5	6	6	5	6
Range	T-0.015	T-0.018	T-0.033	T-0.011	T-0.008
DDE					
Average	0.007	0.007	0.006	0.033	0.007
Positive Composites					
Number	6	6	6	6	6
Range	0.001-0.014	T-0.021	0.003-0.013	0.018-0.048	T-0.022
DIELDRIN					
Average	0.003	0.005	0.005	0.003	0.003
Positive Composites					
Number	4	4	6	6	5
Range	T-0.008	0.001-0.015	0.004-0.009	0.001-0.004	0.002-0.007
PCB'S					
Average	T	T	T	T	0.029
Positive Composites					
Number	4	2	2	2	4
Range	T	T	T	T	T-0.15
CADMIUM					
Average	0.01	0.01	< 0.01	0.01	0.01
Positive Composites					
Number	3	4	3	2	5
Range	0.01-0.02	0.01-0.04	0.01-0.02	0.01	0.01-0.02
ARSENIC					
Average	< 0.1	< 0.1	< 0.1	< 0.1	—
Positive Composites					
Number	2	3	2	2	0
Range	0.1-0.2	0.1-0.3	0.1-0.2	0.2-0.3	—
HEPTACHLOR EPOXIDE					
Average	T	T	0.002	T	T
Positive Composites					
Number	3	5	3	2	5
Range	T-0.003	T	0.001-0.011	T-0.001	T-0.001
MERCURY					
Average	< 0.02	< 0.02	< 0.02	0.02	< 0.02
Positive Composites					
Number	1	3	1	3	2
Range	< 0.02	T-0.03	< 0.02	0.02-0.05	0.02

(Continued next page)

TABLE 2A (cont'd). Levels of pesticide residues commonly found—by food class and region, June 1970-April 1971

CHEMICAL	BALTIMORE	BOSTON	KANSAS CITY	LOS ANGELES	MINNEAPOLIS
III. GRAIN AND CEREAL¹					
RESIDUES, PPM					
DDT					
Average	T	0.001	—	0.002	0.001
Positive Composites					
Number	2	3	0	2	3
Range	T	T-0.005	—	T-0.009	T-0.003
MALATHION					
Average	0.023	0.015	0.016	0.062	0.030
Positive Composites					
Number	6	5	5	6	6
Range	0.008-0.038	0.013-0.023	0.011-0.026	0.020-0.170	0.015-0.041
DIELDRIN					
Average	0.002	T	T	0	T
Positive Composites					
Number	1	1	1	0	1
Range	0.012	0.001	T	—	T
DIAZINON					
Average	0.001	0	0.001	0.003	T
Positive Composites					
Number	2	0	4	4	2
Range	T-0.006	—	T-0.006	T-0.015	T-0.002
CADMIUM					
Average	0.02	0.03	0.02	0.02	0.03
Positive Composites					
Number	5	5	5	6	6
Range	0.01-0.03	0.01-0.07	0.01-0.04	0.01-0.02	0.02-0.03
PCB'S					
Average	0	0.06	T	0.18	0.14
Positive Composites					
Number	0	1	1	1	1
Range	—	0.36	T	0.36	0.82
BROMIDES					
Average	7.8	4.8	5.0	2.7	2.4
Positive Composites					
Number	2	2	1	2	1
Range	22-25	14	30	7.0-9.0	14
LINDANE					
Average	0	0	0	0.001	T
Positive Composites					
Number	0	0	0	2	1
Range	—	—	—	0.003-0.005	0.001
DDE					
Average	T	T	0	0	T
Positive Composites					
Number	2	1	0	0	3
Range	T	T	—	—	T-0.001
IV. POTATOES¹					
RESIDUES, PPM					
DDT					
Average	0.003	0.001	0	T	T
Positive Composites					
Number	1	2	0	1	T
Range	0.020	T-0.004	—	T	0.002
DIELDRIN					
Average	0.001	T	0.001	T	0.001
Positive Composites					
Number	1	2	3	2	2
Range	0.005	T	T-0.003	T-0.001	0.001-0.006
DDE					
Average	0.001	T	0.004	T	T
Positive Composites					
Number	1	2	2	1	2
Range	0.007	T	0.003-0.018	T	T-0.002
CADMIUM					
Average	0.04	0.03	0.04	0.03	0.05
Positive Composites					
Number	5	5	6	6	6
Range	0.02-0.08	0.02-0.04	0.02-0.08	0.02-0.04	0.02-0.09

(Continued next page)

TABLE 2A (cont'd). Levels of pesticide residues commonly found—by food class and region, June 1970-April 1971

CHEMICAL	BALTIMORE	BOSTON	KANSAS CITY	LOS ANGELES	MINNEAPOLIS
V. LEAFY VEGETABLES ¹ RESIDUES, PPM					
DDT					
Average	0.004	0.001	0.001	0.002	T
Positive Composites					
Number	1	5	1	3	1
Range	0.026	T-0.004	0.008	T-0.008	0.002
DDE					
Average	0.003	0.003	0	0.063	0.002
Positive Composites					
Number	2	3	0	4	3
Range	0.004-0.016	T-0.011	—	T-0.008	0.002-0.006
ENDOSULFAN (I, II plus sulfate)					
Average	0.001	0.006	0.003	0.013	0.007
Positive Composites					
Number	1	4	4	4	2
Range	0.006	T-0.020	T-0.008	0.063	0.001-0.018
CADMIUM					
Average	0.03	0.06	0.02	0.05	0.08
Positive Composites					
Number	6	6	4	6	6
Range	0.01-0.05	0.02-0.14	0.02-0.03	0.03-0.08	0.02-0.20
PARATHION					
Average	.002	0.005	T	T	0
Positive Composites					
Number	1	4	1	1	0
Range	0.01	T-0.012	T	0.002	—
VI. LEGUME VEGETABLES ¹ RESIDUES, PPM					
DDT					
Average	0	0.006	0	T	0
Positive Composites					
Number	0	2	0	3	0
Range	—	0.003-0.031	—	T-0.002	—
DDE					
Average	0	0.001	0	0.001	0
Positive Composites					
Number	0	2	0	3	0
Range	—	T-0.004	—	T-0.005	—
CADMIUM					
Average	0.007	0.007	0.007	0.003	0.003
Positive Composites					
Number	3	2	3	1	2
Range	0.01-0.02	0.02	0.01-0.02	0.01	0.01
VII. ROOT VEGETABLES ¹ RESIDUES, PPM					
DDT					
Average	0	0.001	0	T	0
Positive Composites					
Number	0	2	0	2	0
Range	—	T-0.008	—	T-0.001	—
DDE					
Average	0	0.001	0.001	T	0.001
Positive Composites					
Number	0	1	1	3	1
Range	—	0.005	0.006	T-0.002	0.005
CADMIUM					
Average	0.02	0.02	0.01	0.03	0.02
Positive Composites					
Number	6	5	2	5	6
Range	0.01-0.02	0.01-0.04	0.02-0.05	0.01-0.06	0.01-0.03

(Continued next page)

TABLE 2A (cont'd). *Levels of pesticide residues commonly found—by food class and region, June 1970-April 1971*

CHEMICAL	BALTIMORE	BOSTON	KANSAS CITY	LOS ANGELES	MINNEAPOLIS
VIII. GARDEN FRUITS ¹ RESIDUES, PPM					
DDT					
Average	0.006	0.005	0.007	0.008	0.004
Positive Composites					
Number	2	2	3	3	1
Range	0.014-0.023	0.006-0.025	T-0.037	0.003-0.037	0.026
TDE					
Average	0.013	0.015	0.006	0.005	0.007
Positive Composites					
Number	4	2	6	3	4
Range	0.017-0.024	T-0.087	T-0.013	0.010-0.027	T-0.018
DIELDRIN					
Average	0.002	0.003	0.003	0.001	0.002
Positive Composites					
Number	2	5	4	4	3
Range	T-0.010	T-0.006	T-0.006	T-0.003	0.001-0.006
CADMIUM					
Average	0.01	0.01	0.01	0.02	0.02
Positive Composites					
Number	5	4	6	6	5
Range	0.01	0.01-0.02	0.01-0.04	0.01-0.02	0.01-0.05
BHC					
Average	0.002	T	T	T	0.001
Positive Composites					
Number	2	1	2	1	1
Range	0.007-0.009	0.002	T-0.003	T	0.007
IX. FRUITS ¹ RESIDUES, PPM					
ETHION					
Average	0.005	0.004	0.028	0.004	0.017
Positive Composites					
Number	2	2	5	3	3
Range	0.009-0.02	0.007-0.018	0.008-0.073	T-0.015	0.099
KELTHANE					
Average	0.001	0.007	0.014	0.015	0.003
Positive Composites					
Number	1	2	3	4	1
Range	0.007	0.005-0.035	0.015-0.039	T-0.066	0.019
DDT					
Average	0	T	0	T	T
Positive Composites					
Number	0	1	0	3	2
Range	—	T	—	T-0.003	T-0.002
X. OILS, FATS, AND SHORTENING ¹ RESIDUES, PPM					
DIELDRIN					
Average	0.001	0.001	T	0.001	T
Positive Composites					
Number	5	6	4	2	2
Range	T-0.003	T-0.006	T	T-0.005	T
DDE					
Average	0.002	0.002	0.001	0.001	0.002
Positive Composites					
Number	4	5	4	4	4
Range	T-0.005	T-0.006	T-0.003	T-0.008	T-0.008
DDT					
Average	0.001	0.003	0.001	0.001	T
Positive Composites					
Number	4	5	3	4	2
Range	T-0.005	T-0.012	T-0.006	T-0.007	T
MALATHION					
Average	0.024	0.008	0.006	0.007	0.004
Positive Composites					
Number	3	3	2	2	2
Range	0.022-0.097	0.010-0.021	0.009-0.030	0.014-0.029	0.009-0.017
CADMIUM					
Average	0.01	0.01	0.02	0.02	0.03
Positive Composites					
Number	5	4	6	6	6
Range	0.01-0.02	0.01-0.03	0.01-0.03	0.01-0.03	0.02-0.04

(Continued next page)

TABLE 2A (cont'd). Levels of pesticide residues commonly found—by food class and region, June 1970-April 1971

CHEMICAL	BALTIMORE	BOSTON	KANSAS CITY	LOS ANGELES	MINNEAPOLIS
XI. SUGARS AND ADJUNCTS ¹ RESIDUES, PPM					
DDT					
Average	0	0.001	T	0.003	T
Positive Composites					
Number	0	4	1	1	3
Range	—	T-0.004	T	0.017	T-0.003
DDE					
Average	0	T	0	T	T
Positive Composites					
Number	0	3	0	3	2
Range	—	T	—	T-0.002	T-0.001
LINDANE					
Average	0	T	T	0.001	0.001
Positive Composites					
Number	0	2	1	2	3
Range	—	T	0.002	0.002	T-0.004
CADMIUM					
Average	0.01	0.01	0.01	0.01	0.01
Positive Composites					
Number	2	3	3	3	3
Range	0.02	0.01-0.03	0.01-0.02	0.01-0.02	0.01
XII. BEVERAGES ¹ RESIDUES, PPM					
BROMIDES					
Average	0.92	—	0.25	0.33	0.33
Positive Composites					
Number	2	0	1	1	1
Range	2.5-3.0	—	1.5	2.0	2.0

NOTE: — denotes not applicable.

T = Trace: see definition under Analytical Methods.

¹ Six composite samples examined from each of five districts: Baltimore, Boston, Kansas City, Los Angeles, and Minneapolis. Residues listed are averages of the six composites from each site.

TABLE 2B. Pesticides found infrequently—by food class and region, June 1970-April 1971

PESTICIDE	DISTRICT	No. COMPOSITES	AMOUNT
I. DAIRY PRODUCTS ¹ RESIDUES, PPM			
HCB	Boston	1	T
	Kansas City	1	T
	Los Angeles	2	0.001, T
Lindane	Kansas City	2	T, T
TDE	Baltimore	1	T
	Boston	2	T, 0.001
	Kansas City	3	T, T, 0.001
	Los Angeles	2	T, 0.001
	Minneapolis	1	T
Cadmium	Baltimore	1	0.01
	Boston	1	0.06
	Los Angeles	1	0.01
	Minneapolis	1	0.02
HCB	Boston	1	T
	Kansas City	1	T
	Los Angeles	2	T, 0.001
Methoxychlor	Kansas City	2	T, 0.008
	Minneapolis	1	0.006
PCP	Kansas City	1	T
Bromides	Baltimore	2	5.0, 5.0
	Boston	1	1.5
	Kansas City	1	4.0
	Los Angeles	2	2.0, 5.5
	Minneapolis	1	3.0
II. MEAT, FISH, AND POULTRY ¹ RESIDUES, PPM			
Lindane	Boston	1	T
	Kansas City	3	T, T, 0.001
	Los Angeles	1	0.001
	Minneapolis	3	T, T, 0.001
BHC	Boston	3	T, T, T
	Kansas City	2	T, 0.001
	Los Angeles	2	T, T
HCB	Los Angeles	1	T
Bromides	Baltimore	2	7.5, 8.0
	Boston	2	3.5, 4.5
	Los Angeles	2	2.0, 6.5
	Minneapolis	1	5.5

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TABLE 2B (cont'd). Pesticides found infrequently—by food class and region, June 1970-April 1971

PESTICIDE	DISTRICT	NO. COMPOSITES	AMOUNT
III. GRAIN AND CEREAL ¹ RESIDUES, PPM			
Heptachlor Epoxide	Boston	2	T, T
Carbaryl	Boston	2	T, T
	Los Angeles	1	T
BHC	Kansas City	1	T
	Los Angeles	2	T, 0.007
TDE	Baltimore	1	T
	Boston	1	T
	Minneapolis	3	T, 0.001, 0.001
Ronnel	Kansas City	1	0.007
<i>o</i> -Phenylphenol	Los Angeles	1	T
Methoxychlor	Minneapolis	1	T
IV. POTATOES ¹ RESIDUES, PPM			
Botran	Baltimore	1	0.003
Endrin	Boston	1	T
	Los Angeles	1	0.007
CIPC	Los Angeles	1	0.14
TDE	Boston	1	T
Carbaryl	Boston	1	T
	Kansas City	1	T
Endosulfan	Boston	1	0.007
	Los Angeles	1	T
Bromides	Baltimore	2	16.0, 13.0
	Boston	2	1.0, 1.0
	Minneapolis	2	4.0, 2.0
Arsenic	Minneapolis	1	0.1
BHC	Boston	1	0.002
V. LEAFY VEGETABLES ¹ RESIDUES, PPM			
Dieldrin	Boston	3	T, T, 0.001
	Minneapolis	2	0.001, 0.005
Carbaryl	Boston	1	T
2,4-D	Baltimore	1	0.01
	Minneapolis	2	0.02, 0.13
Methyl Parathion	Baltimore	1	T
	Boston	1	T
	Los Angeles	1	0.011
Diazinon	Baltimore	1	T
	Boston	1	0.004
	Los Angeles	1	0.003
	Minneapolis	1	0.020
Bromides	Baltimore	2	4.0, 4.0
	Boston	2	0.5, 1.0
	Kansas City	2	51.0, 3.0
	Los Angeles	1	2.5
	Minneapolis	2	2.5, 1.5
HCB	Boston	1	T
TDE	Boston	2	T, 0.002
	Minneapolis	1	0.001
Dacthal	Boston	1	T
Malathion	Kansas City	1	T
VI. LEGUME VEGETABLES ¹ RESIDUES, PPM			
BHC	Boston	1	T
Dieldrin	Minneapolis	1	T
TDE	Baltimore	1	T
	Boston	2	T, T
	Los Angeles	3	T, 0.001, 0.003
	Minneapolis	1	0.001
Carbaryl	Los Angeles	1	T
Parathion	Kansas City	1	T
Bromides	Baltimore	2	2.0, 4.0
	Boston	2	1.5, 1.5
	Kansas City	1	5.5
	Minneapolis	1	2.0

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TABLE 2B (cont'd). Pesticides found infrequently—by food class and region, June 1970-April 1971

PESTICIDE	DISTRICT	No. COMPOSITES	AMOUNT
VII. ROOT VEGETABLES ¹			
RESIDUES, PPM			
Dieldrin	Boston	1	0.005
	Minneapolis	1	0.001
<i>o</i> -Phenylphenol	Baltimore	2	T, T
TDE	Baltimore	2	0.007, 0.011
Lindane	Boston	1	0.008
	Los Angeles	1	0.023
Toxaphene	Los Angeles	1	T
Carbaryl	Los Angeles	2	T, 0.006
Bromides	Baltimore	2	5.0, 3.5
	Boston	2	0.5, 6.0
	Kansas City	1	1.5
	Los Angeles	1	4.0
	Minneapolis	1	4.0
VIII. GARDEN FRUITS ¹			
RESIDUES, PPM			
Parathion	Baltimore	2	T, 0.004
	Minneapolis	1	0.005
Carbaryl	Boston	2	T, 0.5
	Los Angeles	1	T
Endosulfan	Boston	1	0.061
	Los Angeles	1	T
<i>o</i> -Phenylphenol	Baltimore	1	T
Lindane	Kansas City	1	0.002
	Los Angeles	1	T
	Minneapolis	1	0.003
Kelthane	Kansas City	1	0.019
DDE	Baltimore	1	0.007
	Kansas City	2	T, 0.003
	Los Angeles	2	0.001, 0.002
Bromides	Baltimore	2	4.5, 6.0
	Boston	1	3.5
	Kansas City	1	0.5
	Los Angeles	2	3.0, 3.5
	Minneapolis	1	5.0
IX. FRUITS ¹			
RESIDUES, PPM			
Carbaryl	Baltimore	1	0.15
	Boston	3	T, T, 0.005
	Los Angeles	3	T, T, T
	Minneapolis	1	0.006
Perthane	Boston	4	T, T, 0.022, 0.009
	Los Angeles	1	0.018
Botran	Minneapolis	1	0.006
<i>o</i> -Phenylphenol	Kansas City	1	0.1
	Los Angeles	3	T, T, 0.2
	Minneapolis	3	T, 0.1, 0.25
Phosalone	Boston	1	0.278
TDE	Boston	1	T
	Kansas City	1	0.004
	Los Angeles	1	T
	Minneapolis	1	0.009
Endosulfan	Boston	1	0.011
	Los Angeles	1	T
	Minneapolis	3	T, 0.001, 0.045
Lindane	Los Angeles	1	0.003
Diazinon	Kansas City	1	0.009
Arsenic	Baltimore	1	0.1
	Boston	1	0.1
Cadmium	Baltimore	1	0.01
	Boston	1	0.01
	Kansas City	1	0.03
	Los Angeles	1	0.01
Bromides	Baltimore	2	5.5, 6.0
	Boston	2	0.5, 1.5
	Los Angeles	1	1.5
	Minneapolis	1	6.5
DDE	Boston	2	T, T
	Kansas City	2	T, T
	Los Angeles	2	0.001, 0.002
	Minneapolis	3	0.001, 0.001, T
Dieldrin	Boston	1	0.002
	Los Angeles	1	T
Malathion	Kansas City	1	0.036
	Los Angeles	3	0.039, 0.026, 0.089
	Minneapolis	3	0.021, 0.003, 0.062

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TABLE 2B (cont'd). Pesticides found infrequently—by food class and region, June 1970-April 1971

PESTICIDE	DISTRICT	NO. COMPOSITES	AMOUNT
X. OILS, FATS, AND SHORTENING ¹ RESIDUES, PPM			
Diazinon TDE	Baltimore	1	T
	Baltimore	3	T, T, 0.013
	Boston	2	0.011, 0.009
	Kansas City	3	T, T, T
	Los Angeles	4	T, T, T, 0.007
	Minneapolis	2	T, T
Bromides	Baltimore	2	12.0, 12.0
	Boston	2	2.5, 5.5
	Minneapolis	1	12.0
XI. SUGARS AND ADJUNCTS ¹ RESIDUES, PPM			
TDE	Boston	3	T, T, 0.002
	Los Angeles	1	T
	Minneapolis	2	T, 0.001
Heptachlor Epoxide	Boston	1	T
	Minneapolis	1	T
BHC	Boston	2	0.002, 0.002
	Los Angeles	2	T, T
	Minneapolis	2	T, 0.001
Malathion	Los Angeles	1	0.016
Arsenic	Baltimore	1	0.3
Bromides	Baltimore	2	5.5, 6.0
	Boston	2	7.5, 9.5
	Kansas City	2	0.5, 3.5
	Los Angeles	1	23.0
	Minneapolis	1	12.0
PCP	Kansas City	1	0.011
Diazinon	Minneapolis	1	T
XII. BEVERAGES ¹ RESIDUES, PPM			
DDT	Boston	1	T
TDE	Boston	1	T
Lindane	Los Angeles	1	T
Cadmium	Baltimore	1	0.01
	Kansas City	1	0.01
	Los Angeles	1	0.01

NOTE: T = Trace; see definition under Analytical Methods

¹ Six composite samples examined from each of five districts: Baltimore, Boston, Kansas City, Los Angeles, and Minneapolis.

TABLE 3. Recovery experiments on pesticides found in total diet samples, June 1970-April 1971

PESTICIDE	TYPE OF FOOD COMPOSITE	SPIKE LEVEL, PPM	BLANK LEVEL, ¹ PPM RANGE	TOTAL FOUND, ¹ PPM RANGE	NUMBER OF RECOVERY EXPERIMENTS
HEPTACHLOR EPOXIDE	Fatty	0.005	0-0.006 (0.003)	0.008-0.010 (0.009)	2
	Fatty	0.100	0	0.097	
	Nonfatty	0.005	0	0-0.008 (0.005)	9
<i>p,p'</i> -DDT	Fatty	0.050	0-0.037 (0.016)	0.051-0.072 (0.059)	3
	Nonfatty	0.010	0.002-0.003 (0.003)	0.010-0.012 (0.011)	3
RONNEL	Fatty	0.01	0	0.008-0.010 (0.009)	2
	Nonfatty	0.01	0	0.008-0.011 (0.010)	3
	Nonfatty	0.075	0	0.061-0.078 (0.068)	6
TDE	Fatty	0.01	0-0.007 (0.003)	0.004-0.016 (0.010)	2
	Nonfatty	0.01	0	0.011-0.013 (0.012)	3
DIELDRIN	Fatty	0.010	0.002-0.010 (0.006)	0.010-0.020 (0.015)	2
	Nonfatty	0.050	0	0.049	1
	Nonfatty	0.005	0-0.008 (0.002)	0.003-0.012 (0.006)	5
ENDRIN	Fatty	0.300	0	0.237	1
	Fatty	0.010	0	0.008-0.010	3
	Nonfatty	0.010	0	0.006-0.014 (0.011)	7

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TABLE 3 (cont'd). Recovery experiments on pesticides found in total diet samples, June 1970-April 1971

PESTICIDE	TYPE OF FOOD COMPOSITE	SPIKE LEVEL, PPM	BLANK LEVEL, ¹ PPM RANGE	TOTAL FOUND, ¹ PPM RANGE	NUMBER OF RECOVERY EXPERIMENTS
BHC	Fatty	0.005	0-0.002 (0.001)	0.003-0.007 (0.005)	6
	Nonfatty	0.003	0-0.001 (0)	0.003-0.004 (0.003)	14
ALDRIN	Fatty	0.003	0	0.002-0.003 (0.003)	2
	Nonfatty	0.050	0	0.941-0.043 (0.042)	2
	Nonfatty	0.005	0	0.004-0.007 (0.006)	4
DDE	Nonfatty	0.005	0	0.003-0.008 (0.004)	6
	Fatty	0.005	0.002-0.006 (0.004)	0.008-0.010 (0.009)	3
	Nonfatty	0.10	0	0.111-0.117 (0.114)	2
CHI ORDANE	Fatty	0.20	0.014	0.193	1
	Fatty	0.1	0	0.088	1
	Nonfatty	0.1	0	0.079-0.089 (0.084)	2
	Fatty	0.2	0	0.016-0.158 (0.087)	2
	Nonfatty	0.2	0	0.174-0.207 (0.186)	4
	METHOXYCHLOR	Fatty	0.1	0	0.091-0.099 (0.095)
	Nonfatty	0.1	0	0.072-0.103 (0.086)	4
HEPTACHLOR	Fatty	0.003	0	0.001-0.002 (0.002)	3
	Nonfatty	0.003	0	0.001-0.002 (0.002)	6
PCB'S	Fatty	0.075	0-0.017 (0.008)	0.052-0.059 (0.056)	2
	Nonfatty	0.075	0	0.048-0.072 (0.056)	4
TOXAPHENE	Fatty	0.200	0	0.189-0.203 (0.196)	2
	Nonfatty	0.200	0	0.174-0.212 (0.191)	3
MERCURY	Fatty	0.10	0	0.094-0.130 (0.103)	4
	Fatty	0.02	0-0.024 (0.004)	0.008-0.042 (0.020)	16
	Nonfatty	0.1	0	0.095-0.100 (0.098)	5
	Nonfatty	0.02	0-0.008 (0.001)	0.013-0.034 (0.021)	32
CADMIUM	Fatty	0.1	0-0.030 (0.013)	0.086-0.250 (0.123)	8
	Fatty	0.04	0-0.020 (0.004)	0.024-0.069 (0.036)	20
	Nonfatty	0.10	0-0.051 (0.017)	0.092-0.151 (0.116)	6
	Nonfatty	0.04	0-0.053 (0.007)	0.018-0.192 (0.047)	42
ARSENIC	Fatty	0.5	0-0.125 (0.017)	0.160-0.576 (0.439)	10
	Fatty	0.1	0-0.100 (0.005)	0.030-0.290 (0.116)	21
	Nonfatty	0.5	0-0.03 (0.003)	0.110-0.720 (0.412)	22
	Nonfatty	0.15	0	0.030-0.246 (0.127)	37
	Nonfatty	1.00	0-0.060 (0.005)	0.20-1.05 (0.701)	11
CARBARYL	Nonfatty	1.0	0	0.10-1.79 (0.98)	8
	Nonfatty	0.5	0	0.20-0.50 (0.48)	14
	Nonfatty	0.20	0	0.05-0.30 (0.18)	38
o-PIHENYLPHENOL	Nonfatty	0.5	0	0.25-0.50 (0.33)	10
	Nonfatty	0.2	0	0-0.20 (0.15)	16

(Continued next page)

TABLE 3 (cont'd). *Recovery experiments on pesticides found in total diet samples, June 1970-April 1971*

PESTICIDE	TYPE OF FOOD COMPOSITE	SPIKE LEVEL, PPM	BLANK LEVEL, ¹ PPM RANGE	TOTAL FOUND, ¹ PPM RANGE	NUMBER OF RECOVERY EXPERIMENTS
PARATHION	Fatty	0.02	0	0.010-0.017 (0.014)	4
	Nonfatty	0.02	0	0.017-0.026 (0.021)	8
	Nonfatty	0.10	0-0.020 (0.003)	0.060-0.120 (0.095)	6
MALATHION	Fatty	0.02	0-0.007 (0.002)	0.016-0.030 (0.022)	4
	Nonfatty	0.02	0-0.016 (0.002)	0.013-0.037 (0.021)	8
	Nonfatty	0.10	0-0.038 (0.007)	0.083-0.128 (0.101)	5
DIAZINON	Nonfatty	0.01	0	0.008-0.012 (0.010)	6
	Fatty	0.05	0	0.040-0.064 (0.048)	4
2,4-D	Fatty	0.05	0	0.006-0.040 (0.021)	7
	Nonfatty	0.03	0	0.005-0.037 (0.021)	11
2,4-DB	Fatty	0.03	0	0.004-0.036 (0.021)	8
	Nonfatty	0.03	0	0.009-0.037 (0.027)	16
2,4,5-TP	Fatty	0.20	0	0.032-0.074 (0.059)	3
	Fatty	0.02	0	0-0.016 (0.009)	6
	Nonfatty	0.03	0	0.009-0.027 (0.022)	12

¹ Numbers in parentheses represent average residue levels.

GENERAL

Residue Accumulation in Selected Vertebrates Following a Single Aerial Application of Mirex Bait, Louisiana—1971-72¹

H. L. Collins,² G. P. Markin,³ and John Davis¹

ABSTRACT

A survey to monitor accumulation of mirex residues in 61 species of vertebrates and certain components of the human food chain was conducted in Louisiana from May 1971 to May 1972 following a single application of mirex bait. All gas-liquid chromatographic analyses were performed on composited, whole-body homogenates. Levels of residues detected ranged from less than 0.001 to 8.483 ppm.

Highest concentrations of mirex were detected in loggerhead shrikes and mockingbirds 3 months after treatment. Although mirex was detected in 89 percent of the total samples analyzed, residues noted were usually less than 1 ppm.

Introduction

Because of increased interest in environmental effects of chlorinated pesticides, as well as increasingly refined and exacting analytical techniques, numerous papers and unpublished reports on the accumulation of mirex residues in nontarget organisms have appeared in recent years (1-5). Most of these studies have dealt with residues following multiple applications of mirex bait employed in attempts to eradicate or suppress isolated imported fire ant infestations. Other papers have reported on residues following massive doses of mirex administered to test animals in the laboratory (6-9).

The majority of treated acreage now receives a single mirex application (1¼ lb bait or 1.7 g actual toxicant/acre) in State and Federal control programs aimed at providing short-term relief for landowners (10). A scarcity of information on residue levels to be expected from this type of program prompted the present study. The primary objective is to investigate and compare

accumulation of mirex residues in selected vertebrates and certain components of the human food chain for 1 year following a single application of mirex bait. Vertebrates chosen represent certain families or orders whose members occupy the same general habitat, have similar food habits, and are available at all times of the year. Preliminary results of this study are reported in this paper.

DESCRIPTION OF STUDY AREA

The 2-square-mile study area was located in Washington Parish in the east central corner of Louisiana near the town of Bogalusa. Agricultural practices in the area are generally limited to dairy and timber farming. Permanent pastureland and hardwood bottom land predominate although hills are usually covered by stands of pine interspersed with hardwoods and underbrush. The topography is diversified enough to provide an abundance of food and cover for numerous species of vertebrates. This diversity and the fact that there had been no previous mirex treatments in the area provided the basis for its selection as a study site.

The area is drained by several small streams whose flow is often interrupted during dry periods. Pushepetapa Creek, a tributary of the Pearl River, flows through the center of the study area year-around. Researchers monitored two species of fish which inhabit this body of water. Numerous farm ponds averaging less than 1 acre in size are scattered over the area and usually contain sizable populations of warm-water fish such as bluegills, green sunfish, and mosquito fish. Eight of these ponds were chosen as study sites; all fish samples except for those from Pushepetapa Creek were taken in these ponds.

Methods and Materials

BAIT APPLICATION

The study area was treated with mirex bait by a Piper Pawnee aircraft on May 4 and 5, 1971. The plane was

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equipped with a Swathmaster granular spreader calibrated to deliver the present recommended dosage of 1.25 lb. standard 4X mirex bait per acre (1.7 g actual toxicant/acre). Ground personnel guided the aircraft with helium-filled Kytoons.

SAMPLING PROCEDURES

Terrestrial animals were collected by shooting or trapping. Havahart live traps baited with canned sardines and peanut butter were employed to capture opossums and rodents; armadillos, birds, and rabbits were shot. A .22-caliber pistol loaded with No. 12 dust shot was used to collect frogs, snakes, and lizards. Fish were collected by seining or trapping with a common fish trap constructed of 1-inch mesh poultry netting and baited with cottonseed meal. These collections, while seemingly incomplete in some instances, represent 1,120 person-hours of work. A complete phylogenetic listing

of the vertebrates sampled is presented in Table 1. Scientific names and phylogenetic arrangements generally follow those given by Blair et al. (11).

Only the central portion of the treated area was utilized for sampling. A buffer zone one-half to one-fourth mile wide was maintained to reduce migration of study animals in and out of the treated area. Some migration of the more mobile species did doubtless occur; however the home range of most animals sampled was probably restricted to the test area.

Sampling was carried out in seven excursions at 1- to 3-month intervals from April 1971 until May 1972. Unfortunately, replication of samples and thus statistical interpretation of the data were not possible because of limitations of gas-liquid chromatography (GLC) time and personnel required to replicate sampling. All individuals of a given species were lumped together at

TABLE 1. Phylogenetic listing of selected vertebrates sampled for mirex residues

MAMMALIA	Icteridae
ROENTIA	<i>Sturnella magna</i> (Linnaeus)—Eastern meadowlark
Cricetidae	<i>Agelaius phoeniceus</i> (Linnaeus)—Red-winged blackbird
<i>Reithrodontomys humulus</i> (Audubon & Bachman)—Eastern harvest mouse	<i>Quiscalus quiscula</i> (Linnaeus)—Common grackle
LAGOMORPHA	<i>Molothrus ater</i> (Boddaert)—Brown-headed cowbird
Leporidae	Thraupidae
<i>Sylvilagus floridanus</i> (Allen)—Eastern cottontail	<i>Pyrhithoxia cardinalis</i> (Linnaeus)—Cardinal
MARSUPIALIA	REPTILIA
Didelphidae	SQUAMATA
<i>Didelphis marsupialis</i> (Linnaeus)—Common opossum	Colubridae
XENARTHRA	<i>Coluber constrictor constrictor</i> (Linnaeus)—Southern black racer
Dasypodidae	<i>Natrix rhombifera rhombifera</i> (Hallowell)—Diamond-backed water snake
<i>Dasypus novemcinctus</i> (Linnaeus)—Nine-banded armadillo	<i>Natrix erythrogaster flavigaster</i> (Conant)—Yellow-bellied water snake
AVES	Iguanidae
CICONIIFORMES	<i>Anolis carolinensis</i> (Voigt)—Green anole
Ardeidae	<i>Sceloporus undulatus</i> (Latreille)—Eastern fence lizard
<i>Egretta thula</i> (Molina)—Snowy egret	Scincidae
<i>Casmerodius albus</i> (Linnaeus)—Greater egret	<i>Lygosoma laterale</i> (Say)—Ground skink
<i>Hydranassa tricolor</i> (P. L. S. Muller)—Louisiana heron	<i>Eumeces fasciatus</i> (Linnaeus)—Five-lined skink
<i>Butorides virescens</i> (Linnaeus)—Green heron	CHELONIA
<i>Ardeola ibis</i> (Linnaeus)—Cattle egret	Kinosterninae
<i>Florida caerulea</i> (Linnaeus)—Little blue heron	<i>Kinosternon subrubrum</i> (Lacépède)—Mud turtle
FALCONIFORMES	Emydinae
Accipitridae	<i>Terrapene carolina</i> (Linnaeus)—Gulf Coast box turtle
<i>Accipiter cooperii</i> (Bonaparte)—Cooper's hawk	Testudinidae
GALLIFORMES	<i>Gopherus polyphemus</i> (Daudin)—Gopher tortoise
Phasianidae	AMPHIBIA
<i>Colinus virginianus</i> (Linnaeus)—Bobwhite quail	SALIENTA
<i>Gallus gallus</i> (Linnaeus)—Domestic chicken	Bufonidae
CHARADRIIFORMES	<i>Bufo terrestris</i> (Bonaparte)—Southern toad
Charadriidae	Microhylidae
<i>Charadrius vociferus</i> (Linnaeus)—Killdeer	<i>Gastrophryne carolinensis</i> (Holbrook)—Narrow-mouthed toad
CUCULIFORMES	Ranidae
Cuculidae	<i>Rana catesbeiana</i> (Shaw)—Bullfrog
<i>Coccyzus americanus</i> (Linnaeus)—Yellow-billed cuckoo	<i>Rana pipiens</i> (Schreber)—Leopard frog
PICIFORMES	CAUDATA
Picidae	Plethodontidae
<i>Melanerpes carolinus</i> (Linnaeus)—Red-bellied woodpecker	<i>Plethodon glutinosus</i> (Green)—Slimy salamander
<i>Melanerpes erythrocephalus</i> (Linnaeus)—Red-headed woodpecker	OSTEICHTHYES
PASSERIFORMES	CYPRINIFORMES
Tyrannidae	Cyprinidae
<i>Tyrannus tyrannus</i> (Linnaeus)—Eastern kingbird	<i>Notemigonus crysoleucas</i> (Mitchill)—Golden shiner
Corvidae	Ictaluridae
<i>Cyanocitta cristata</i> (Linnaeus)—Blue jay	<i>Ictalurus nebulosus</i> (LeSueur)—Brown bullhead
Mimidae	Poeciliidae
<i>Mimus polyglottus</i> (Linnaeus)—Mockingbird	<i>Gambusia affinis</i> (Baird & Girard)—Mosquitofish
<i>Toxostoma rufum</i> (Linnaeus)—Brown thrasher	Centrarchidae
Turdidae	<i>Micropterus salmoides</i> (Lacépède)— largemouth bass
<i>Turdus migratorius</i> (Linnaeus)—American robin	<i>Chaenobryttus coronarius</i> (Bartram)—Warmouth
Laniidae	<i>Lepomis cyanellus</i> (Rafinesque)—Green sunfish
<i>Lanius ludovicianus</i> (Linnaeus)—Loggerhead shrike	<i>Lepomis megalotis</i> (Rafinesque)—Longear sunfish
	<i>Lepomis macrochirus</i> (Rafinesque)—Bluegill

each collection date and the composite was analyzed. Thus each sample usually consisted of three or more individuals except for less accessible specimens such as certain birds, opossums, and armadillos (Table 2).

All samples were placed on ice immediately after capture and returned to the laboratory where they were kept frozen until GLC analysis could be performed.

SURVEY OF ITEMS IN HUMAN FOOD CHAIN

Several recent studies have dealt with mirex residues in the human food chain. Ford et al. (12) reported on mirex residues in beef fat samples collected from cattle raised on pastures which had been treated two or more times. Others have reported on mirex residues in seafood and catfish samples (2,4,13).

Certain human food items such as milk, chicken eggs, various species of fish, and game birds and animals that are occasionally consumed by man were also monitored in the present study. Milk samples were taken from a dairy located within the treated area. Eggs and domestic chickens were obtained from a flock of poultry that ranged freely over their owner's farm.

METHOD OF ANALYSIS

Analytical techniques sensitive to 0.001 ppm as described by Markin et al. (10) were used to determine residues in all samples. Compositated samples of blended whole-body tissues were processed by grinding a 5-g portion

of the blended tissue homogenate with 5 g Na₂SO₄ in a mortar and pestle, added to 200 ml of 3:1 nanograde hexane and isopropanol, mixed for 1 hour on a concentric rotor, and placed in a separatory funnel. The solution was washed three times with 200 ml distilled water to remove the isopropanol. After separation, the hexane was cleaned in 11-by-500-mm chromatographic columns packed with 10 g florisil with a 2.5-cm Na₂SO₄ layer above and below the florisil. The hexane was concentrated to 15 ml in a three-ball Snyder column on an explosion-proof hotplate and stored in glass-stoppered conical test tubes. Further concentration was performed when necessary by heating the extract in a water bath with an airstream filtered through a Drierite filter. Portions of the final extract measuring 1 to 7.5 µl were injected into a twin-column Microtek gas chromatograph. Instrument parameters were:

Column: (A) Glass, 1.24 m by 17 mm, packed with 3 percent DC-200 on Supelcoport 100-120 mesh.
(B) Glass, 2.48 m by 17 mm, packed with a mixture of equal portions of separately coated 1.5 percent OV-17, and 1.95 percent QF-1.
Detector: Electron capture using 130 MC tritium as the ionizing source.
Temperatures: Injector 225°C.
Columns 190°C.
Detector 210°C.
Carrier Gases: Purified nitrogen at 75 ml/min.

Recovery averaged 97 percent when fortified samples were processed and analyzed by this procedure. Results presented have not been corrected for percent recovery.

TABLE 2. Mirex residues (ppm) in selected vertebrates from pretreatment to 1 year after single mirex application

BIOTIC GROUP AND SPECIES	PRETREATMENT		2 WK		1 MO		3 MO		6 MO		9 MO		12 MO	
	NO. ANALY.	RESIDUE FOUND	NO. ANALY.	RESIDUE FOUND	NO. ANALY.	RESIDUE FOUND	NO. ANALY.	RESIDUE FOUND	NO. ANALY.	RESIDUE FOUND	NO. ANALY.	RESIDUE FOUND	NO. ANALY.	RESIDUE FOUND
MAMMALS														
Eastern harvest mouse	2	0.013	3	0.310	1	0.450	2	0.049	2	0.014	4	0.003	1	0.010
Eastern cottontail	0	—	1	ND	1	ND	0	—	1	ND	1	0.254	0	—
Opossum	1	0.120	2	0.044	0	—	1	0.099	1	0.004	0	—	0	—
Armadillo	0	—	1	0.076	0	—	0	—	0	—	0	—	1	0.054
BIRDS														
Annual Residents														
Bobwhite quail	1	0.113	1	0.012	1	0.475	2	1.502	0	—	1	0.064	2	0.036
Cardinal	1	0.113	1	0.685	1	0.105	2	0.222	1	0.064	3	0.043	2	0.051
Mockingbird	1	0.030	1	1.579	2	3.627	1	4.549	3	0.807	2	1.936	1	0.282
Loggerhead shrike	1	0.346	1	0.706	0	—	1	8.483	2	0.754	2	3.560	1	3.666
Blue jay	1	0.007	2	0.027	2	0.035	2	0.113	2	0.181	2	0.071	1	0.198
Meadowlark	2	0.010	1	0.312	1	0.870	3	2.455	1	0.201	2	1.241	1	0.299
Killdeer	1	0.100	1	0.096	1	0.132	1	0.015	2	0.473	1	0.448	1	0.346
Brown thrasher	0	—	0	—	1	0.669	0	—	0	—	1	ND	1	0.624
Purple grackle	1	0.018	2	0.734	2	2.427	0	—	0	—	1	1.140	1	0.073
Eastern cowbird	1	0.015	0	—	1	0.713	0	—	3	0.088	3	0.028	1	0.012
Redwinged blackbird	0	—	0	—	1	0.072	1	0.280	0	—	1	0.084	2	0.208
Red-headed woodpecker	1	0.006	2	1.826	0	—	1	0.088	0	—	0	—	1	0.061
Red-bellied woodpecker	0	—	1	0.015	0	—	0	—	2	0.070	2	0.035	0	—
Summer Residents														
Cattle egret	2	0.514	1	0.085	1	0.090	3	0.163	0	—	0	—	1	0.221
Eastern kingbird	1	0.018	1	0.121	0	—	0	—	0	—	0	—	2	0.065
Yellow-billed cuckoo	0	—	1	0.042	0	—	1	0.023	0	—	0	—	0	—
Green heron	0	—	1	0.001	1	0.409	1	0.260	0	—	0	—	1	0.082
Winter Residents														
American robin	0	—	0	—	0	—	0	—	1	0.021	2	0.054	0	—
Transients														
Little blue heron	0	—	0	—	1	0.101	0	—	0	—	0	—	0	—
Cooper's hawk	0	—	0	—	1	0.087	0	—	0	—	0	—	0	—
Snowy egret	0	—	0	—	0	—	1	0.054	0	—	0	—	0	—
Louisiana heron	0	—	0	—	0	—	1	0.005	0	—	0	—	0	—
Greater egret	0	—	0	—	0	—	1	0.096	0	—	0	—	0	—

(Continued next page)

TABLE 2 (cont'd). *Mirex residues (ppm) in selected vertebrates from pretreatment to 1 year after single mirex application*

	PRETREATMENT		2 Wk		1 Mo		3 Mo		6 Mo		9 Mo		12 Mo	
	NO. OF ANALY.	RESIDUE FOUND												
REPTILES														
Aquatic														
Diamondback water snake	2	0.005	1	ND	1	0.029	0	—	0	—	3	0.037	1	0.054
Yellow-bellied water snake	0	—	1	0.002	0	—	0	—	1	0.078	0	—	0	—
Mud turtle	0	—	1	0.015	0	—	1	0.013	0	—	2	0.273	0	—
Terrestrial														
Gofer tortoise	1	0.001	0	—	1	ND	1	0.002	0	—	0	—	1	ND
Gulf coast box turtle	2	ND	2	ND	1	0.009	0	—	0	—	0	—	0	—
Southern black racer	1	ND	1	0.002	0	—	2	0.053	0	—	0	—	2	0.111
Southern fence lizard	0	—	1	0.003	2	0.065	5	0.191	0	—	3	0.040	2	0.025
Ground skink	2	ND	0	—	0	—	4	0.032	2	0.091	4	0.037	3	0.042
Five-lined skink	0	—	0	—	1	0.658	2	0.076	0	—	2	0.126	2	0.216
Green anole	2	ND	1	0.011	1	0.183	0	—	3	0.072	4	0.019	3	0.017
AMPHIBIANS														
Slimy salamander	1	ND	1	ND	2	0.097	4	0.828	0	—	2	0.254	2	0.020
Southern toad	2	ND	2	0.001	26	0.144	3	0.030	0	—	3	0.026	8	0.008
Leopard frog	0	—	4	0.002	1	0.015	0	—	0	—	0	—	0	—
Bullfrog	0	—	1	ND	0	—	0	—	0	—	1	0.001	0	—
Eastern narrow-mouthed toad	0	—	2	0.044	0	—	0	—	0	—	0	—	1	0.074
Tadpoles (undetermined species)	3	0.016	4	0.005	0	—	43	0.024	0	—	0	—	0	—
FISH														
Lentic Habitat														
Largemouth bass	1	ND	1	0.018	1	0.032	1	0.624	0	—	0	—	0	—
Warmouth	4	ND	0	—	0	—	1	0.009	9	0.005	2	0.005	8	0.012
Bluegill	23	0.002	15	0.012	23	0.019	79	0.025	29	0.013	36	0.009	10	0.026
Green sunfish	22	0.003	5	0.003	30	0.014	71	0.014	47	0.007	36	0.002	43	0.005
Longear sunfish	1	ND	0	—	4	0.016	4	0.039	1	0.016	0	—	0	—
Golden shiner	22	0.001	19	0.005	21	0.024	87	0.027	45	0.007	38	0.008	38	0.009
Mosquitofish	51	0.003	21	0.109	109	0.131	136	0.010	144	0.015	347	0.008	51	0.006
Brown bullhead	5	0.001	6	0.004	20	0.113	4	0.086	7	0.007	4	0.003	10	0.010
Lotic Habitat														
Bluegill	5	0.004	0	—	2	ND	2	0.057	5	0.006	0	—	5	0.011
Longear sunfish	5	0.002	4	0.003	0	—	3	0.007	2	0.007	4	0.021	2	0.006

NOTE: ND = no detectable residues; — = not sampled.

Results and Discussion

MIREX IN SELECTED VERTEBRATES

Mirex residues in selected vertebrates are shown in Table 2. With few exceptions these levels were quite low (0.001-0.005 ppm) although certain birds did accumulate residues in the range of 1 to 8 ppm. Of particular interest are the relatively high levels detected in loggerhead shrikes and mockingbirds. Authors assume that the residues reflect the diet of these birds. It is interesting to note that green herons did not accumulate high levels of residues as expected by virtue of their position in the aquatic food web. The extensive home range of the herons could account for their relatively low residue levels because it is possible that they derived the majority of their food outside the treated area. In general, birds such as cardinals, Eastern cowbirds, and quail, whose diets consisted primarily of seeds, fruits, and other vegetable matter, had lower levels than did the more carnivorous species such as shrikes, mockingbirds, and meadowlarks.

Of the four mammal species sampled, Eastern harvest mice contained the largest amount of residues: 0.450 ppm 1 month after treatment.

Reptiles and amphibians generally accumulated lower residues (0.001-0.828 ppm) than did birds and mam-

mals (0.001-8.483 ppm). Surprisingly, carnivorous reptiles such as water snakes, lizards, and skinks did not appear to concentrate mirex as did birds with similar feeding habits. This may be related to the greater volume of food consumed by birds as opposed to reptiles. Birds usually consume more food per unit weight in any given time and may thus encounter and concentrate greater residues.

As expected, predatory species of fish such as largemouth bass contained more residues than did omnivorous species such as brown bullheads and sunfish. In general, residues detected in fish agreed fairly closely with those reported in an earlier study by Collins et al. (14)

An overview of various vertebrate trophic levels reveals that strict herbivorous species such as Eastern cottontails and gopher tortoises contained significantly less mirex than did either omnivorous or carnivorous species (Fig. 1). Regardless of trophic levels, however, residues in most animals peaked 1 to 3 months after treatment and decreased afterward.

ITEMS IN HUMAN FOOD CHAIN

Results of the survey of items in the human food chain are shown in Table 3. Mirex was detected in 77 per-

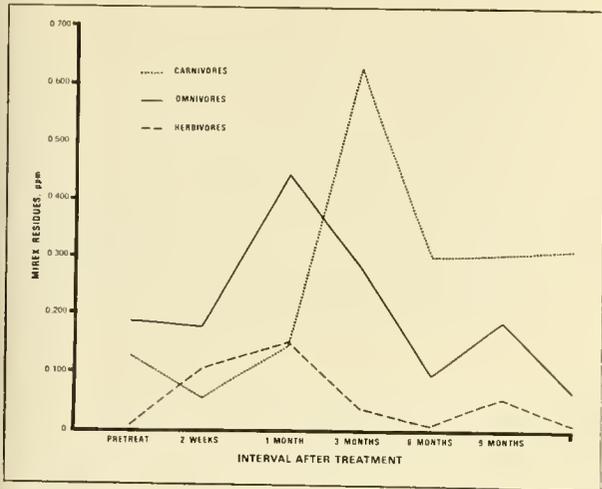


FIGURE 1. Residue fluctuations in various vertebrate trophic levels following a single application of mirex bait

cent of the samples analyzed. Detectable residues were still present in most samples 1 year after treatment. Highest concentrations found were in bobwhite quail (0.012-1.502 ppm) and largemouth bass (0.018-0.624 ppm). Mirex was not detected in beef fat prior to or 1 year after treatment. Low levels were found in milk (0.001-0.022 ppm), chicken eggs (0.001-0.493 ppm), and chickens (0.004-0.515 ppm). These results are in general agreement with those reported by Baetke et al (5). Their results indicated that mirex residues in milk ranged from 0.007 to 0.016 ppm; beef fat contained 0.012 to 0.042 ppm; chicken adipose tissue contained 0.087 ppm; and residues in quail ranged from 0.016 to 3.148 ppm.

This and other studies have demonstrated conclusively that low levels of mirex residues remain in the environment and are concentrated by some species (4,5,10,13). All residue levels reported here are well below the level reported by others as causing acute toxicity to test animals such as rats, mice, birds, and fish (7,9,15-17).

However, there is virtually no information available on the long-range effects of low, chronic dosages on nontarget organisms.

Future research in the area of mirex residues should not merely monitor residues; research has already shown that they exist in virtually all components of the ecosystem. Instead, future research should attempt to divulge whether these residues are harmful, and if so, to which organisms.

LITERATURE CITED

- (1) Butler, P. A. *Monitoring pesticide pollution*. 1969. *Bioscience* 19(10):889-891.
- (2) McKenzie, M. D. 1970. Fluctuations in abundance of the blue crab and factors affecting mortalities. S. C. Wildl. Resour. Div. Marine Resour. Div. Tech. Rep. No. 1. 45 pp.
- (3) Lowe, J. I., P. R. Parrish, A. J. Wilson, Jr., P. D. Wilson, and T. W. Duke. 1971. Effects of mirex on selected estuarine organisms. Trans. 36th North American Wildlife and Natural Resources Conference. Gulf Breeze Contribution No. 124. pp. 175-186.
- (4) Markin, G. P., J. C. Hawthorne, H. L. Collins, and J. H. Ford. 1974. Levels of mirex and some other organochlorine residues in seafood from Atlantic and Gulf Coastal States. *Pestic. Monit. J.* 7(3/4):139-143.
- (5) Baetke, K. P., J. D. Cain, and W. E. Poe. 1972. Mirex and DDT residues in wildlife and miscellaneous samples in Mississippi—1970. *Pestic. Monit. J.* 6(1): 14-22.
- (6) Ludke, J. L., M. T. Finlay, and C. Lusk. 1971. Toxicity of mirex to crayfish, *Procambarus blandingi*. *Bull. Environ. Contamin. Toxicol.* 6(1):89-96.
- (7) Van Valin, C. C., A. K. Andrews, and L. L. Eller. 1968. Some effects of mirex on two warm-water fishes. *Trans-American Fish. Soc.* 97(2):185-196.
- (8) Naber, E. C., and G. W. Ware. 1965. Effects of Kepone and mirex on reproductive performance in the laying hen. *Poul. Sci.* 44:875-880.
- (9) Gaines, T. B. 1969. Acute toxicity of pesticides. *Toxicol. Appl. Pharmacol.* 14(3):515-534.
- (10) Markin, G. P., J. H. Ford, J. C. Hawthorne, J. C. Spence, J. Davis, H. L. Collins, and C. D. Loftis. 1972. The insecticide mirex and techniques for its monitoring. *APHIS* 81-3. 19 pp.
- (11) Blair, W. F., A. P. Blair, P. Brodkorb, F. R. Cagle,

TABLE 3. Mirex residues (ppm) in human food chain from pretreatment to 1 year after single mirex application

FOOD ITEM	PRETREATMENT		2 Wk		1 Mo		3 Mo		6 Mo		9 Mo		12 Mo	
	SAMPLE SIZE	RESIDUE FOUND	SAMPLE SIZE	RESIDUE FOUND	SAMPLE SIZE	RESIDUE FOUND	SAMPLE SIZE	RESIDUE FOUND	SAMPLE SIZE	RESIDUE FOUND	SAMPLE SIZE	RESIDUE FOUND	SAMPLE SIZE	RESIDUE FOUND
Milk	1 qt	0.015	1 qt	ND	1 qt	0.022	1 qt	0.001	1 qt	ND	1 qt	ND	1 qt	ND
Chicken Eggs	12	ND	12	0.493	12	0.005	12	0.007	12	ND	12	0.011	12	0.001
Domestic Chickens	2	—	2	0.004	2	0.036	2	0.515	2	0.010	2	0.201	2	0.014
Beef Fat	1 lb	ND	0	—	0	—	0	—	0	—	0	—	1 lb	ND
Fish ¹														
Bluegills	28	0.003	15	0.012	25	0.019	79	0.041	34	0.009	36	0.009	15	0.018
Brown bullheads	5	0.001	6	0.004	20	0.113	4	0.086	7	0.007	4	0.003	10	0.010
Largemouth bass	1	ND	1	0.018	1	0.032	1	0.624	0	—	0	—	0	—
Game Animals and Birds														
Eastern cottontails	0	—	1	ND	1	ND	0	—	1	ND	1	0.254	0	—
Opossums	1	0.120	2	0.044	0	—	1	0.099	1	0.004	0	—	0	—
Bobwhite quail	1	0.113	1	0.012	1	0.475	1	1.502	0	—	1	0.064	2	0.036

NOTE: ND = no detectable residues; — = not sampled.
Average of all samples collected from entire study area at indicated sampling interval.

- and G. A. Moore. 1957. Vertebrates of the United States. McGraw-Hill Book Company, Inc., New York, N.Y.
- (12) Ford, J. H., J. C. Hawthorne, and G. P. Markin. 1971. Monitoring for mirex and other organochlorine pesticides in beef cattle in the Southeastern United States. *Pestic. Monit. J.* 7(2):87-94.
- (13) Hawthorne, J. C., J. H. Ford, C. W. Collier, and G. P. Markin. 1971. Residues of mirex and other chlorinated pesticides in commercially raised catfish. *Bull. Environ. Contam. Toxicol.* (In Press)
- (14) Collins, H. L., J. R. Davis, and G. P. Markin. 1973. Residues of mirex in channel catfish and other aquatic organisms. *Bull. Environ. Contam. Toxicol.* 10(2): 73-77.
- (15) Gaines, T. B., and R. D. Kimbrough. 1970. Oral toxicity of mirex in adult and suckling rats. *Arch. Environ. Health* 21:7-14.
- (16) Ware, G. W., and E. E. Good. 1966. Effects of insecticide on reproduction in the laboratory mouse. *Toxicol. Appl. Pharmacol.* 10:54-61.
- (17) Stickel, L. 1964. Wildlife Studies. Patuxent Wildlife Research Center. Pp. 77-116. In *Pesticide-Wildlife Studies, 1963. A review of fish and wildlife service investigations during the calendar year.* U.S. Dept. of Interior, Fish and Wildl. Serv. Circ. 199.

Residues of the Insecticide Mirex in Terrestrial and Aquatic Invertebrates Following a Single Aerial Application of Mirex Bait, Louisiana—1971-72¹

G. P. Markin,² H. L. Collins,³ and J. Davis⁴

ABSTRACT

Samples of 25 invertebrates were collected for 1 year following a broadcast application of mirex bait to 1,000 hectares of land in southeastern Louisiana for control of the imported fire ant. Immediately following the treatment, residues of 5.504 to 22.153 ppm were found in scavengers such as the imported fire ant which fed directly upon the bait. Predatory invertebrates accumulated residues more slowly; a maximum level of 10.010 ppm was found in spiders 10 weeks after the treatment. Herbivorous invertebrates usually did not accumulate significant amounts of mirex. Residue levels in all terrestrial and aquatic invertebrates decreased greatly during the following year; no detectable residues were found in 68 percent of the samples at the end of the study.

Introduction

In 1971 an extensive monitoring program for mirex was undertaken in southeastern Louisiana. The purpose of the study was to determine mirex residue levels in representative groups of animals and the physical environment, and the rate of accumulation or loss of residues over a 1-year period following a single treatment with bait for control of imported fire ants. A general description of the study and results of vertebrate monitoring have been presented by Collins et al. (1); results of the study of residues in the physical environment were published by Spence et al. (2). This paper presents data on mirex residues in invertebrate fauna.

Although some information exists on mirex residues in invertebrate populations, most of it is based on studies of animals collected from an area which received sev-

eral closely spaced treatments with bait applied to determine the feasibility of eradicating the ant from isolated areas (3,4). Samples were usually collected at one time and do not present any information on the rate of buildup or decline of residues in the overall population. Because mirex is annually applied to over 10 million acres (4) to control this ant, information pertaining to residues following such routine single-application control programs is more valuable in understanding the overall residue picture for this pesticide than are data primarily concerning experimental eradication programs. The present study was designed specifically to observe the residue picture following the normal practice of using a single application of bait to control this ant.

Sampling

The treated area was a 1,000-hectare (ha.) block of pasture and forest land in Washington Parish, La. A blanket treatment of 2.5 kg/ha. mirex 4X bait was applied to the total area May 4 and 5, 1971. The study area and method of bait application were reported by Collins et al. (1). Researchers chose 25 groups of invertebrates to represent the general invertebrate fauna of the area and collected them prior to treatment and at various intervals over the following year. Initially, it was hoped that individual species could be used as indicators, but this was impractical because the brief life cycle and short season of occurrence of most invertebrates made it impossible to obtain most species during the entire year. It was then decided to concentrate on particular families or orders of invertebrates, the members of which occupied the same general habitat, had similar food habits, and were available at all times of the year.

Aquatic samples were collected from two small farm ponds approximately one-tenth ha. in size, lying in open improved pasture, and from a 100-m section of a

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small permanent stream (flow rate: 10 to 1,000-plus liters/min) just above its junction with Pushepetapa Creek. The drainage system of all three bodies of water lay entirely within the treated area. From each location, bottom organisms were collected by taking 10 bottom samples in 10 to 25 cm of water. Each sample consisted of the bottom sediment from an area one-tenth m² and 5 cm deep. It was washed through a 20-mesh screen and the desired organisms were collected. Free-swimming organisms were collected with a hand-held sweep net.

Soil insects were collected at three study sites 1 to 3 ha. in size scattered throughout the treatment area. At each site 10 soil samples, each representing an area one-tenth m², were randomly selected; the vegetation was removed by clipping and the upper layer of duff was scraped off. Soil was excavated to a depth of 10 cm, placed on a plastic sheet, and sorted by hand to retrieve the desired animals. Surface-living arthropods were collected from the same three sites by 30 pitfall traps. Pitfall traps were plastic-lined paper cups 7.5 cm in diameter and 18 cm deep. The cup was buried with the lip level at the soil surface; each cup contained 5 cm 50 percent alcohol. Traps were left out for 24 hours and animals which had fallen into the trap were immediately strained from the alcohol upon collection. Immediate removal of the animals from the alcohol and use of a solution which was only 50 percent alcohol were necessary to prevent the loss of mirex residues to the alcohol (4).

Miscellaneous animals such as web spiders, grasshoppers, and leaf hoppers were collected at the same three study sites by sweeping with a sweep net 40 cm in diameter.

Samples were restricted to the six study sites: three aquatic sites and the three terrestrial sites. Nests of mud dauber wasps (*Sceliphron* sp.) were collected from several old barns in the study area. The six sampling sites were all located well within the treated area. A 1-km buffer area was set up to minimize the chance of animal migration from the untreated area into the treated block.

At the time of collection, all samples were placed in glass vials which had been prewashed in hexane and checked by gas-liquid chromatography (GLC) for contamination; aluminum foil was used to line lids. The vials were placed on ice until they were brought to the laboratory; samples were washed in tap water, sorted, identified, weighed, and counted. Samples were deep-frozen in glass vials until processed. Collections from the three sampling sites were combined into a single composite sample for each of the 25 indicator organisms at each collection interval. Samples usually contained between 20 and 100 individuals and were usually over 1 g in weight. However, it was sometimes

necessary to use smaller samples during the winter. The smallest sample used was one-tenth g but contained at least five individual animals.

Analytical Procedures

Analytical procedures were basically the same as those used by Collins et al. (1), who collected vertebrates from the same treatment area. Frozen samples were ground whole with a mortar and pestle with 5 g Na₂SO₄, added to 200 ml nanograde hexane and isopropyl alcohol (3:1), mixed for 1 hour in a concentric rotor, and placed in a separatory funnel. Samples were washed three times with 200 ml distilled water to remove the isopropyl alcohol. After separation, the hexane was cleaned in an 11-by-500-mm chromatographic column packed with 10 g florisil (or silica gel for fish) with a 2.5-cm Na₂SO₄ layer above and below the florisil. The hexane was concentrated in a three-ball Snyder column on an explosion-proof hotplate to 15 ml and was stored in glass-stoppered, conical-based test tubes. Further concentration was performed when necessary by heating the hexane in a water bath with an airstream filtered through a Drierite filter. Technicians injected 1- to 7.5- μ l portions of the final extract into a twin column Microtek 220 gas chromatograph. Instrument parameters were:

Column:	(A) Glass, 1.24 m by 17 mm, packed with 3 percent DC-200 on Supelcoport 100-120 mesh.
	(B) Glass, 2.48 m by 7 mm, packed with mixture of equal portions of separately coated 1.5 percent OV-17 and 1.95 percent QF-1 on 60-80 mesh Chromosorb.
Detector:	Electron capture using 130 MC Tritium as ionizing source.
Temperatures:	Injector 225°C. Columns 190°C. Detector 210°C.
Carrier Gases:	Purified nitrogen at 75 ml/min.

The level of sensitivity with 1 g or larger samples was 0.001 ppm. Sensitivity of 0.1 g samples was 0.01 ppm. Recovery using this procedure averaged 97 percent when fortified samples were run through the processing and analytical procedures. Results presented have not been corrected for percent recovery.

Polychlorinated biphenyls (PCB's) are the major contaminants which complicate analyses for mirex (4). Particular effort was made to watch for the characteristic series of peaks which identify these contaminants. However, because no evidence of PCB contamination was found, no more extensive cleanup was undertaken. For a more detailed discussion of the problems of PCB's, the types of equipment, reagents, and confirmation procedures used, see Markin et al. (4).

Results

Table I presents mirex residues found in 25 invertebrate groups before treatment and for 1 year afterward. Several pretreatment samples contained small residues of mirex, indicating that it had been used in or near the test

area before the study. However, the three aquatic and three terrestrial sites sampled were specifically known not to have a history of mirex treatment; this was one reason for their selection as sampling locations. It can be presumed then, that specimens containing residues must have migrated from adjacent fields or perhaps even from outside the treatment area. Because mirex is commonly used in Louisiana to control the fire ant, pretreatment residues were not unexpected. In general, it was felt that the small number of pretreatment samples which had mirex residues were too few to be significant in inter-

preting the overall results of this study.

Mirex residues were detected in all but one of the groups sampled, white fringed beetle larvae. Amounts found usually corresponded very closely to group feeding habits. General scavengers that would be attracted to oil, such as the imported fire ant, fed directly upon the bait and contained the highest mirex levels found immediately after the treatment. Predacious invertebrates received mirex indirectly through the food chain and therefore showed slow but progressive buildup for 20

TABLE 1. Residue levels of mirex in 25 invertebrate groups sampled for 1 year following a single bait application for control of the imported fire ant

SPECIMEN	PRE-TREATMENT	MIREX RESIDUES, PPM										
		24 HR	1 WK	2 WK	4 WK	10 WK	3 MO	6 MO	8 MO	10 MO	1 YR	
<i>Aquatic</i>												
Dragonfly Larvae												
Insecta: Odonata	Neg	0.003	0.005	0.005	0.011	0.013	Neg	Neg	Neg	Neg	Neg	Neg
Water Scorpion												
Insecta: Hemiptera: Nepidae	Neg	0.076	0.017	0.124	0.015	0.028	0.008	0.003	0.003	0.002	0.003	
Water Boatmen												
Insecta: Hemiptera: Corixidae	Neg	—	1.003	0.146	—	Neg	Neg	0.016	Neg	—	Neg	
Back Swimmers												
Insecta: Hemiptera: Notonectidae	Neg	5.504	—	0.141	0.011	—	—	—	—	Neg	0.022	
Giant Water Bugs												
Insecta: Hemiptera: Belostomatidae	0.001	0.038	Neg	0.013	0.038	0.004	0.004	0.009	—	—	Neg	
Predacious Diving Beetles												
Insecta: Coleoptera: Dytiscidae	0.018	Neg	0.033	—	0.073	—	—	—	—	0.009	Neg	
Water Scavenger Beetles												
Insecta: Coleoptera: Hydrophilidae	Neg	0.043	0.015	0.018	Neg	0.005	0.011	Neg	Neg	Neg	Neg	
Midge Larvae												
Insecta: Diptera: Chironomidae	Neg	0.003	0.007	0.003	0.188	Neg	Neg	Neg	Neg	Neg	Neg	
Crayfish												
Crustacea: Decapoda: Astacidae	Neg	0.737	—	0.687	0.115	0.153	0.004	Neg	0.003	0.002	0.004	
Leeches												
Hirudinea: Glossiphoniidae	Neg	—	0.152	0.003	0.004	0.006	0.011	0.007	—	—	Neg	
<i>Soil</i>												
Earthworms												
Oligochaeta: Opisthoptera: Lumbricidae	Neg	Neg	—	0.002	—	0.038	Neg	Neg	0.026	0.004	0.005	
Centipede												
Myriapoda: Chilopoda	Neg	Neg	—	0.248	—	0.225	0.336	—	0.038	0.192	0.044	
Millipedes												
Myriapoda: Diplopoda	Neg	Neg	—	Neg	—	0.006	Neg	—	0.076	Neg	Neg	
White Grubs (June beetle larvae)												
Insecta: Coleoptera: Scarabaeidae	Neg	Neg	—	0.005	—	Neg	0.004	Neg	0.032	Neg	Neg	
White Fringe Beetle Larvae												
Insecta: Coleoptera: Curculionoidea	Neg	Neg	—	Neg	—	—	—	—	Neg	Neg	Neg	
<i>Pitfall Traps</i>												
Crickets												
Insecta: Orthoptera: Gryllidae	Neg	1.630	—	0.072	0.040	0.030	0.003	0.009	—	Neg	Neg	
Darkling Beetles												
Insecta: Coleoptera: Tenebrionidae	Neg	Neg	—	0.079	0.109	0.242	0.071	0.031	—	0.163	0.008	
Scarab Beetles												
Insecta: Coleoptera: Scarabaeidae	Neg	0.018	—	0.008	0.830	0.010	0.020	Neg	—	Neg	Neg	
Imported Fire Ants												
Insecta: Hymenoptera: Formicidae	Neg	22.153	—	—	—	Neg	Neg	Neg	—	Neg	Neg	
Wolf Spiders												
Arachnida: Araneida: Lycosidae	Neg	—	—	Neg	0.159	0.012	0.019	0.014	—	Neg	Neg	
<i>Sweep Net Samples</i>												
Leafhoppers												
Insecta: Homoptera: Cicadellidae	Neg	Neg	—	Neg	0.030	Neg	—	0.018	—	—	Neg	
Grasshoppers												
Insecta: Orthoptera: Acrididae	Neg	—	—	Neg	0.023	—	Neg	0.008	—	Neg	Neg	
Wild Bees												
Insecta: Hymenoptera: Apidae	Neg	Neg	—	Neg	0.008	0.002	Neg	Neg	—	—	Neg	
Crab and Web Spiders												
Arachnida: Araneida	Neg	0.211	—	0.535	1.890	10.010	0.708	0.069	—	0.205	0.092	
<i>Other</i>												
Mud daubers												
Insecta: Hymenoptera: Sphecidae												
Adults	0.008	—	—	—	—	Neg	—	0.158	—	—	0.076	
Larvae	Neg	—	—	—	—	0.524	—	0.126	—	—	0.020	

NOTE: All samples were adults unless otherwise noted.
All analysis was performed on a wet, whole-body basis.
Neg = no mirex at level of detection; — = no sample collected.

to 90 days after treatment. Smallest residues were found in herbivorous animals. Most residues began to decline after 90 days and had decreased significantly in all groups by 1 year after the treatment. Detectable residues were found in only 8 of the 25 invertebrates sampled a year after treatment.

LITERATURE CITED

- (1) Collins, H. L., G. P. Markin, and J. Davis. 1974. Residue accumulation in selected vertebrates following a single application of mirex bait, Louisiana—1971-72. *Pestic. Monit. J.* 8(2):125-130.
- (2) Spence, J. H., and G. P. Markin. 1974. Mirex residues in the physical environment following a single bait application. 1971-72. *Pestic. Monit. J.* 8(2):135-139.
- (3) Baetcke, K. P., J. D. Cain, and W. E. Poe. 1972. Mirex and DDT residues in wildlife and miscellaneous samples in Mississippi, 1970. *Pestic. Monit. J.* 6(1):14-22.
- (4) Markin, G. P., J. H. Ford, J. C. Hawthorne, J. H. Spence, J. Davis, H. L. Collins, and C. D. Loftis. 1972. The insecticide mirex and techniques for its monitoring. USDA, APHIS 81-3, Nov. 1972, 19 pp.

Mirex Residues in the Physical Environment Following a Single Bait Application, 1971-72

James H. Spence¹ and George P. Markin²

ABSTRACT

*In 1971 and 1972, samples of soil, sediment, water, and Bahia grass were collected at various intervals in Louisiana and Mississippi after the areas had been aerially treated with mirex to control the red imported fire ant (*Solenopsis invicta* Buren). In Louisiana, samples were collected throughout the first year after spraying; in Mississippi, they were taken for the first 4 months. Samples had also been collected from the physical environment in both States before spraying began. Residues in the sediment at the bottom of ponds increased gradually after treatment, indicating that mirex was being carried in by runoff water. Residues reached maximum levels (0.7 and 1.1 ppb) about 1 month after treatment, and gradually declined thereafter. Soil residues in the Louisiana study built up to a peak of 2.5 ppb after 1 month and gradually declined over the remainder of the year. Bahia grass in Louisiana had residues in both roots and blades, indicating that some translocation occurred from the roots upward.*

In Mississippi, residue patterns of pond sediment were less predictable than in sediment of Louisiana ponds, but levels peaked at about the same interval: 1 month after treatment. Water in the pond showed the highest residue levels immediately after treatment, 0.020 and 0.530 ppb, and still had detectable levels of 0.001 to 0.005 ppb as long as 3 months after treatment. Bahia grass roots and blades were combined for analysis; the highest residue levels (26 ppb) occurred between 3 and 4 months after treatment.

Introduction

Mirex is presently the major chemical used to control the red imported fire ant (*Solenopsis invicta* Buren; formerly referred to as *Solenopsis saevissima richteri* Forel). Information about the environmental impact

of mirex in bait form is very limited. Although some of the mirex that is applied as bait soon enters the biomass of an area, the degradation pattern of the remaining mirex, which is presumably in the physical portion of the environment, has yet to be determined.

In 1971 an in-depth study was undertaken to determine the movement and degradation pattern of mirex in an area where it had been applied to control the imported fire ant. Mirex residue levels occurring in various indicator species or groups of animals in that study have been presented in two previous papers (1,2). This paper reports levels of mirex residues occurring in portions of the physical environment, soil, sediment, and water at various intervals up to 1 year after treatment. Also included in this report are the residue levels found in Bahia grass (*Paspalum notatum* Flugge), the most abundant pasture grass in the area and the only plant monitored during the study.

This study was set up in Washington Parish, La. Unfortunately, it was determined that the system used for monitoring water was not satisfactory after the study had been under way for several months. Therefore, data for water from the first study site were discarded. In February 1972 a second study was set up in Harrison County, Miss., which concentrated on mirex levels in water. The newer method of sampling was not totally satisfactory but was believed to present data accurate enough for publication in this paper.

Study Area

The first study ran for 1 year in Washington Parish, La., on a 2,000-acre area of land that is farmed, grazed, or forested. The open area of the treated block was predominantly Bahia grass, hay fields, or pastures. Most of the pastures, however, contained small artificial ponds used for stock watering. Authors chose three separate

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pastures, each with its own pond, as sampling sites. Study sites were the same as those used by Markin et al. (2) to collect invertebrates and were in the same general area where many of the vertebrates reported by Collins et al. (1) had been collected.

The second study site was a 100-acre block of cutover pine forest and Bahia grass pastures located east of Saucier, Miss., in the northern part of Harrison County. The center of this plot was dominated by a 2-acre pond, the entire drainage system of which lay within the treated area. Water in the pond was sampled at both the surface and at its deepest point, approximately 1.5 m.

Both study sites were aerially treated with one application of standard 4X mirex bait (1.25 lb bait containing 1.74 g actual mirex/acre). The Louisiana block was treated May 4 and 5, 1971; the Mississippi block was treated February 15, 1972.

Sampling Procedures

Sediment samples were collected with a hand-thrown grab sampler at 10 locations around the ponds. Samples were combined at the site and a subsample was removed for analysis in the laboratory. Soil was collected from 10 random sites, each 0.1 m², where vegetation had been clipped and litter brushed away. Soil was removed to a depth of 7.5 cm. The 10 samples were combined on the field into a composite sample and a subsample was removed and brought to the laboratory. Grass was clipped from these areas and set aside. Dirt was shaken from the roots which were also sampled.

In the Louisiana study, stems and leaves of grass were saved as one sample; roots were a separate sample. Residues found in biological indicators that were collected have been presented elsewhere (1,2). In the Mississippi study, biological indicators were not collected because the main emphasis was on determining mirex residues in water. For a more detailed description of the collection techniques used, see Markin et al. (3).

In both Louisiana and Mississippi, sampling varied according to weather conditions and accessibility of the sampling sites. A sample was taken from both sites before treatment; the next sample was obtained 1-3 hours later. Subsequent collections were made 24, 48, and 72 hours after treatment; then sampling continued at various intervals for a given period of time: 4 months in Louisiana and 1 year in Mississippi.

Water was sampled with a pair of filters. The first filter, a Sears sediment filter containing a replaceable cellulose cartridge, removed suspended particulate matter. The second filter, a Sears taste/odor filter containing a replaceable activated charcoal cartridge, removed dissolved material. Water was pumped through the filters using a 115-volt submersible pump. Rate of flow varied from 25 gallons an hour at the start of a

sampling period to less than 1 gallon an hour 24 hours later. Variation in flow was caused by clogging in the sediment filter which automatically reduced flow rate. To determine the total volume of water sampled during each period, three 55-gallon drums were set up in series below the filtering system to collect the filtered water so that it could be measured.

Water was collected at two locations in the pond, the pond surface and the bottom at the deepest point, 1.5 m. Surface water was taken by floating the pump in a styrofoam boat so that the pump inlet was just under the pond surface. Bottom water was sampled as water emerged from a drainage pipe under the dam. Researchers used two pumps and two separate filter systems; each had its own pump and collection barrels.

Analytical Procedures

To begin soil extraction, a 5-gallon cream can was partly filled with 5 kg moist soil, and sufficient 3:1 acetone:hexane to cover the soil to a depth of 3 cm. After 2 hours of rotation, the extract was poured through prewashed fluted filter paper into a separatory funnel. The acetone was washed out with water and the remaining hexane extract was dried over anhydrous sodium sulfate. The extract was treated with concentrated sulfuric acid until it was clear and colorless; then it was injected into the gas chromatograph. Sediment was extracted similarly except that 10-kg samples were used and the water that rose from the sediment while standing was extracted separately. Total mirex in this sample was added to mirex from the sediment sample. The Bahia grass was ground in a Waring blender with a small amount of water, extracted with acetone, then processed as the soil and sediment had been. For a detailed description of the analytical procedures above, see Markin et al. (3).

The wet cellulose cartridge used to extract water was soaked with acetone, allowed to drain into a separatory funnel, soaked with methylene chloride, allowed to drain, and then soaked again with acetone. After draining was completed, the acetone was washed out with water, the bottom layer was dried over sodium sulfate, and the extract was concentrated into hexane using a Snyder column. The sample was then treated with concentrated sulfuric acid and analyzed without further concentration.

The wet charcoal from the activated charcoal filter was removed from the plastic housing and subjected to Soxhlet extraction with methylene chloride for 3 hours. After drying, the extract was concentrated into hexane and treated with concentrated sulfuric acid. The extract was then ready for analysis without further concentration. After completion of the study it was determined that extracting the activated charcoal could have been improved by multiple extractions using a wet

solvent such as water-saturated benzene to remove more mirex. This method is described by Thornburg (4).

Primary identification and quantification of mirex was accomplished on a Hewlett-Packard 402 gas chromatograph. Researchers employed two columns with different characteristics. Instrument parameters were:

- Columns: (A) Glass, 3 ft by 1/4 in., packed with 3 percent DC-200 on 100/120 mesh Supelcoport.
 (B) Glass, 3 ft by 1/4 in., packed with a mixture of equal portions of separately coated 3 percent DC-200 on 100/120 mesh Supelcoport and 5 percent XE-60 on 60/80 mesh Chromosorb W.
- Detectors: Electron capture, with 130 MC tritium ionizing source.
- Temperatures: Injector 235°C.
 Column 190°C.
 Detector 210°C.
- Carrier Gas: Prepurified nitrogen flowing at 90 ml/min (Column A) and 36 ml/min (Column B).
- Purge Gas: Methane: 5 percent; argon: 95 percent.

Confirmation and Recovery

Because residue levels were low, confirmation was limited to extraction p-values and retention time comparisons of spiked samples to a mirex standard. The

typical responses of PCB's were not observed in any sample; presumably no PCB's were present. Recovery rates were established for the samples by spiking them with a known concentration of mirex at approximately the same level as mirex found in the samples. Recoveries were: sediment, 95 percent; soil, 97 percent; and grass, 97 percent. Tabular values for these samples have been corrected for recovery. The rate of recovery for filtered water was 70 percent, but the recovery method was not considered valid; thus tabular values for filtered water have not been corrected for recovery. Sensitivity for soil, sediment, and grass was 0.01 ppb; it was 0.001 ppb for water.

Results and Discussion

Pretreatment samples of sediment and grass showed detectable mirex residues. Although the land had never received aerial applications of bait, some landowners in both treated areas were known to have used mirex on an individual basis.

TABLE 1. Mirex residues in sediment collected in Mississippi (1972) and Louisiana (1971-72)

DAYS POSTTREATMENT	MIREX, PPB	CUMULATIVE RAINFALL, IN.
MISSISSIPPI		
Pretreatment	0.06	0.0
1-3 hours	0.16	0.0
1	0.41	0.0
2	0.17	0.0
3	0.51	0.0
7	0.11	0.3
14	0.11	0.4
21	0.30	2.4
28	0.93	4.1
35	1.1	5.3
42	0.85	6.0
49	0.04	7.1
56	0.03	7.6
63	0.20	7.6
70	0.01	7.6
77	0.02	9.5
84	0.05	11.3
91	0.10	16.1
98	0.01	19.5
105	0.76	19.5
LOUISIANA ¹		
Pretreatment	Neg	
1-3 hours	Neg	
3	Neg	
4	Neg	
7	0.02	
17	0.04	
25	0.30	
31	0.70	
38	0.60	
45	0.03	
54	0.08	
69	0.10	
77	0.10	
90	0.60	
117	0.30	
164	0.20	
185	0.09	
223	0.06	
268	0.50	
337	0.16	
374	0.40	

NOTE: Neg = no mirex at level of detection. Louisiana rainfall not recorded.

TABLE 2. Mirex residues in soil collected in Mississippi (1972) and Louisiana (1971-72)

DAYS POSTTREATMENT	MIREX, PPB
MISSISSIPPI	
Pretreatment	—
1-3 hours	6.3
1	0.71
2	0.31
3	4.2
7	0.87
14	0.41
21	0.22
28	1.2
35	1.3
42	4.0
49	0.78
56	2.7
63	8.2
70	1.5
77	1.2
84	2.0
91	10.4
98	2.4
105	1.1
112	0.31
LOUISIANA	
Pretreatment	—
1-3 hours	0.70
3	0.70
4	0.30
7	0.80
17	0.70
25	2.0
31	2.0
38	2.5
45	2.5
54	2.5
69	1.4
77	1.4
90	1.0
117	1.0
164	0.60
185	0.90
223	0.90
268	0.20
337	0.20
374	—

NOTE: — = no data.

Mirex residues in sediment collected from the bottom of the study pond in Louisiana (1971-72) and Mississippi (1972) are shown in Table 1. Rainfall records were kept for the duration of the Mississippi studies. Mirex residues in soil collected from the two study sites are shown in Table 2. Given the rate of application, 1.7 g of actual mirex per acre, the expected residue level for mirex in the upper 7.5 cm of the soil was 3.76 ppb. In Louisiana the residue level found immediately after treatment was much below this and possibly indicates that a foraging insect such as the fire ant had collected much of the material from the soil surface. Buildup of soil residues in Louisiana over the next 54 days has been interpreted as an indication that the mirex was slowly returning to the soil through decomposition of dead insects or excretion. The decline in residues after 54 days could be caused by either degradation of mirex or translocation out of the soil. Residue levels found in soil in Mississippi are much more variable and show no distinctive pattern. A possible explanation is that bait was applied during winter months when animal activity was minimal.

Mirex residues in Bahia grass from Mississippi and Louisiana are shown in Table 3. In the Louisiana study where grass was not sampled until 69 days after treatment, the blades and roots were analyzed separately to determine mirex distribution in the Bahia grass. Mirex findings in the above-ground parts of the grass, even after thorough cleaning to remove all external dirt, indicate that some translocation was taking place from the roots to the blades. This agrees with Mehendale et al. (5), who found an uptake and translocation of mirex by beans and pea seedlings in laboratory tests. In Mississippi the roots and blades were combined for analysis.

Table 4 shows mirex residues in water collected from the two sites in the Mississippi pond, using the double filter systems. Water samples from the bottom of the pond show residue values which remain higher and

TABLE 3. Mirex residues in Bahia grass (*Paspalum notatum* Flugge) collected in Mississippi (1972) and Louisiana (1971-72)

DAYS POSTTREATMENT	BLADES, PPB	ROOTS, PPB	BLADES AND ROOTS, PPB
MISSISSIPPI			
Pretreatment	—	—	0.14
1-3 hours	—	—	6.0
1	—	—	2.7
2	—	—	4.4
3	—	—	1.8
7	—	—	4.0
14	—	—	9.0
21	—	—	1.8
28	—	—	3.2
35	—	—	1.7
42	—	—	3.7
49	—	—	14.0
56	—	—	10.0
63	—	—	4.7
70	—	—	16.0
77	—	—	12.0
84	—	—	3.9
91	—	—	16.0
98	—	—	13.0
105	—	—	26.0
112	—	—	3.1
LOUISIANA			
69	17.0	9.0	26.0
77	2.0	1.0	3.0
90	1.6	0.3	1.9
117	4.0	0.6	4.6
164	6.5	2.7	9.2
185	3.6	0.8	4.4
223	2.6	2.3	4.9
268	5.7	4.9	10.6
337	6.0	17.0	23.0
374	0.01	0.07	0.08

NOTE: — = no data.

TABLE 4. Mirex residues in filtered water collected in Mississippi, 1972

DAYS POSTTREATMENT	FILTER SYSTEM 1 (DEEPEST POINT)			FILTER SYSTEM 2 (POND SURFACE)		
	CARTRIDGE: SEDIMENT, PPB	CARTRIDGE: ACTIVATED CARBON, PPB	TOTAL MIREX, PPB	CARTRIDGE: SEDIMENT, PPB	CARTRIDGE: ACTIVATED CARBON, PPB	TOTAL MIREX, PPB
Pretreatment	Neg	Neg	Neg	Neg	Neg	Neg
1-3 hours	0.033	Neg	0.033	0.007	0.009	0.016
1	0.530	Neg	0.530	0.008	0.012	0.020
2	0.001	Neg	0.001	0.003	0.004	0.007
3	0.001	0.006	0.007	0.001	0.002	0.003
7	0.001	0.007	0.008	0.005	0.001	0.006
14	0.003	0.010	0.013	0.006	0.001	0.007
21	0.002	0.012	0.014	0.002	0.003	0.005
28	Neg	0.010	0.010	0.001	0.002	0.003
35	0.001	0.012	0.012	Neg	0.002	0.002
42	Neg	0.003	0.003	Neg	0.001	0.001
49	0.004	0.004	0.008	Neg	0.002	0.002
56	0.002	0.003	0.005	Neg	Neg	Neg
63	0.001	0.009	0.010	0.001	0.001	0.002
70	0.001	0.010	0.011	0.001	0.001	0.001
77	0.001	0.005	0.006	0.001	0.001	0.001
84	0.001	0.010	0.011	0.002	Neg	0.002
91	0.002	0.003	0.005	0.002	0.001	0.003
98	0.001	0.015	0.016	0.003	Neg	0.003
105	0.001	0.003	0.004	0.007	0.003	0.010
112	0.001	0.002	0.003	0.005	0.002	0.007

NOTE: Neg = no mirex at level of detection.

more constant than those from the surface of the pond. Because sample water flowed through both the sediment and the activated charcoal filters, the total mirex residue load for each sampling period is determined by adding the figures for the two different filters. In general, highest residue levels were found immediately after treatment.

Acknowledgment

For assistance and suggestions, authors are indebted to Dudley J. Adams, Animal and Plant Health Inspection Service, U.S. Department of Agriculture, Gulfport, Miss.

LITERATURE CITED

(1) Collins, H. L., G. P. Markin, and J. Davis. 1974. Res-

idue accumulation in selected vertebrates following a single aerial application of mirex bait, Louisiana—1971-72. *Pestic. Monit. J.* 8(2):125-130.

- (2) Markin, G. P., H. L. Collins, and J. Davis. 1974. Residues of the insecticide mirex in terrestrial and aquatic invertebrates following a single aerial application of mirex bait, Louisiana—1971-72. *Pestic. Monit. J.* 8(2): 131-134.
- (3) Markin, G. P., J. H. Ford, J. C. Hawthorne, J. H. Spence, J. Davis, H. L. Collins, and C. D. Loftis. 1972. The insecticide mirex and techniques for its monitoring. APHIS 81-83 U.S. Department of Agriculture, Animal and Plant Health Inspection Service. 19 pp.
- (4) Thornburg, W. W. 1972. Analytical methods for pesticides, plant growth regulators and food additives. Vol. 1. Academic Press, New York and London. p. 97.
- (5) Mehendale, H. M., L. Fishbein, M. Fields, and H. B. Matthews. 1972. Fate of mirex-c¹⁴ in the rat and plants. *Bull. Environ. Contam. Toxicol.* 8(4):200-207.

BRIEFS

*Organochlorine Insecticide Residues in Carpeting*¹

David L. Mick,² Herbert Hetzler,¹ and Edwin Slach¹

ABSTRACT

Organochlorine insecticide (OCI) residues were detected by gas-liquid chromatography in carpet samples in 1973. Dieldrin was found in largest quantities; it was also found most frequently, existing in 84 percent of the samples. Wool carpet had higher residue levels than did synthetic carpet. OCI residues were also found in raw wool, but at much lower levels, indicating that most of the residues had been absorbed at the carpet mill rather than on the farm.

Introduction

Insect damage to carpeting can be prevented at carpet mills by treating fibers with insecticides during the manufacturing process. Garrison and Hill found dieldrin residues while monitoring the aqueous effluent of a mill (1). Their research stimulated this study to determine organochlorine insecticide residue levels in carpeting. The authors wished to explore carpeting as a possible source of insecticide residues in organic samples, particularly human tissue, which have no apparent exposure to chlorinated hydrocarbons.

Sampling and Analytical Procedures

Carpet remnants were obtained from carpet retailers and homes around Iowa City, Iowa, in 1973. Selection was not based upon any specific manufacturer, fiber, or color. No chlorinated hydrocarbon insecticides had been applied in the vicinity of the carpets while in the store or home.

Researchers extracted 10-g samples of one-inch carpet squares by immersing them in 500-ml, glass-stoppered, Erlenmeyer flasks with 200 ml n-hexane for 15 minutes,

hand-shaking the flasks for 5 minutes, and filtering the solutions through Whatman No. 1 filter paper. The n-hexane extract was concentrated by flash evaporation to approximately 5 ml prior to cleanup on a florisisil column. The column was first eluted with 200 ml 6 percent diethyl ether in petroleum ether and then with 200 ml 15 percent diethyl ether in petroleum ether.

Eluates were concentrated to approximately 5 ml and subsequently analyzed by gas-liquid chromatography using QF-1/SF-30 and DEGS columns. Sensitivity was approximately 0.001 ppm for aldrin, dieldrin, lindane, and *p,p'*-DDE, and 0.002 ppm for *p,p'*-DDT. Thin-layer chromatography was used to confirm detected residues.

Results and Discussion

Every carpet sampled revealed residues of at least one chlorinated hydrocarbon: aldrin, DDE, DDT, dieldrin, or lindane (Table 1). DDT and dieldrin were found most frequently, occurring in 15 and 21 of the 25 samples, respectively; Dieldrin was found in considerably higher quantities than any other insecticide. Highest residue levels of DDT and dieldrin appeared in wool carpeting. These levels probably result from treatment at the mill rather than on the farm, although the current study produces only limited evidence to support this conclusion.

To establish a control for wool samples, raw wool was obtained from a central Iowa farm and processed as the carpet samples had been. Although wool was sampled from only one farm (25-30 sheep), authors consider it representative of raw wool throughout the West and Midwest which is used in the manufacture of carpeting. Chlorinated hydrocarbon insecticides detected in a 6.7-g sample of raw wool are shown in Table 2. The fact that the raw wool contained residues indicated that the environment of sheep contributes to insecticide residue levels found in wool carpet samples. But these

¹ Iowa Community Pesticides Study, Institute of Agricultural Medicine, College of Medicine, University of Iowa. (Reprints are available from this address.) Work was performed pursuant to U.S. Environmental Protection Agency—Office of Pesticides Programs, Technical Services Division Contract No. 68-02-0746.

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TABLE 1. Chlorinated hydrocarbon insecticide residues in carpeting, Iowa City, Iowa—1973

FIBER	RESIDUE LEVELS, PPM				
	ALDRIN	DIELDRIN	<i>p,p'</i> -DDT	<i>p,p'</i> -DDE	LINDANE
Wool	0	27,638	0.638	0.036	0
"	0	9,684	0.424	0.159	0
"	0.105	9,331	0.234	0	0
"	0.022	7,391	0.030	0	0
Synthetic	0	25,393	0.142	0	0
"	0.070	2,383	0	0	0
"	0	0.956	0.240	0.032	0
"	0.011	0.825	0	0	0
"	0	0.497	0.028	0	0
"	0	0.361	0	0	0
"	0	0.119	0.082	0	0
"	0	0.116	0.095	0	0
"	0	0.075	0	0	0
"	0.026	0.071	0	0	0
"	0	0.040	0.021	0	0
"	0	0.026	0.051	0	0
"	0	0.019	0	0	0
"	0	0.010	0	0	0
"	0.010	0.008	0	0	0.007
"	0	0.007	0	0	0
"	0	0.004	0	0	0
"	0.041	0	0.063	0	0.015
"	0.049	0	0.086	0	0
"	0	0	0.025	0	0
"	0	0	0.863	0	0

TABLE 2. Chlorinated hydrocarbon insecticide residues in raw wool, Iowa—1973

INSECTICIDE	RESIDUE LEVELS, PPM
<i>p,p'</i> -DDT	0.064
<i>p,p'</i> -DDE	0.009
<i>o,p'</i> -DDT	0.015
Dieldrin	0.017

levels were not great enough to account for all residues detected in the samples.

Recovery studies indicate that the extraction process detected 85 to 100 percent of the residues in both wool and synthetic carpet. This is based upon the difference

in insecticide residues recovered from nonspiked samples contrasted to those recovered from spiked samples. As postulated earlier, results of this study provide evidence for a potential source of human exposure to chlorinated hydrocarbon insecticides. Findings may help explain why insecticide residue levels are sometimes detected in organic samples, such as human tissue, with no apparent source of exposure.

LITERATURE CITED

- (1) Garrison, A. W., and D. W. Hill. 1972. Organic pollutants from mill persist in downstream waters. Amer. Dyest. Rep. 61(2):21-23.

Organochlorine Pesticide Residue Levels in North American Timber Wolves—1969-71

James C. Schneeweis,¹ Yvonne A. Greichus,² and Raymond L. Linder³

ABSTRACT

Tongue and muscle tissue samples from 51 timber wolves captured in Minnesota and northwest Ontario in 1969-71 were analyzed for organochlorine pesticide residues in an attempt to determine the level of insecticide contamination in their environment. No determined residue levels exceeded the minimum analytical confidence limits established in a previous study by one of the authors. The implementation of new State, national, and international legislation protecting timber wolves makes this study especially valuable because samples from a wide range of age groups will no longer be readily available for analysis.

Introduction

The timber wolf (*Canis lupus*) has recently become a symbol of wilderness environments. Because these mammals are at the top of their food chain, one would expect their tissues to contain pesticide residues if their environment were contaminated by organochlorine compounds. The purpose of this paper is to report results of analyses of timber wolf tissues for selected pesticides. This study is especially valuable because recent State, national, and international legislation protecting timber wolves has made samples from a wide variety of age groups more difficult to obtain for analysis.

Analytical Methods

Tongue and muscle tissue samples were taken from 51 timber wolves captured by hunters and trappers: 30 from

the winter of 1969-70 and 21 from 1970-71. No animals were collected specifically for this study. Wolves were assigned an age class based on examination of the gross size and weight of the carcass, wear and development of the teeth, and, in some cases, development of the cranium (Table 1). Wolves were from Koochiching and northwest St. Louis Counties, Minn., and from northwest Ontario, Canada. The area is wild to semiwild in nature and is primarily coniferous forest with little or no human disturbance.

Samples were kept frozen until they were analyzed in the Experiment Station Biochemistry Laboratory, South Dakota State University. Analytical procedures were those reported by Greichus, et al. (1,2).

Results

No determined residue levels exceeded the minimum analytical confidence limits established by Greichus in 1973 (2). These limits are: lindane, heptachlor, heptachlor epoxide, aldrin, dieldrin, and DDE—0.01 parts per million (ppm); DDT and DDD—0.05 ppm; and PCB's, endrin, and methoxychlor—1.00 ppm. These data suggest that pesticide contamination was quite low in specified areas of Minnesota and Ontario.

LITERATURE CITED

- (1) Greichus, Yvonne, D. Lamb, and C. Garrett. 1968. Efficiency of extraction of metabolically incorporated HEOD (Carbon-14) from pheasant tissues, eggs and feces. *Analyst* 93:323-325.
- (2) Greichus, Yvonne A., A. Greichus, and R. J. Emerick. 1973. Insecticides, polychlorinated biphenyls and mercury in wild cormorants, pelicans, their eggs, food and environment. *Bull. Environ. Contam. Toxicol.* 9(6): 321-328.

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TABLE 1. Sex and age class¹ of 51 North American timber wolves analyzed for insecticide residues, 1969-71

YEAR ²	NUMBER ANALYZED						
	MALES			FEMALES			
	ADULTS	JUVENILES	AGE UNKNOWN	ADULTS	JUVENILES	AGE UNKNOWN	TOTAL
1969-70	12	0	2	5	5	6	30
1970-71	ND	ND	8	ND	ND	13	21
Total	12	0	10	5	5	19	51

NOTE: ND = no data.

¹ Juveniles were those born around the preceding spring.

² Samples were obtained both winters between December and March.

APPENDIX

Chemical Names of Compounds Discussed in This Issue¹

ALDRIN	Not less than 95% of 1,2,3,4,10,10-Hexachloro-1,4,4a,5,8,8a-hexahydro-1,4-endo-exo-5,8-dimethanonaphthalene
AMIBEN	3-Amino-2,5-dichlorobenzoic acid
AMITROLE	3-Amino-1,2,4-triazole
ATRAZINE	2-Chloro-4-ethylamino-6-isopropylamino-s-triazine
BHC (BENZENE HEXACHLORIDE)	1,2,3,4,5,6-Hexachlorocyclohexane (mixture of isomers). Commercial product contains several isomers of which <i>gamma</i> is most active as an insecticide.
BIDRIN ®	See dicrotophos.
BOTRAN ®	See dichloran.
CAPTAN	<i>N</i> -Trichloromethylthio-4-cyclohexane-1,2-dicarboximide
CARBARYL	1-Naphthyl <i>N</i> -methylcarbamate
CHLORDANE	1,2,3,4,5,6,7,8,8-Octachloro-2,3,3a,4,7,7a-hexahydro-4,7-methanoindane. The technical product is a mixture of several compounds including heptachlor, chlordene, and two isomeric forms of chlordane.
CHLORPROPHAM	Isopropyl <i>N</i> -(3-chlorophenyl) carbamate
CIPC	See chlorpropham.
COTORAN ®	See fluometuron.
2,4-D	2,4-Dichlorophenoxyacetic acid
DACTHAL ®	See DCPA.
DCPA	Dimethyl 2,3,5,6-tetrachloroterephthalate
DDD	See TDE.
DDE	Dichlorodiphenyl dichloro-ethylene (degradation product of DDT). Main component (<i>p,p'</i> -DDE): 1,1-Dichloro-2,2-bis(<i>p</i> -chlorophenyl) ethylene <i>o,p'</i> -DDE: 1,1-Dichloro-2-(<i>o</i> -chlorophenyl)-2-(<i>p</i> -chlorophenyl) ethylene
DDT	Main component (<i>p,p'</i> -DDT): α -Bis(<i>p</i> -chlorophenyl) β,β,β -trichloroethane Other isomers are possible and some are present in the commercial product. <i>o,p'</i> -DDT: [1,1,1-Trichloro-2-(<i>o</i> -chlorophenyl)-2-(<i>p</i> -chlorophenyl) ethane] <i>S,S,S</i> -Tributyl phosphorotrithioate
DEF ®	<i>o,o</i> -Diethyl <i>o</i> -(2-isopropyl 4-methyl-6-pyrimidyl) phosphorothioate
DIAZINON	2,6-Dichloro-4-nitroaniline
DICHLORAN	4,4'-Dichloro- α -trichloromethylbenzhydrol
DICOFOL	3-(Dimethoxyphosphinyloxy)- <i>N,N</i> -dimethyl- <i>cis</i> -crotonamide
DICROTOPHOS	Not less than 85% of 1,2,3,4,10,10-Hexachloro-6,7-epoxy-1,4,4a,5,6,7,8,8a-octahydro-1,4-endo-exo-5,8-dimethanonaphthalene
DIELDRIN	3-(3,4-Dichlorophenyl)-1,1-dimethyl-urea
DIURON	6,7,8,9,10,10-Hexachloro-1,5,5a,6,9,9a-hexahydro-6,9-methano-2,4,3-benzodioxathiepin 3-oxide
ENDOSULFAN	1,2,3,4,10,10-Hexachloro-6,7-epoxy-1,4,4a,5,6,7,8,8a-octahydro-1,4-endo-endo-5,8-dimethanonaphthalene
ENDRIN	3-(<i>m</i> -Trifluoromethylphenyl)-1,1-dimethylurea
FLUOMETURON	Tributyl phosphorotrithioate
FOLEX	Hexachlorobenzene
HCB	
HEPTACHLOR	1,4,5,6,7,8,8-Heptachloro-3a,4,7,7a-tetrahydro-4,7-endo-methanoindane
HEPTACHLOR EPOXIDE	1,4,5,6,7,8,8-Heptachloro 2,3-epoxy-3a,4,7,7a-tetrahydro-4,7-methanoindane
KELTHANE ®	See dicofol.
LINDANE	Gamma isomer of Benzene Hexachloride (1,2,3,4,5,6-hexachlorocyclohexane) of 99+ % purity
MALATHION	<i>S</i> -[1,2-Bis(ethoxycarbonyl)ethyl] <i>o,o</i> -dimethyl phosphorodithioate
METHOXYCHLOR	1,1,1-Trichloro-2,2-bis(<i>p</i> -methoxyphenyl) ethane
METHYL PARATHION	<i>o,o</i> -Dimethyl <i>o-p</i> -nitrophenyl phosphorothioate
MIREX	Dodecachlorooctahydro-1,3,4-metheno-1H-cyclobuta[cd]pentalene
MSMA	Methanearsonic acid, monosodium salt
PARATHION	<i>o,o</i> -Diethyl- <i>o-p</i> -nitrophenyl phosphorothioate
PCB's (POLYCHLOR- INATED BIPHENYLS)	Mixtures of chlorinated biphenyl compounds having various percentages of chlorine.
PCP	Pentachlorophenol
PERTHANE	1,1-Dichloro-2,2-bis(<i>p</i> -ethylphenyl) ethane
<i>o</i> -PHENYLPHENOL	orthophenylphenol
PHOSALONE	<i>o,o</i> -Diethyl <i>S</i> -(6-chloro-2-oxo-benzoxazolin-3-yl) methyl phosphorodithioate
PROPACHLOR	2-Chloro- <i>N</i> -isopropylacetanilide
RAMROD ®	See propachlor.
RONNEL	Dimethyl 2,4,5-trichlorophenyl phosphorothioate
TDE	2,2-Bis (<i>p</i> -chlorophenyl)-1,1-dichloroethane (including isomers and dehydrochlorination products)
TOXAPHENE	Chlorinated camphene (67-69% chlorine); product is a mixture of polychlor bicyclic terpenes with chlorinated camphenes predominating.
TRIFLURALIN	α,α,α -Trifluoro-2,6-dinitro- <i>N,N</i> -dipropyl- <i>p</i> -toluidine

¹ Does not include chemicals listed only in tables of papers by Crockett et al. and Manske/Corneliusen.

ERRATUM

PESTICIDES MONITORING JOURNAL, Volume 7, Number 1. In the paper "Mercury, Lead, Cadmium, and Arsenic Residues in Starlings—1971," page 69, Table 1, first two columns: analysis was performed in the city of Laurel, Maryland, rather than in Patuxent, Maryland.

Information for Contributors

The PESTICIDES MONITORING JOURNAL welcomes from all sources qualified data and interpretive information which contribute to the understanding and evaluation of pesticides and their residues in relation to man and his environment.

The publication is distributed principally to scientists and technicians associated with pesticide monitoring, research, and other programs concerned with the fate of pesticides following their application. Additional circulation is maintained for persons with related interests, notably those in the agricultural, chemical manufacturing, and food processing industries; medical and public health workers; and conservationists. Authors are responsible for the accuracy and validity of their data and interpretations, including tables, charts, and references. Accuracy, reliability, and limitations of the sampling and analytical methods employed must be clearly demonstrated through the use of appropriate procedures, such as recovery experiments at appropriate levels, confirmatory tests, internal standards, and inter-laboratory checks. The procedure employed should be referenced or outlined in brief form, and crucial points or modifications should be noted. Check or control samples should be employed where possible, and the sensitivity of the method should be given, particularly when very low levels of pesticides are being reported. Specific note should be made regarding correction of data for percent recoveries.

- Preparation of manuscripts should be in conformance to the CBE STYLE MANUAL, 3d ed. Council of Biological Editors, Committee on Form and Style, American Institute of Biological Sciences, Washington, D. C., and/or the STYLE MANUAL of The United States Government Printing Office.
- An abstract (not to exceed 200 words) should accompany each manuscript submitted.
- All material should be submitted in duplicate (original and one carbon) and sent by first-class mail in flat form—not folded or rolled.
- Manuscripts should be typed on 8½ x 11 inch paper with generous margins on all sides, and each page should end with a completed paragraph.
- All copy, including tables and references, should be double spaced, and all pages should be numbered. The first page of the manuscript must contain authors' full names listed under the title, with affiliations, and addresses footnoted below.
- Charts, illustrations, and tables, properly titled, should be appended at the end of the article with a notation in text to show where they should be inserted.

—Charts should be drawn so the numbers and texts will be legible when considerably reduced for publication. All drawings should be done in black ink on plain white paper.

—Photographs should be made on glossy paper. Details should be clear, but size is not important.

—The "number system" should be used for literature citations in the text. List references in the order in which they are cited in the text, giving name of author/s/, year, full title of article, exact name of periodical, volume, and inclusive pages.

The Journal also welcomes "brief" papers reporting monitoring data of a preliminary nature or studies of limited scope. A section entitled *Briefs* will be included, as necessary, to provide space for papers of this type to present timely and informative data. These papers must be limited in length to two journal pages (850 words) and should conform to the format for regular papers accepted by the Journal.

Pesticides ordinarily should be identified by common or generic names approved by national scientific societies. The first reference to a particular pesticide should be followed by the chemical or scientific name in parentheses—assigned in accordance with CHEMICAL ABSTRACTS nomenclature. Structural chemical formulas should be used when appropriate. Published data and information require prior approval by the Editorial Advisory Board; however, endorsement of published information by any specific Federal agency is not intended or to be implied. Authors of accepted manuscripts will receive edited typescripts for approval before type is set. After publication, senior authors will be provided with 100 reprints.

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The WORKING GROUP is comprised of representatives of the U.S. Departments of Agriculture; Commerce; Defense; the Interior; Health, Education, and Welfare; State; Transportation; and Labor; and the U.S. Environmental Protection Agency.

The pesticide MONITORING PANEL consists of representatives of the Agricultural Research Service, Animal and Plant Health Inspection Service, Extension Service, Forest Service, Department of Defense, Fish and Wildlife Service, Geological Survey, Food and Drug Administration, Environmental Protection Agency, National Marine Fisheries Service, National Science Foundation, and Tennessee Valley Authority.

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Pesticide monitoring activities of the Federal Government, particularly in those agencies represented on the pesticide MONITORING PANEL which participate in operation of the national pesticides monitoring network, are expected to be the principal sources of data and interpretive articles. However, pertinent data *in summarized form*, together with interpretive discussions, are invited from both Federal and non-Federal sources, including those associated with State and community monitoring programs, universities, hospitals, and nongovernmental research institutions, both domestic and foreign. Results of studies in which monitoring data play a major or minor role or serve as support for research investigation also are welcome; however, the *Journal* is not intended as a primary medium for the publication of basic research. Manuscripts received for publication are reviewed by an Editorial Advisory Board established by the MONITORING PANEL. Authors are given the benefit of review comments prior to publication.

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EDITORIAL

New Publications from Monitoring Panel

Journal subscribers have recently received in the mail *Guidelines on Sampling and Statistical Methodologies for Ambient Pesticide Monitoring*. Newest publication of the Monitoring Panel of the Federal Working Group on Pest Management, the *Guidelines* represent an attempt to standardize sampling procedures among the various components of the National Pesticide Monitoring Program. Guideline compilers hope by this means to minimize variations encountered by personnel sampling various media in widely differing geographic regions.

For 10 years the Monitoring Panel has coordinated various Federal activities concerned with pesticide monitoring. The National Pesticide Monitoring Program, begun in 1964 as an interagency cooperative effort, is the prime result of this coordination. Other charter responsibilities of the Monitoring Panel include disseminating data obtained from pesticide monitoring activities, maintaining awareness of monitoring programs and plans of all Federal agencies, and developing manuals or guidelines to encourage acceptable sampling and analytical methodologies in pesticide monitoring.

Since its initial appearance in June 1967, the *Pesticides Monitoring Journal* has fulfilled the first responsibility mentioned above. Another charge of the charter inspired the *Catalog of Federal Pesticide Monitoring Activities*, originally published in 1968 and now being revised for publication in spring 1975. The new edition will cover activities in effect through June 1973,

greatly enlarging its predecessor. The catalog is a reference source identifying types and locations of all Federal pesticide monitoring activities. The Panel is also putting final touches on its *Guidelines on Analytical Methodologies for Ambient Pesticide Monitoring* which is targeted for publication next summer.

A decade ago the Panel undertook to develop a continuing network to monitor pesticide residue levels in air, water, soil, wildlife, fish, and humans; an ambitious goal for six different agencies, each with different and sometimes divergent reasons for undertaking the task. Today pesticide residue levels are monitored on a national scale and resulting data are disseminated widely by countless scientists and authors from Federal, State, and local agencies, and academic and international sources, through the *Pesticides Monitoring Journal*.

This tradition of interagency cooperation is further reinforced by the catalog and two sets of guidelines. We trust that these three publications will prove invaluable to individuals and organizations concerned with pests, pesticides, and pest management.

Anthony Inglis
Assistant Executive Secretary

PESTICIDES IN PEOPLE

Organochlorine Insecticide Residues in Human Milk in Portugal¹

Isabel Graca, A. M. S. Silva Fernandes, and H. C. Mourão

ABSTRACT

A total of 222 samples of human milk collected in several parts of Portugal were analyzed by gas chromatography in 1970 and 1972. The highest rate of insecticide contamination was observed in the 1970 study in a sample taken from an employee who for 6 years had been cleaning glass equipment used in the analysis of pesticide formulations. Her milk contained 1.38 ppm total DDT 73 days after her child had been delivered.

DDT, the most frequently detected insecticide, was found in 99.5 percent of the samples. Mean residues of total DDT were similar to those of other European and North American countries. Dieldrin was detected in 15 samples; values ranged from 0.005 to 0.031 ppm.

In the 1972 study, p,p'-DDE residues ranged from 0.006 to 0.699 ppm and p,p'-DDT residues ranged from 0.003 to 0.345 ppm. The highest mean value of total DDT, 0.326 ± 0.175 ppm, was from the district of Lisbon.

Potatoes, fruits, and vegetables were the most important items in the women's diets except in coastal districts where the staple was fish. Most of the participating women were homemakers.

Introduction

Widespread use of persistent pesticides has led to unintentional pollution of the environment; it is becoming increasingly difficult to find any being in inhabited regions of the globe which does not contain residues of DDT or its metabolites. Owing to its liposolubility, an inherent property of numerous organochlorine insecticides, DDT is readily absorbed by living organisms; it is stored in certain organs but accumulates primarily in the adipose tissues.

DDT is detected with greater frequency than are other organochlorines because it was widely used in agriculture and public health for so many years, but

residues of other insecticides such as dieldrin, heptachlor epoxide, and BHC (known in European countries as HCH) are also fairly common.

In addition to organochlorines, other substances which have been detected recently are polychlorinated biphenyls (PCB's). Widely used in industry, PCB's are approximately as persistent and as liposoluble as are organochlorines. It may be concluded that they also cause considerable, if unintentional, contamination of the environment.

Because humankind is in direct contact with these products, unintentionally ingesting them in foodstuffs or intentionally using them as pesticides, it is not surprising that insecticide residues are found in human adipose tissues, blood, urine, and milk. Residue levels vary with the type of exposure to which the individual is subjected and the individual's daily intake of residues in foodstuffs. This accounts for the variations in levels observed in different professions, between rural and urban zones, between countries, and even between developed and underdeveloped areas.

The first research into pesticide residues in human milk was undertaken in 1950 by Laug et al. (1), who detected DDT in 30 of 32 samples examined. However, it was only upon introduction of organochlorine insecticide residue analysis by gas chromatography that these studies were intensified. To date, innumerable studies on this matter have been published in various countries.

In Portugal, no research into unintentional insecticide contamination was carried out before 1966. In that year, samples of cows' milk, butter, and cream were analyzed for the first time. Results disclosed the presence of DDT and its metabolites in all these dairy products. In subsequent years, studies were extended to embrace residues in wildlife. As expected, work undertaken to date has revealed widespread organochlorine pesticide contamination in Portugal.

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In 1970 a preliminary study of human milk entailing analysis of 54 samples was made. A sample was obtained from an employee of the Laboratório de Fitofarmacologia who assisted in analyses of pesticide formulations. Other samples were taken at two Lisbon maternity hospitals from lactating women whose case histories were unknown.

In light of the results of this preliminary study and the absence of details in the women's case histories, a more detailed study was undertaken which involved individuals from various parts of Portugal. The present report describes results of both the preliminary study and the 1972 study.

Analytical Methods

The amount of milk sampled varied among the individual women and ranged between 5 and 20 ml. Samples were refrigerated until analysis. Upon collection, 1 ml of a potassium dichromate saturated aqueous solution having 1 percent amyl alcohol was added to act as a preservative.

A method devised by de Faubert Maunder et al. (2) was used to extract and purify samples; the residues were determined by gas chromatography using an electron-capture detector. The method detected residues as low as 0.001 ppm for DDT isomers and metabolites, dieldrin, HCB, and BHC. Results were confirmed by using different column packings (10 percent DC 200, 6 percent QF₁ + 4 percent SE-30, and 5 percent QF₁ on 80/100 mesh Gas Chrom Q). In addition, one-fifth the samples were submitted to alkaline hydrolysis to confirm the DDT residues. Residue values given in the tables are not corrected for recovery, which ranged from 84 to 96 percent.

Fat content was determined by drying a subsample extracted with acetone and weighing the respective residue.

RESULTS OF 1970 PRELIMINARY STUDY

The first milk sample analyzed was obtained from an employee of the Laboratório de Fitofarmacologia who for 6 years had been cleaning glass equipment used in analyses of pesticide formulations. This woman had therefore been in daily contact with these products. Her milk was extracted at 73, 77, 85, 92, and 98 days after delivery of her child, who happened to be the firstborn. Results are summarized in Table 1.

All the remaining 53 samples collected at two Lisbon maternity hospitals contained residues of *p,p'*-DDE and *p,p'*-DDT. Dieldrin was found in four of the samples; *o,p'*-DDT was found in one. DDE residues ranged from 0.020 to 0.390 ppm and *p,p'*-DDT ranged from 0.008 to 0.136 ppm. Total DDT residues varied from 0.032 to 0.497 ppm; the mean was 0.177 and the standard

deviation was ± 0.108 ppm. Dieldrin residues ranged from 0.018 to 0.031 ppm.

RESULTS OF 1972 STUDY

Authors collected and analyzed 168 milk samples from 12 districts in Portugal. Each sample was accompanied by a data sheet identifying the mother and containing relevant particulars such as date and number of deliveries, occupation, and normal intake of staple foods.

Results of the analyses are summarized in Tables 2-13. Of the 168 samples examined, 167 showed residues of *p,p'*-DDE and *p,p'*-DDT. Dieldrin was detected in four samples from the district of Bragança, one from Setúbal, and six from Viseu. In a negligible number of samples, residues of γ BHC and hexachlorobenzene were identified but were not quantified because levels were very low.

Mean values, standard deviations, and maximum and minimum residues of total DDT for each set of samples from the various districts are contained in Table 14. Converted means relating to total DDT were transformed by \sqrt{X} and are summarized in Table 15. This transformation was suggested by the detected correlation between the logarithm of the mean and the logarithm of the variance for each district (3).

Having established that Bragança was the district theoretically least polluted with DDT, authors determined the significance of the differences for all the remaining means (4). Highly significant differences of 1 percent were observed for Odivelas, Amadora, Loures, Caneças (all within the district of Lisbon); Portalegre; Aveiro; Evora; and Setúbal. Differences for Damaia (in the district of Lisbon), Guarda, and Porto were significant (5 percent). Differences for Faro, Vila Real, Viana do Castelo, and Viseu did not reach the level of significance.

Results of the inquiry into dietary habits of the lactating women revealed that in most cases potatoes, fruits, and vegetables were important items in their diets. Only a few women claimed to drink milk frequently and, in some districts, the number of nursing mothers who never drank it at all was very high. In the coastal districts the staple food was usually reported to be fish.

Table 16 indicates that most of the mothers were homemakers. Sample 6 from the district of Setúbal was obtained from a farmworker; sample 1 from Faro and sample 3 from Caneças were from factory workers. The mother from Faro was working in an almond-shelling factory; no details are available on the specific type of factory work being done by the woman from Caneças.

Discussion

References cited in this paper show that the pesticide most widely found in human milk is DDT and its metabolites, mainly DDE (5-23); TDE has been detected

in some cases (6,10,18,22). The *o,p'*-DDT isomer was detected by Ritcey et al. (22) and by Curley and Kimbrough (6). The latter authors also detected the *o,p'*-DDE isomer.

In the present study DDT was by far the most frequently detected insecticide; it was found in 99.5 per cent of the samples analyzed. Both *p,p'*-DDT and *p,p'*-DDE were present in all samples containing DDT; residue levels of the latter usually were higher than those of the former. Juszkiwicz (17) and Ritcey et al. (22) arrived at similar conclusions.

The lactating woman who was employed by our Laboratório de Fitofarmacologia revealed the highest level of DDT, 1.38 ppm, 73 days after delivery. The

closest value mentioned in the literature reviewed was reported by Gracheva (8), who detected 1 mg/liter total DDT.

Table 1 shows that the DDT level in milk decreased as the number of days between sampling and delivery increased.

TABLE 1. DDT residues detected in milk of an employee of Laboratório de Fitofarmacologia, Oeiras, Portugal—1976

DAYS BETWEEN DELIVERY AND SAMPLING	RESIDUES, PPM		TOTAL DDT, PPM
	<i>p,p'</i> -DDE	<i>p,p'</i> -DDT	
73	0.938	0.444	1.38
77	0.680	0.292	0.97
85	0.850	0.350	1.20
92	0.408	0.140	0.55
98	0.263	0.097	0.36

TABLE 2. Pesticide residues in human milk from district of Aveiro, Portugal—1972

SAMPLE	NUMBER OF DELIVERIES	DAYS BETWEEN DELIVERY AND SAMPLING	FAT CONTENT, %	ON WHOLE-MILK BASIS, PPM				ON FAT BASIS, PPM		
				Dieldrin	<i>p,p'</i> -DDE	<i>p,p'</i> -DDT	TOTAL DDT	<i>p,p'</i> -DDE	<i>p,p'</i> -DDT	TOTAL DDT
1	2	172	0.66	ND	0.025—	0.022	0.047—	3.79	3.33	7.12
2	1	33	3.67	ND	0.123	0.042	0.165	3.35	1.14—	4.49
3	1	52	2.20	ND	0.063	0.039	0.102	2.86	1.75	4.61
4	1	143	4.48	ND	0.491+	0.205	0.696	10.95+	4.58	15.53+
5	2	171	3.21	ND	0.076	0.042	0.118	2.35	1.31	3.66
6	1	113	0.70	ND	0.117	0.091	0.208	1.57—	1.30	2.87—
7	5	240	4.86	ND	0.312	0.196	0.508	6.42	4.03	10.45
8	6	141	0.47	ND	0.030	0.019—	0.049	6.28	4.04	10.32
9	1	48	3.36	ND	0.116	0.073	0.189	3.45	2.17	5.62
10	1	78	5.67	ND	0.398	0.345+	0.743+	7.01	6.08+	13.09

NOTE: ND = not detected.
 — = lowest value.
 + = highest value.

TABLE 3. Pesticide residues in human milk from district of Bragança, Portugal—1972

SAMPLE	NUMBER OF DELIVERIES	DAYS BETWEEN DELIVERY AND SAMPLING	FAT CONTENT, %	ON WHOLE-MILK BASIS, PPM				ON FAT BASIS, PPM		
				Dieldrin	<i>p,p'</i> -DDE	<i>p,p'</i> -DDT	TOTAL DDT	<i>p,p'</i> -DDE	<i>p,p'</i> -DDT	TOTAL DDT
1	2	113	6.15	ND	0.045	0.020	0.065	0.72	0.39—	1.11
2	6	46	2.24	ND	0.024	0.024	0.048	1.06	1.07	2.13
3	1	225	3.33	ND	0.041	0.016	0.057	1.24	0.48	1.72
4	3	31	2.01	ND	0.013	0.008	0.021	0.65	0.40	1.05
5	4	152	4.44	ND	0.039	0.031	0.070	0.89	0.70	1.59
6	1	37	2.82	ND	0.067	0.023	0.090	2.39+	0.82	3.21
7	4	33	2.55	0.013	0.022	0.016	0.038	0.87	0.63	1.50
8	2	44	3.46	ND	0.078	0.028	0.106	2.24	0.81	3.05
9	2	213	3.71	ND	0.053	0.045	0.098	1.42	1.21	2.63
10	1	326	7.84	ND	0.097+	0.052+	0.149—	1.24	0.66	1.90
11	4	157	1.29	ND	0.017	0.009	0.026	1.31	0.70	2.04
12	11	30	2.06	ND	0.026	0.020	0.046	1.28	0.97	2.25
13	10	186	2.53	ND	0.028	0.013	0.041	1.11	0.51	1.62
14	6	196	2.11	ND	0.020	0.019	0.039	0.95	0.90	1.85
15	8	284	4.21	0.006	0.025	0.021	0.046	0.58	0.50	1.08
16	2	31	2.84	0.013	0.063	0.035	0.098	2.22	1.23+	3.45+
17	5	287	5.86	0.009	0.025	0.029	0.054	0.64	0.75	1.39
18	3	67	2.91	ND	0.051	0.024	0.075	1.75	0.82	2.57
19	11	222	2.20	ND	0.006—	0.004—	0.010—	0.27—	0.18	0.45—
20	1	131	3.80	ND	0.066	0.016	0.082	1.74	0.42	2.16

NOTE: ND = not detected.
 — = lowest value.
 + = highest value.

TABLE 4. Pesticide residues in human milk from district of Évora, Portugal—1972

SAMPLE	NUMBER OF DELIVERIES	DAYS BETWEEN DELIVERY AND SAMPLING	FAT CONTENT, %	ON WHOLE-MILK BASIS, PPM				ON FAT BASIS, PPM		
				DIELDRIN	p,p'-DDE	p,p'-DDT	TOTAL DDT	p,p'-DDE	p,p'-DDT	TOTAL DDT
1	3	4	3.76	ND	0.224	0.081	0.305	5.94	2.15	8.09
2	1	3	1.58	ND	0.111	0.026	0.137	7.03	1.65	8.68
3	1	4	4.80	ND	0.198	0.079	0.277	4.13	1.65	5.78
4	2	14	1.70	ND	0.081	0.028	0.109	4.75	1.65	6.40
5	3	8	1.76	ND	0.019—	0.012—	0.031—	1.10—	0.68—	1.78—
6	1	22	2.62	ND	0.330	0.165+	0.495	12.60+	6.30+	18.90+
7	2	2	3.23	ND	0.156	0.064	0.220	4.83	1.98	6.81
8	2	10	7.62	ND	0.699+	0.138	0.837+	9.17	1.82	10.99
9	1	5	0.73	ND	0.046	0.017	0.063	6.30	2.33	8.63
10	1	3	1.68	ND	0.174	0.037	0.211	10.36	2.20	12.56

NOTE: ND = not detected.
 — = lowest value.
 + = highest value.

TABLE 5. Pesticide residues in human milk from district of Portalegre, Portugal—1972

SAMPLE	NUMBER OF DELIVERIES	DAYS BETWEEN DELIVERY AND SAMPLING	FAT CONTENT, %	ON WHOLE-MILK BASIS, PPM				ON FAT BASIS, PPM		
				DIELDRIN	p,p'-DDE	p,p'-DDT	TOTAL DDT	p,p'-DDE	p,p'-DDT	TOTAL DDT
1	4	43	2.50	ND	0.059	0.015—	0.074	2.34—	0.60	2.94—
2	1	28	3.24	ND	0.162	0.058	0.220	5.00	1.79	6.79
3	3	180	3.52	ND	0.239	0.066	0.305	6.79	1.88	8.67
4	2	139	1.39	ND	0.061	0.025	0.086	4.39	1.80	6.19
5	4	90	6.46	ND	0.333	0.273+	0.606+	5.15	4.23+	9.38
6	1	55	4.96	ND	0.221	0.029	0.250	4.45	0.58—	5.03
7	1	79	4.33	ND	0.364+	0.124	0.488	8.41+	2.86	11.27+
8	1	131	3.77	ND	0.090	0.068	0.158	2.37	1.80	4.17
9	1	150	3.94	ND	0.230	0.088	0.318	5.84	2.23	8.07
10	3	134	1.58	ND	0.039—	0.018	0.057—	2.44	1.14	3.58

NOTE: ND = not detected.
 — = lowest value.
 + = highest value.

TABLE 6. Pesticide residues in human milk from district of Faro, Portugal—1972

SAMPLE	NUMBER OF DELIVERIES	DAYS BETWEEN DELIVERY AND SAMPLING	FAT CONTENT, %	ON WHOLE-MILK BASIS, PPM				ON FAT BASIS, PPM		
				DIELDRIN	p,p'-DDE	p,p'-DDT	TOTAL DDT	p,p'-DDE	p,p'-DDT	TOTAL DDT
1	1	15	4.14	ND	0.216+	0.056+	0.272+	5.22	1.35	6.57
2	3	211	0.69	ND	0.025—	0.013—	0.038—	3.57—	1.88+	5.45—
3	1	45	1.28	ND	0.048	0.023	0.071	3.71	1.80	5.51
4	1	158	2.27	ND	0.128	0.029	0.157	5.64+	1.28—	6.92+
5	2	45	3.40	ND	0.138	0.052	0.190	4.06	1.53	5.59

NOTE: ND = not detected.
 — = lowest value.
 + = highest value.

TABLE 7. Pesticide residues in human milk from district of Guarda, Portugal—1972

SAMPLE	NUMBER OF DELIVERIES	DAYS BETWEEN DELIVERY AND SAMPLING	FAT CONTENT, %	ON WHOLE-MILK BASIS, PPM				ON FAT BASIS, PPM		
				DIELDRIN	p,p'-DDE	p,p'-DDT	TOTAL DDT	p,p'-DDE	p,p'-DDT	TOTAL DDT
1	1	9	2.07	ND	0.122	0.019—	0.141	5.88	0.92	6.80
2	1	240	5.66	ND	0.163	0.050	0.213	2.07	0.88	2.95
3	4	90	3.55	ND	0.048—	0.024	0.072—	1.34	0.68	2.02
4	4	31	5.56	ND	0.118	0.056	0.174	2.11	1.01	3.12
5	2	9	3.02	ND	0.229	0.096+	0.325	7.60+	3.18+	10.78+
6	1	35	3.38	ND	0.059	0.024	0.083	1.75	0.71	2.46
7	3	44	5.59	ND	0.056	0.019—	0.075	1.02—	0.34—	1.36—
8	1	40	5.70	ND	0.282+	0.084	0.366+	4.95	1.47	6.42
9	8	103	3.43	ND	0.050	0.053	0.103	1.46	1.55	3.01
10	1	121	3.86	ND	0.070	0.027	0.097	1.81	0.70	2.51

NOTE: ND = not detected.
 — = lowest value.
 + = highest value.

TABLE 8. Pesticide residues in human milk from district of Lisbon, Portugal—1972

SAMPLE	NUMBER OF DELIVERIES	DAYS BETWEEN DELIVERY AND SAMPLING	FAT CONTENT, %	ON WHOLE-MILK BASIS, PPM				ON FAT BASIS, PPM		
				DIFLURIN	p,p'-DDE	p,p'-DDT	TOTAL DDT	p,p'-DDE	p,p'-DDT	TOTAL DDT
1	1	23	3.84	ND	0.278	0.180	0.458	7.24	4.68	11.92
2	1	9	2.43	ND	0.353	0.099	0.452	14.53	4.06	18.59
3	1	30	2.00	ND	0.140	0.043	0.183	5.00	1.54	6.54
4	1	33	4.64	ND	0.410	0.134	0.544	8.84	2.89	11.73
1 a	1	38	6.49	ND	0.087	0.059	0.146	1.34	0.91	2.25
2 a	1	48	1.66	ND	0.158	0.040	0.198	9.52	2.41	11.93
3 a	1	324	5.37	ND	0.230	0.068	0.298	4.28	1.27	5.55
4 a	3	28	4.64	ND	0.185	0.081	0.266	3.99	1.75	5.74
5 a	2	198	6.06	ND	0.198	0.128	0.326	3.27	2.11	5.38
1 b	2	104	2.76	ND	0.180	0.051	0.231	6.52	1.85	8.37
2 b	1	23	3.35	ND	0.134	0.044	0.178	3.99	1.31	5.30
3 b	1	26	4.37	ND	0.152	0.073	0.225	3.48	1.67	5.15
4 b	2	24	6.41	ND	0.140	0.095	0.235	2.19	1.48	3.67
1 c	2	120	2.15	ND	0.054	0.029	0.083	2.52	1.35	3.87
2 c	2	30	3.06	ND	0.129	0.056	0.185	4.22	1.83	6.05
3 c	1	99	3.95	ND	0.108	0.034	0.142	2.73	0.86	3.39
4 c	1	36	1.93	ND	0.600+	0.180	0.780+	31.09+	8.70+	39.79+
5 c	3	52	2.15	ND	0.267	0.084	0.351	12.40	3.91	16.31
6 c	3	Unknown	0.98	ND	0.095	0.041	0.136	9.70	4.18	13.88
7 c	1	58	4.11	ND	0.268	0.186	0.454	6.53	4.53	11.06
8 c	1	182	4.36	ND	0.202	0.072	0.274	4.62	1.65	6.27
9 c	3	14	4.32	ND	0.138	0.089	0.227	3.20	2.06	5.26
10 c	2	182	6.16	ND	0.251	0.103	0.354	4.07	1.67	5.74
11 c	2	29	4.71	ND	0.180	0.064	0.244	3.82	1.36	5.18
1 d	1	33	4.52	ND	0.371	0.086	0.457	8.21	1.90	10.11
2 d	1	93	2.83	ND	0.177	0.065	0.242	6.25	2.30	8.55
3 d	3	156	4.81	ND	0.404	0.187	0.591	8.39	3.89	12.28
4 d	1	35	5.62	ND	0.357	0.340+	0.697	6.35	6.05+	12.40
5 d	2	50	5.52	ND	0.315	0.189	0.504	9.98	5.35	15.33

NOTE: ND = not detected.
 — = lowest value.
 + = highest value.

TABLE 9. Pesticide residues in human milk from district of Porto, Portugal—1972

SAMPLE	NUMBER OF DELIVERIES	DAYS BETWEEN DELIVERY AND SAMPLING	FAT CONTENT, %	ON WHOLE-MILK BASIS, PPM				ON FAT BASIS, PPM		
				DIFLURIN	p,p'-DDE	p,p'-DDT	TOTAL DDT	p,p'-DDE	p,p'-DDT	TOTAL DDT
1	6	9	1.89	ND	0.089	0.048	0.137	4.71	2.52+	7.23
2	1	65	6.60	ND	0.248+	0.105+	0.353+	3.75	1.59	5.34
3	4	24	4.05	ND	0.075	0.028	0.103	1.84	0.69	2.53
4	3	114	2.41	ND	0.094	0.025	0.119	3.90	1.04	4.94
5	2	360	2.62	ND	0.077	0.023	0.100	2.91	0.88	3.79
6	3	234	1.92	ND	0.025	0.019	0.044	1.28	0.99	2.27
7	1	57	2.04	ND	0.032	0.028	0.060	1.55	1.37	2.92
8	1	33	2.05	ND	0.031	0.015	0.046	1.51	0.73	2.24
9	2	29	3.91	ND	0.237	0.071	0.308	6.06+	1.82	7.88+
9a	Unknown	89	1.97	ND	0.068	0.032	0.100	3.43	1.62	5.05
10	Unknown	77	3.92	ND	0.145	0.057	0.202	3.70	1.44	5.14
11	Unknown	63	3.54	ND	0.104	0.045	0.149	2.94	1.27	4.21
12	Unknown	32	1.83	ND	0.040	0.016	0.056	2.23	0.87	3.10
13	Unknown	47	2.53	ND	0.059	0.028	0.087	2.33	1.11	3.44
14	1	211	4.37	ND	0.162	0.036	0.198	3.71	0.82	4.53
15	2	65	4.40	ND	0.200	0.066	0.266	4.55	1.50	6.05
16	6	174	2.21	ND	0.022	0.048	0.070	0.93	2.17	3.15
17	1	328	2.02	ND	0.026	0.015	0.041	1.29	0.74	2.03
18	1	176	1.94	ND	0.059	0.027	0.086	3.04	1.39	4.43
19	4	69	4.08	ND	0.084	0.071	0.155	2.06	1.74	3.80
20	1	60	2.78	ND	0.127	0.045	0.172	4.57	1.62	6.19

NOTE: ND = not detected.
 — = lowest value.
 + = highest value.

TABLE 10. Pesticide residues in human milk from district of Setúbal, Portugal—1972

SAMPLE	NUMBER OF DELIVERIES	DAYS BETWEEN DELIVERY AND SAMPLING	FAT CONTENT, %	ON WHOLE-MILK BASIS, PPM				ON FAT BASIS, PPM		
				DIELDRIN	<i>p,p'</i> -DDE	<i>p,p'</i> -DDT	TOTAL DDT	<i>p,p'</i> -DDE	<i>p,p'</i> -DDT	DDT TOTAL
1	Unknown	56	0.41	ND	0.031—	0.014—	0.045—	7.56	3.41	10.97
2	Unknown	Unknown	1.98	ND	0.067	0.035	0.102	3.38	1.77	5.15
3	Unknown	8	2.27	ND	0.309	0.176	0.485	13.61	7.75+	21.36+
4	Unknown	238	5.27	ND	0.166	0.130	0.296	3.14—	2.47	5.61
5	Unknown	124	5.51	ND	0.220	0.085	0.305	3.99	1.54	5.53
6	Unknown	28	4.83	ND	0.403	0.183+	0.586	8.34	3.79	12.13
7	5	11	1.38	ND	0.058	0.028	0.086	4.17	2.03	6.20
8	1	17	2.51	ND	0.087	0.047	0.134	3.48	1.87	5.35
9	2	186	2.02	ND	0.066	0.029	0.095	3.27	1.44	4.71—
11	1	210	2.57	ND	0.190	0.075	0.265	7.40	2.92	10.32
12	2	63	5.93	ND	0.229	0.076	0.305	3.86	1.28—	5.14
13	4	68	2.70	ND	0.112	0.061	0.173	4.13	2.26	6.39
14	3	164	1.17	0.006	0.038	0.024	0.062	3.28	2.05	5.33
15	1	40	2.97	ND	0.516+	0.113	0.629+	17.37+	3.80	21.17

NOTE: ND = not detected.
 — = lowest value.
 + = highest value.

TABLE 11. Pesticide residues in human milk from district of Viana do Castelo, Portugal—1972

SAMPLE	NUMBER OF DELIVERIES	DAYS BETWEEN DELIVERY AND SAMPLING	FAT CONTENT, %	ON WHOLE-MILK BASIS, PPM				ON FAT BASIS, PPM		
				DIELDRIN	<i>p,p'</i> -DDE	<i>p,p'</i> -DDT	TOTAL DDT	<i>p,p'</i> -DDE	<i>p,p'</i> -DDT	TOTAL DDT
1	1	61	2.34	ND	0.072	0.031	0.103	3.09	1.32	4.41
2	2	50	2.75	ND	0.076	0.053	0.129	2.76	1.93	4.69
3	1	5	0.40	ND	0.020	0.019	0.039	5.00	4.75+	9.75+
4	2	178	1.94	ND	0.123	0.048	0.171	6.44+	2.47	8.91
5	1	43	5.08	ND	0.146+	0.113+	0.259+	2.87	2.22	5.09
6	2	18	1.52	ND	0.042	0.015	0.057	2.74	0.99	3.73
7	2	324	3.89	ND	0.083	0.047	0.130	2.14	1.21	3.35
8	2	232	1.58	ND	0.019	0.010	0.029	1.17—	0.63—	1.80—
10	3	110	0.45	ND	0.007—	0.003—	0.010—	1.56	0.67	2.23

NOTE: ND = not detected.
 — = lowest value.
 + = highest value.

TABLE 12. Pesticide residues in human milk from district of Vila Real, Portugal—1972

SAMPLE	NUMBER OF DELIVERIES	DAYS BETWEEN DELIVERY AND SAMPLING	FAT CONTENT, %	ON WHOLE-MILK BASIS, PPM				ON FAT BASIS, PPM		
				DIELDRIN	<i>p,p'</i> -DDE	<i>p,p'</i> -DDT	TOTAL DDT	<i>p,p'</i> -DDE	<i>p,p'</i> -DDT	TOTAL DDT
1	3	129	2.02	ND	0.043	0.020	0.063	2.11	0.99	3.10
2	1	159	3.97	ND	0.100	0.047	0.147	2.52	1.18	3.70
3	9	78	1.31	ND	0.025—	0.010—	0.035—	1.87	0.76—	2.63
4	10	132	1.27	ND	0.043	0.024	0.067	3.41	1.89	5.30
5	1	41	4.01	ND	0.155	0.058+	0.213	3.86	1.44	5.30
6	1	16	1.69	ND	0.107	0.044	0.151	6.33+	2.60	8.93+
7	4	62	3.94	ND	0.065	0.033	0.098	1.66—	0.84	2.50—
8	1	20	3.99	ND	0.204+	0.048	0.252+	5.11	1.20	6.31
9	4	30	1.32	ND	0.054	0.055	0.109	4.06	4.17+	8.23

NOTE: ND = not detected.
 — = lowest value.
 + = highest value.

TABLE 13. Pesticide residues in human milk from district of Viseu, Portugal—1972

SAMPLE	NUMBER OF DELIVERIES	DAYS BETWEEN DELIVERY AND SAMPLING	FAT CONTENT, %	ON WHOLE-MILK BASIS, PPM				ON FAT BASIS, PPM		
				DIELDRIN	p,p'-DDE	p,p'-DDT	TOTAL DDT	p,p'-DDE	p,p'-DDT	TOTAL DDT
1	3	65	1.67	ND	0.066	0.042	0.108	3.92	2.51	6.43
2	4	88	1.85	ND	0.021	0.018	0.039	1.14	0.97	2.11
3	4	208	1.40	ND	0.015	0.011	0.026	1.04	0.79	1.83
5	1	18	1.91	ND	0.036	0.012	0.048	1.86	0.63	2.49
6	1	17	3.42	0.009	0.057	0.057	0.114	1.67	1.67	3.34
7	4	193	3.71	0.005	0.008	0.009	0.017	0.22-	0.24-	0.46-
8	1	90	1.05	ND	0.027	0.013	0.040	2.57	1.24	3.81
9	2	128	3.63	0.017	0.032	0.016	0.048	0.87	0.44	1.31
11	1	164	2.19	ND	0.044	0.022	0.066	1.99	1.00	2.99
12	1	218	1.84	0.015	0.021	0.016	0.037	1.13	0.85	1.98
13	6	164	0.80	0.005	0.006-	0.004-	0.010	0.62	0.44	1.06
14	2	83	1.81	ND	0.020	0.020	0.040	1.10	1.11	2.21
15	2	18	2.75	ND	0.109+	0.158+	0.267+	3.97	5.73+	9.70+
16	2	93	0.96	ND	0.041	0.014	0.055	4.22+	1.46	5.68
17	1	42	3.19	ND	0.047	0.025	0.072	1.47	0.78	2.25
18	3	69	2.54	0.021	ND	ND	0.01-	ND	ND	-
19	1	20	1.49	ND	0.029	0.028	0.057	1.92	1.88	3.80
20	5	22	2.12	ND	0.018	0.011	0.029	0.83	0.52	1.35

NOTE: ND = not detected.
 - = lowest value.
 + = highest value.

Tables 14 and 15 show that lowest mean levels of DDT were found in the rural districts Bragança and Viseu. The highest mean level was found in the district of Lisbon. Various other authors have reported lower contamination levels in rural areas than in urban areas (16,18,21).

Kroger (12) observed that mothers nursing firstborn children showed higher levels of DDT than did other mothers. This may account for the difference observed between mean levels in nursing mothers in the district of Lisbon and those in Bragança, but could hardly justify the difference in relation to Viseu. However, it is not only the number of deliveries that influences an individual's contamination levels, but also the number of days separating sampling from delivery, and the individual's dietary habits. Authors have not drawn conclusions regarding the influence of each of these factors.

Dieldrin was detected in 15 of 222 samples examined; levels ranged from 0.006 to 0.031 ppm. The district of Viseu showed the highest percentage of samples containing this insecticide; it was found in 33 percent of the samples collected in that area. In Bragança, 20 percent of the samples had dieldrin residues. Similar dieldrin levels have been reported by various authors (6,7,10,13,16,19-22). Most significant is the Japanese study in which residues of this insecticide were found in 74.6 percent of 398 samples of human milk (16). In Australia, Newton observed that in 67 samples examined, about 43 percent contained dieldrin residues (18).

Apart from DDT and dieldrin, BHC isomers are the pesticides which have been most widely reported in human milk. In the present case, γ BHC was detected in some samples but, because of its low level, was not measured. This was the only isomer reported by Westoo et al. in human milk in Sweden (10) but the β isomer has been detected at very high levels by various authors (13,16,19-21).

TABLE 14. Total DDT residues in human whole milk, Portugal—1972

DISTRICT	RESIDUES, MG/KG			AVERAGE STANDARD DEVIATION	NUMBER OF DELIVERIES
	MINIMUM	MAXIMUM	MEAN		
Aveiro	0.047	0.743	0.283	± 0.265	2.1
Bragança	0.010	0.149	0.063	± 0.034	4.4
Évora	0.031	0.837	0.269	± 0.241	1.7
Faro	0.038	0.272	0.146	± 0.094	1.6
Guarda	0.072	0.366	0.165	± 0.106	2.6
Lisbon	0.083	0.780	0.326	± 0.175	1.6
Porto	0.041	0.353	0.136	± 0.088	Unknown
Portalegre	0.057	0.606	0.256	± 0.181	2.1
Setúbal	0.032	0.629	0.252	± 0.197	Unknown
Vila Real	0.035	0.252	0.126	± 0.072	3.8
Viana do Castelo	0.010	0.259	0.103	± 0.079	1.8
Viseu	<0.010	0.343	0.064	± 0.075	2.4

TABLE 15. Converted mean of total DDT residues in human whole milk submitted to the \sqrt{x} transformation, Portugal—1972

COUNTY OR DISTRICT	CONVERTED MEAN, MG/KG	SIGNIFICANCE LEVEL, % ¹
Odivelas ²	0.4778	1
Amadora ²	0.3831	1
Loures ²	0.2570	1
Caneças ²	0.2396	1
Damaia ²	0.2163	5
Portalegre	0.2122	1
Aveiro	0.2067	1
Évora	0.2051	1
Setúbal	0.1962	1
Guarda	0.1453	5
Faro	0.1243	NS
Porto	0.1178	5
Vila Real	0.1121	NS
Viana do Castelo	0.0798	NS
Viseu	0.0415	NS
Bragança	0.0564	NS

NOTE: NS = not significant.
¹ Significance levels determined by the Dunnet test (Dunnet, 1964).
² Towns in the district of Lisbon.

In the present study of human milk in Portugal, samples also contained traces of HCB which were not measured. HCB was detected in human milk in Australia (18) and in France (13,20).

TABLE 16. Professions of lactating women whose milk was analyzed, Portugal—1972

DISTRICT	NUMBER OF MOTHERS QUESTIONED	HOMEMAKERS	CIVIL SERVANTS	FACTORY WORKERS	FARMWORKERS	OTHER ¹
Aveiro	10	9				1
Bragança	19	19				
Evora	10	8	1			1
Faro	5	4		1		
Guarda	10	9				1
Lisbon	29	25	1	1		2
Porto	22	20	2			
Portalegre	10	9	1			
Setúbal	15	14			1	
Vila Real	10	8	1			
Viano do Castelo	10	10				1
Viseu	20	19	1			

¹ Dressmakers, office assistants, and shop assistants.

Some authors have also detected lindane (7,10,22,23), heptachlor epoxide (6,7,13,20,22,23), endrin (16), aldrin (16), and PCB's (10,19), but none of these products was detected in human milk in Portugal. PCB's were not even sought during this work.

Comparing mean residues of total DDT detected in each of the districts of Portugal with values published in other countries and tabulated in a paper presented by Ritcey et al. (22), values found in Portugal are all higher than those in the Netherlands (0.048 ppm) and are all lower than those published in works on Romania (0.530 ppm) and Poland (0.40 ppm). It may be concluded that mean residues of total DDT in Portugal were generally similar to those of other European and North American countries.

The sale of DDT, BHC, and heptachlor was forbidden in Portugal after January 1, 1974, and the use of aldrin, dieldrin, and endrin has been greatly restricted. It is hoped that the problem of unintentional contamination by organochlorine pesticides in our country will begin to right itself, however slowly.

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LITERATURE CITED

- (1) Laug, E. P., F. M. Kunze, and C. S. Prickett. 1951. Occurrence of DDT in human fat and milk. *Arch. Industr. Hyg.* 3(3):245-246.
- (2) De Faubert Maunder, M. J., H. Egan, E. W. Godly, E. W. Hammond, J. Roburn, and J. Thomson. 1964. Cleanup of animal fats and dairy products for the analysis of chlorinated pesticide residues. *Analyst* 89: 168-174.

- (3) Jeffers, J. N. R. 1960. Experimental design and analysis in forest research. Almqvist and Wiksell, Stockholm.
- (4) Dunnet, C. W. 1964. New tables for multiple comparison with a control. *Biometrics* 20:482-491.
- (5) Quinby, G. E., J. F. Armstrong, and W. F. Durham. 1965. DDT in human milk. *Nature* 207:726-728.
- (6) Curley, A., and R. Kimbrough. 1969. Chlorinated hydrocarbon insecticides in plasma and milk of pregnant and lactating women. *Arch. Environ. Health* 18:156-164.
- (7) Heyndrickx, A., and R. Maes. 1969. The excretion of chlorinated hydrocarbon insecticides in human mother milk. *J. Pharm. Belg.* 24:459-463.
- (8) Gracheva, G. V. 1969. The possibility of DDT accumulation in the organism of persons not having occupational contact with it. *Faktery Vneshn. Sredy i ikh Znachen. dlia Zdorov'ia Naseleni* 1:125-129. Cited from *Health Aspects Pestic. Abstr. Bull.* 1970, 3:1304.
- (9) Komorova, L. I. 1970. DDT excretion with the breast milk and its effect on the body of the mother and child. *Pediatr. Akusherstvo Hinekol.* 35(1):19-20. Cited from *Health Aspects Pestic. Abstr. Bull.* 1971, 4:474.
- (10) Westoo, G., K. Norén, and M. Anderson. 1970. The levels of organochlorine pesticides and polychlorinated biphenyls in margarine, vegetable oils, and some foods of animal origin on the Swedish market in 1967-1969. *Klorpesticid-och polyklorbi fenylhalter i margarin, vegetabla matoljor och vissa animala livsmedel i svensk handel åren 1967-1969. Vår föda* 22(2-3): 9-31.
- (11) Tuinstra, L. G. M. Th. 1971. Organochlorine insecticide residues in human milk in the Leiden region. *Ned. Melk-Zuiveltijdschr.* 25(1):24-32. Cited from *Health Aspects Pestic. Abstr. Bull.* 1971, 4:2118.
- (12) Kontek, M., S. Kubacki, S. Paradowski, and B. Wierzychowiecka. 1971. Study of the level of organochlorine pesticides in human milk. *Badanie zawartosci pestycydow chloroorganicznych w mleku kobiecym. Pediat. Pol.* 46(2):183-188. Cited from *Health Aspects Pestic. Abstr. Bull.* 1971, 4:1619.
- (13) Goursaud, J., F. M. Luquet, and J. Casalis. 1971. Pesticide residue contamination of human milk in the northern provinces of France and Pas-de-Calais. *Sur la pollution des laits de femme par les résidues de pesticides dans les départements du Nord et du Pas-de-Calais. Lait* 51:559-567.
- (14) Dymont, P. G., L. M. Hebertson, E. D. Gomes, J. S. Wiseman, and R. W. Hornabrook. 1971. Absence of

- polychlorinated biphenyls in human milk and serum from Texas and human milk from New Guinea. *Bull. Environ. Contam. Toxicol.* 6:532-534.
- (15) *Sugaya, T., et al.* 1971. Organochlorine pesticide residues in human milk. *Nippon Noson Igakkai Zasshi* 19(4):379-380. Cited from *Health Aspects Pestic. Abstr. Bull.* 1972, 5:1644.
- (16) *Anonymous.* 1972. BHC and DDT residues in human milk on the decline in Japan. *Noyaku Bijinesu (Pestic. Business)* 56:458. Cited from *Health Aspects Pestic. Abstr. Bull.* 1972, 5:1660.
- (17) *Juszkiewicz, T., J. Stec, T. Radomanski, and B. Trebicka-Kwiatkowska.* 1972. Residues of organochlorine insecticides in the colostrum and milk of women after delivery *Pol. Tyg. Lek.* 27(17):616-619. Cited from *Health Aspects Pestic. Abstr. Bull.* 1972, 5:1875.
- (18) *Newton, K. G., and N. C. Greene.* 1972. Organochlorine pesticide residue levels in human milk—Victoria, Australia—1970. *Pestic. Monit. J.* 6(1):4-8.
- (19) *Hidaka, K., T. Ohe, and K. Fujiwara.* 1972. PCB and organochlorine pesticides in mother's milk. *Igaku No Ayumi (Progr. Med.)* 82(8):519-520. Cited from *Health Aspects Pestic. Abstr. Bull.* 1972, 5:2306.
- (20) *Luquet, F. M., J. Goursaud, and B. Gaudier.* 1972. Study of the pollution of human milk by residual pesticides. *Etude de la pollution des laits humains par les residues de pesticides. Pathol. Biol.* 20:137.
- (21) *Kuroda, H., T. Yano, K. Kagawa, and M. Mitsumune.* 1972. On the residual organochlorine pesticides in mother's milk. *Shikoku Koshu Eiseigakkai Zasshi (J. Shikoku Pub. Health Soc.)* 17:79-80. Cited from *Health Aspects Pestic. Abstr. Bull.* 1972, 5:2331.
- (22) *Ritcey, W. R., G. Savary, and K. A. McCully.* 1972. Organochlorine insecticide residues in human milk, evaporated milk and some milk substitutes in Canada. *Can. J. Pub. Health* 63:125-133.
- (23) *Kroger, M.* 1972. Insecticide residues in human milk. *J. Pediat.* 80:401-405.

PESTICIDES IN WATER

*A Study of the Distribution of Polychlorinated Biphenyls in the Aquatic Environment*¹

Hans J. Crump-Wiesner,² Herman R. Feltz,³ and Marvin L. Yates⁴

ABSTRACT

Data gathered from monitoring activities and project studies indicate the ubiquitous occurrence and distribution of polychlorinated biphenyls (PCB's) in the aquatic environment. By 1972 residues had been detected in samples from 19 States representing nearly every region of the country. These findings permit a preliminary assessment of PCB contamination across the Nation: concentrations ranged from 0.1 to 4.0 µg/liter in unfiltered water samples and from 5.0 to 3,200 µg/kg in bottom sediments. PCB residues were also found in fish and aquatic plants. Samples were prepared by the same techniques used for general chlorinated insecticide detection, with special attention to cleanup and separation of PCB's from other compounds. Basic identification and quantification were made by dual-column electron-capture/gas-liquid chromatography and confirmed by gas-liquid chromatography/mass spectrometry whenever possible. In sediment samples from a south Florida drainage ditch, polychlorinated naphthalenes (PCN's) were observed. This is possibly the first evidence of PCN's in an environmental sample and illustrates the importance of developing analytical capability for the surveillance of other organochlorine compounds that may behave like chlorinated hydrocarbon pesticides.

The sampling program is broadening geographically and gradually increasing to more adequately define the distribution of PCB residues in major drainage basins of the United States.

Introduction

Within the past few years, polychlorinated biphenyls (PCB's) have been identified as a major environmental contaminant. Their detection has caused widespread concern and has generated intense interest in data relating to the presence and effects of these compounds, particularly in the aquatic environment. First produced about 40 years ago, PCB compounds have become increasingly useful in such industrial applications as components in transformers and capacitors, heat exchangers, paints, inks, dyes, and dust control agents.

Although much attention has been focused on estimating levels and potential hazards of PCB's in aquatic organisms, few data are available on the occurrence of PCB's in water and bottom sediments. The Geological Survey, U.S. Department of Interior, through its water-quality-monitoring activities and water-resources-assessment projects, has been alert to the PCB problem since it was first reported by Widmark in 1967 (1). Although the Geological Survey has no nationwide PCB assessment program, sufficient data have accumulated from pesticide residue programs to permit a preliminary assessment of PCB contamination of the Nation's hydrologic environment. This paper presents data gathered from these activities, showing the widespread occurrence of PCB's in significant concentrations in unfiltered surface water and ground water, bottom sediments, flora, and fauna.

Analytical Techniques

PCB residues were analyzed by the multiple-pesticide-residue methods for water, suspended sediment, and bottom material described by Goerlitz and Brown (2). Analytical procedures are appropriate for chlorinated pesticides as well as the general class of organochlorine

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compounds. Special attention was given to cleanup and separation of PCB's from coextractives.

EXTRACTION OF WATER, SEDIMENT, AND BIOTA

One-liter unfiltered water samples were collected in pre-cleaned glass bottles and extracted three times with hexane. The hexane portions were combined, dried with anhydrous Na_2SO_4 , and concentrated to 1 ml before cleanup and analysis by electron-capture/gas-liquid chromatography (EC/GLC).

Fifty-gram sediment samples (dry-weight basis) were extracted with an acetone-hexane solvent. The sediment was dispersed first in acetone, and hexane was added to recover the acetone and the desorbed material. The extract was washed with distilled water, dried over Na_2SO_4 , and concentrated to 5 ml for cleanup before EC/GLC analysis.

The two extraction procedures used for biota are described in an analytical manual issued by the Food and Drug Administration, U.S. Department of Health, Education, and Welfare (3). Fish samples were extracted with petroleum ether in a blender; aquatic plants were extracted with acetonitrile. The chlorinated hydrocarbon fraction was partitioned between petroleum ether and acetonitrile, dried, and concentrated to a final volume of 5 ml.

SEPARATION

Bottom sediment, fish, and plant extracts were cleaned following the Law and Goerlitz technique (4) requiring less time and smaller volumes of solvents for elution than do other widely used methods. Liquid/solid column chromatography was employed using two different types of semimicro columns in sequence (Fig. 1). Hexane extracts were first passed through an alumina column, and one fraction was further chromatographed on silica gel to separate PCB's from chlorinated insecticides. Successive chromatography on alumina and silica gel results in a simultaneous cleanup and separation of PCB's from the common insecticides, except aldrin, and a slight overlap of *p,p'*-DDE. To achieve a reduction in background interference, mercury was added to remove sulfur from bottom sediment extracts before they were applied to the silica column.

In order to insure reproducible chromatographic conditions, the activity of the adsorbents was carefully controlled. Water extracts were cleaned on a deactivated alumina microcolumn (5). When PCB's were detected in the cleaned water extracts, they were also separated on a semimicro silica gel column.

IDENTIFICATION

Basic identification was made by dual-column EC/GLC (DC-200 and QF-1/OV-17) and confirmed by gas-liquid chromatography/mass spectrometry (GLC/MS) when sample size and concentrations were sufficient. The amount of PCB's was determined by matching the

unknown peaks on the chromatogram to the nearest commercial formulation and measuring the areas of four corresponding peaks. Retention time and peak area measurements were made with a digital electronic integrator. The lower detection limit for PCB residues was $0.1 \mu\text{g}/\text{liter}$ in water and $5.0 \mu\text{g}/\text{kg}$ in bottom sediment. Reported levels are subject to considerable error because of the complexity of multiple peaks, some peak alteration, and the occasional presence of mixtures of PCB's in environmental samples. At best, reported values are estimates that may be as much as 50 percent in error.

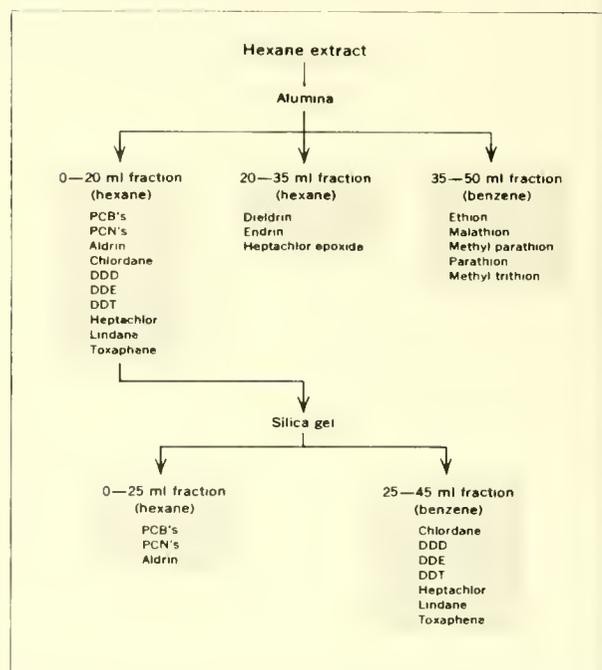


FIGURE 1. Scheme for separating polychlorinated biphenyls (PCB's) and polychlorinated naphthalenes (PCN's) from pesticides

DATA DESCRIPTION

Occurrences of pesticide residues in the aquatic environment have been documented over a period of years through monitoring programs of several Federal agencies. As early as 1957, studies of chlorinated hydrocarbon pesticides in major river basins were made by the Federal Water Pollution Control Administration, now a part of the U.S. Environmental Protection Agency, by use of the carbon-adsorption technique (6). In 1964 interagency cooperation in pesticide monitoring programs culminated in a proposal to begin a national monitoring program. The original program for water was described in 1967 in the first issue of the *Pesticides Monitoring Journal* (7). The purpose of this program, which was revised in 1971 (8), is to provide continuing information on levels of pesticide residues in the water resources of the Nation and to identify possible problem areas. Because PCB's are analyzed by the

multiple-pesticide residue techniques, routine reporting of these compounds has been incorporated into current pesticide programs. At present, samples from 20 of the 161 proposed network sites are collected and analyzed by the Geological Survey. All samples are collected from sites west of the Mississippi River and provide continuity with a network established to evaluate the quality of water used for irrigation (9,10). Budgetary restrictions have prevented further implementation of the network.

After development of the technique to separate PCB's from pesticide residues, examination for the presence of PCB's in water and suspended and bottom sediment samples collected for the National Monitoring Program began in January 1971. Funding was requested to increase the number of network stations to 50 in 1973, and to 100 in 1974, allowing a better assessment of PCB's and pesticides in major drainage basins throughout the United States. Analysis of 194 water samples and 33 bottom sediment samples revealed no positive identifications of PCB's; however, these data are not truly representative of the entire Nation because of the limited number of sites sampled.

In 1958, the Geological Survey began operation of a bench-mark network to provide basic hydrologic data

on selected stream basins throughout the United States that are expected to remain in their present natural condition or are not expected to be significantly altered by humans. Locations of the 57 bench marks established in 37 States are shown in Figure 2.

To insure minimum interference by humans, many of the hydrologic bench marks are in national parks, wilderness areas, State parks, national forests, and areas set aside for scientific study. A detailed description of the network basins, including drainage, climate, topography, geology, vegetation, hydrology, water quality, and personmade influences, appears in a report by Cobb and Biesecker (11). Data gathered from 46 of these sites are presented in Table 1. Despite the careful screening for pristine location of bench-mark sites, two bottom sediment samples analyzed in the 1972 water year contained PCB residues. A value of 5.2 $\mu\text{g}/\text{kg}$ was measured in the sample from South Fork Rocky Creek near Briggs, Tex., and 8.8 $\mu\text{g}/\text{kg}$ was found in the sample from Upper Twin Creek at McGaw, Ohio.

The majority of the Geological Survey water resources studies are conducted in cooperation with State water resources and pollution control agencies, or in response to requests from other Federal agencies. PCB data from these programs in 35 States are presented in Tables 2-4.

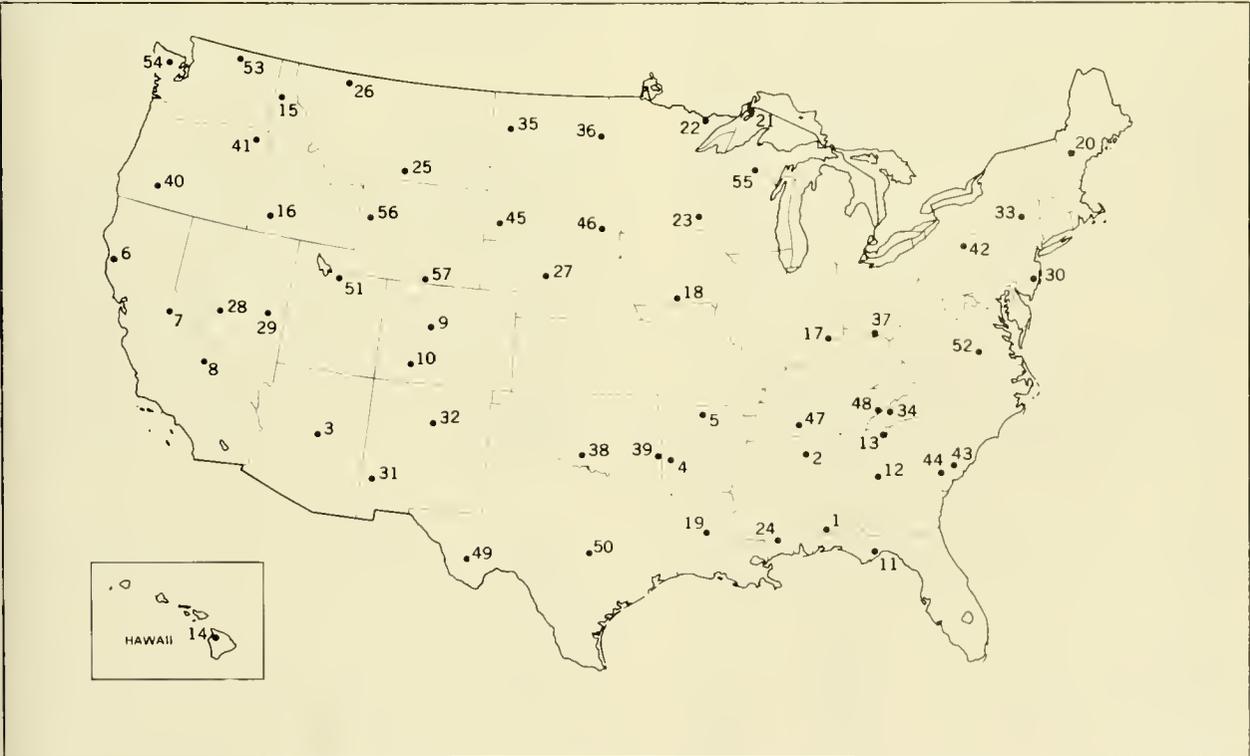


FIGURE 2. Map showing hydrologic bench-mark stations. (Numbers refer to list in Cobb and Biesecker; refer to Literature Cited, reference 1.)

TABLE 1. Summary of PCB residue data, national hydrologic bench-mark network, January 1971-June 1972

TYPE OF SAMPLE	UNIT	NO. SAMPLES	OCCURRENCES	CONCENTRATION
Water	μg/liter	54	0	
Bottom sediment	μg/kg	51	2	5.2, 8.8

TABLE 4. Summary of PCB residue data from selected sampling sites in Florida, January 1971-June 1972

TYPE SAMPLE	NO. SAMPLES	OCCURRENCES	CONCENTRATION, RANGE ¹	MEDIAN CONCENTRATION ¹
Water	231	12	0.1-2.1	0.2
Bottom sediment	118	50	5-3,200	30
Flora	16	5	10-50	20
Fauna	43	36	6-1,000	40

¹ Unit of measure: μg/liter for water samples, μg/kg for other samples.

TABLE 2. Summary of PCB residue data for surface and ground water, January 1971-June 1972

STATE	NO. SAMPLES	OCCURRENCES	CONCENTRATION, μg/LITER	MEDIAN CONCENTRATION, μg/LITER
Alaska	3	0	ND	ND
Arizona	8	0	ND	ND
Arkansas	32	0	ND	ND
California	161	2	0.1, 0.1	ND
Colorado	32	1	0.3	ND
Connecticut	13	6	0.1-0.2	0.1
Hawaii	5	0	ND	ND
Iowa	24	0	ND	ND
Kansas	10	0	ND	ND
Kentucky	7	0	ND	ND
Louisiana	9	0	ND	ND
Maine	2	0	ND	ND
Maryland	6	1	0.1	ND
Massachusetts	5	1	0.2	ND
Michigan	2	0	ND	ND
Minnesota	3	2	0.1, 0.3	ND
Mississippi	8	0	ND	ND
Missouri	21	0	ND	ND
Montana	47	0	ND	ND
Nebraska	44	0	ND	ND
New Jersey	11	3	0.1	0.1
New Mexico	36	0	ND	ND
New York	325	52	0.1-4.0	0.3
North Dakota	40	0	ND	ND
Oklahoma	19	0	ND	ND
Oregon	13	0	ND	ND
Pennsylvania	2	1	0.2	ND
Puerto Rico	7	1	0.1	ND
South Dakota	18	0	ND	ND
Texas	660	12	0.1-3.0	0.4
Virginia	4	1	0.1	ND
Washington	25	0	ND	ND
West Virginia	4	0	ND	ND
Wisconsin	3	0	ND	ND
Wyoming	18	0	ND	ND

NOTE: ND = not detected.

TABLE 3. Summary of PCB residue data for bottom sediments, January 1971-June 1972

STATE	NO. SAMPLES	OCCURRENCES	CONCENTRATION, μg/kg	MEDIAN CONCENTRATION, μg/kg
Alaska	3	0	ND	ND
Arkansas	3	4	20-2,400	60
California	13	3	20-190	85
Connecticut	1	1	40	ND
Hawaii	4	0	ND	ND
Georgia	12	10	10-1,300	300
Maryland	11	5	10-1,200	30
Mississippi	8	2	50:170	ND
New Jersey	12	10	8-250	20
Oregon	4	2	15:140	ND
Pennsylvania	16	11	10-50	20
South Carolina	11	8	30-200	50
Texas	293	23	7.9-290	80
Virginia	10	8	5-80	40
Washington	10	0	ND	ND
West Virginia	2	1	10	ND

NOTE: ND = not detected.

Water samples alone, because of the low water solubility of PCB's, are not a good indicator of the widespread occurrence of the compounds, and show an incidence of slightly over 5 percent. Unfiltered water samples from 12 of the 35 States had PCB concentrations ranging from 0.1 to 4.0 μg/liter. However, a significant number of suspected traces of PCB's were not reported because of several analytical limitations. Generally, re-sampling of areas where PCB's were first detected revealed that the compounds were still present several months later.

Bottom sediments were collected concurrently with many of the water samples reported in Table 2. These samples were taken from lakes and streams that drain a variety of land-use areas generally located away from industrial centers. Data in Table 3 show that bottom sediment samples may be used as an indicator of PCB contamination in the Nation's hydrologic environment. Significantly, of samples collected at random from 16 States, 13 contained PCB's in the range of 5.0 to 2,400 μg/kg. Across the Nation, one of every five bottom sediment samples contained PCB's.

Data available from Florida (Table 4) merit special attention because they reveal the distribution of residues in several environmental components. Only 12 of 231 unfiltered water samples contained PCB's ranging from 0.1 to 2.1 μg/liter, but over 40 percent of the associated bottom sediments analyzed during the same period were contaminated with PCB's ranging from 5.0 to 3,200 μg/kg. Median PCB concentrations of 20 μg/kg and 40 μg/kg found in aquatic plants and fish, respectively, follow the scheme of the biological accumulation of the DDT family in southern Florida (12).

Results and Discussion

Preliminary data presented in this report indicate that significant concentrations of PCB's are widespread in the water resources of the Nation. However, there are some shortcomings of data compiled from pesticide residue programs. First is the problem of nonrepresentative sampling within States and some repetition of sampling in a given basin. Second, the lower limit of detection for PCB residues on the basis of a one-liter water sample is inadequate for critical evaluation. Trace amounts of less than 0.1 μg/liter were detected in a

significant number of samples but were excluded from the tabulation because they could not be confirmed. Third, because of the low solubility of PCB's in water, especially the higher chlorinated ones, the bulk of PCB residues in streams are associated with suspended sediment and bottom material. Therefore, PCB concentrations may be expected to vary directly with the suspended sediment concentration in the cross section of a stream. Most surface water samples were collected by depth integration at the center of flow, which usually does not provide a representative sample of suspended sediment. Future investigations should be made with a depth-integrating sampler using the equal-transit-rate procedure (12). In spite of these shortcomings, evidence for the ubiquity of PCB's in the hydrologic environment is clearly established.

As others have pointed out (13), polychlorinated naphthalenes (PCN's) are compounds that have uses similar to PCB's and may possibly be present in environmental samples. They can be separated from chlorinated hydrocarbon insecticides and are eluted in the same fraction as PCB's by alumina/silica gel column chromatography. Sediment samples collected from a south Florida drainage ditch contained mixtures of PCN's ranging from 1,250 to 5,000 $\mu\text{g}/\text{kg}$, whereas water samples overlying the sediments averaged 5.7 $\mu\text{g}/\text{liter}$. Identification was confirmed by both microcoulometry and GLC/MS. This is possibly the first evidence of PCN's in an environmental sample and illustrates the importance of developing analytical capability for the surveillance of other organochlorine compounds that may behave like chlorinated hydrocarbon pesticides.

It is probable that PCB's enter the aquatic environment through low-temperature incineration of solid wastes, industrial waste disposal into waterways, and sewage outfalls. The highest levels are usually associated with industrial areas and nearby aquatic food chains. In contrast, authors have noticed significant concentrations in the bottom sediments of drainage ditches, multipurpose canals, and suburban real estate lakes remote from major industrial and metropolitan areas. The presence of PCB's in real estate lakes has been attributed to a variety of construction materials used in the housing industry. PCB's in surface and ground water used for public water supplies were detected through cooperative programs. The highest concentration was 4.0 $\mu\text{g}/\text{liter}$ in an untreated source for a city in the State of New York.

It is clear that the presence of PCB's and other organochlorine compounds in the aquatic environment merits continuing observation because of the limited evaluation that can be made from the meager data available. It is important to measure baseline levels of PCB's in streams and lakes in order to determine trends. Long-term monitoring on a systematic basis will provide the data necessary to assess the presence of PCB residues and concurrently reveal problem areas.

LITERATURE CITED

- (1) *Widmark, G.* 1967. Pesticide residues, possible interference by chlorinated biphenyls. In Proceedings of the IUPAC Commission on the Development, Improvement, and Standardization of Methods of Pesticide Residue Analysis, J. Ass. Offic. Anal. Chem. 50(5):1069.
- (2) *Goerlitz, D. F., and Eugene Brown.* 1972. Methods for analysis of organic substances in water. U.S. Geol. Survey Techniques Water Resources Inv. TWI 5-A3. 40 pp. (Book 5, Laboratory Analysis.)
- (3) *U.S. Department of Health, Education, and Welfare—Food and Drug Administration.* 1971. Pesticide analytical manual. Vol. 1.
- (4) *Goerlitz, D. F., and L. M. Law.* 1974. Determination of chlorinated insecticides in suspended sediment and bottom material. J. Ass. Offic. Anal. Chem. 57(1):176-181.
- (5) *Law, L. M., and D. F. Goerlitz.* 1970. Microcolumn chromatographic cleanup for the analysis of pesticides in water. J. Ass. Offic. Anal. Chem. 53:1276-1286.
- (6) *Breidenbach, A. W., et al.* 1964. The identification and measurement of chlorinated hydrocarbon pesticides in surface waters. U.S. Pub. Health Serv. Publ. 1241. 70 pp.
- (7) *Green, R. S., and S. K. Love.* 1967. Network to monitor hydrologic environment covers major drainage rivers. Pestic. Monit. J. 1(1):13-16.
- (8) *Feltz, H. R., W. T. Sayers, and H. P. Nicholson.* 1971. National monitoring program for the assessment of pesticide residues in water. Pestic. Monit. J. 5(1):54-62.
- (9) *Brown, Eugene, and Y. A. Nishioka.* 1967. Pesticides in selected western streams—a contribution to the National Program. Pestic. Monit. J. 1(2):28-46.
- (10) *Manigold, D. B., and J. A. Schulze.* 1969. Pesticides in selected western streams—a progress report. Pestic. Monit. J. 3(2):124-135.
- (11) *Cobb, E. D., and J. E. Biesecker.* 1971. The national hydrologic bench-mark network. U.S. Geol. Surv. Circ. 460-D. 38 pp.
- (12) *Feltz, H. R., and J. A. Culbertson.* 1972. Sampling procedures and problems in the determination of pesticide residues in the hydrologic environment. Pestic. Monit. J. 6(3):171-178.
- (13) *Goerlitz, D. F., and L. M. Law.* 1972. Chlorinated naphthalenes in pesticide analysis. Bull. Environ. Contam. Toxicol. 7:243-251.

RESIDUES IN FISH, WILDLIFE, AND ESTUARIES

*Chlorinated Hydrocarbon Pesticide Residues in Oysters (*Crassostrea commercialis*) in Moreton Bay, Queensland, Australia, 1970-72¹*

Donald Edward Clegg

ABSTRACT

A 2-year survey was carried out to monitor levels of DDT, DDD, DDE, and dieldrin in oysters (*Crassostrea commercialis*) in Moreton Bay, Queensland, Australia. Samples were taken at quarterly intervals from eight stations located at or near the mouths of streams entering the bay.

Highest levels of 0.94 ppm DDT, 0.51 ppm DDD, 0.20 ppm DDE, and 0.34 ppm dieldrin were found in July 1970 at the sampling station on the Brisbane River 16 km downstream from the center of Brisbane, a city of 700,000. Maximum values at other stations were substantially lower.

Residue levels varied considerably throughout the 2-year period. Authors attribute this at least in part to seasonal rainfall patterns in the catchment areas.

Introduction

A program to monitor chlorinated hydrocarbon pesticide residues in oysters (*Crassostrea commercialis*) in Moreton Bay, Queensland, Australia, was begun in April 1970 and continued approximately at quarterly intervals until March 1972. The oyster was chosen as an indicator organism partly because of its ubiquity and immobility but mainly because Butler et al. have shown that it has a marked ability to concentrate certain chlorinated hydrocarbons from the surrounding water and, when subsequently placed in clean water, is able to purge itself rapidly of these compounds (1). These characteristics are useful not only in helping to determine geographical distribution of pesticides in this region but also in facilitating observation of seasonal variations of pesticide levels, particularly as a result of changes in the flow volume of fresh water in adjacent streams.

Moreton Bay is formed by two large sandy islands, Moreton and Stradbroke. The bay is fed by several rivers, the chief being the Brisbane River, and a number of smaller streams. The southern end is estuarine and the north coast faces relatively open water (Fig. 1).

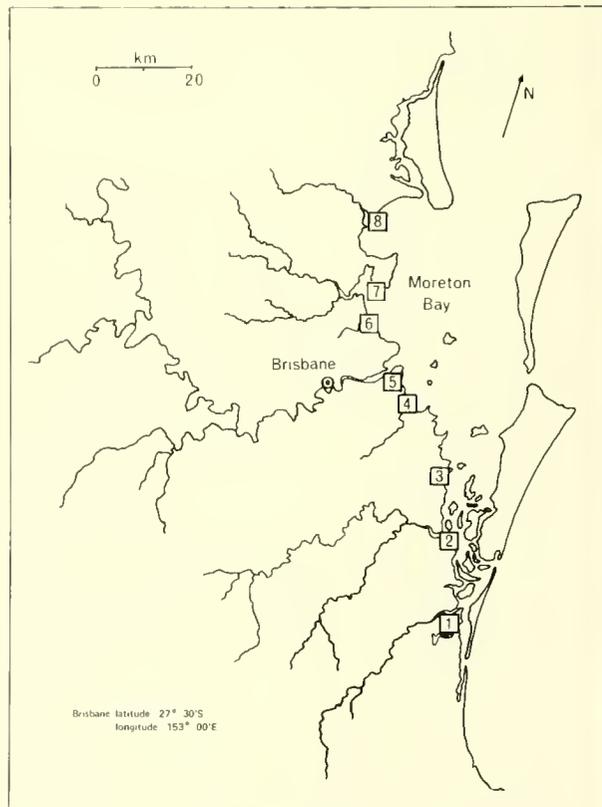


FIGURE 1. Map of Moreton Bay area, Queensland, Australia, surveyed for pesticide contamination in oysters, 1970-72

¹ Animal Research Institute, Department of Primary Industries, Queensland, Australia.

The city and suburbs of Brisbane occupy much of the central region of Moreton Bay, extending about 24 km inland. Industry is concentrated along the banks of the Brisbane River, especially toward the mouth. Smaller outlying towns, such as Caboolture, Cleveland, and Beenleigh, are centers for fruit, vegetable, sugar cane, and dairy farming; they also serve as dormitory towns for city commuters. The bay waters yield commercial quantities of fish, prawns, crabs, and oysters. Although there was little evidence that viability of these marine-based industries has been affected by proximity of an urban-industrial center and surrounding intensive agricultural areas, it was felt that a survey providing information dealing with extent and distribution of persistent pesticides in the bay would provide data against which future investigations might be compared. It would also allow comparisons to be made between pesticide residue levels in this area and those in other regions.

Sampling

Sampling points were located as near as possible to mouths of streams flowing into the bay in the hope of determining the relationship between residue levels in the oysters and the land use of the catchment area (Fig. 1). All oysters were collected from rocks or mangrove roots in the intertidal zone. Table 1 describes individual sites and land use and population of the catchment area.

Analytical Procedures

Oysters were collected in their shells and kept on ice during transportation to the laboratory where they were stored at -4°C pending analysis.

Whole oyster-meat samples of approximately 10 g were submitted to the cleanup procedure for nonfatty foods described in the *Pesticide Analytical Manual* Vol. 1, Section 212.13a (1971) published by the Food and Drug Administration, U.S. Department of Health, Education, and Welfare. Appropriate adjustments were made for sample size. An aliquot of homogenized meat was extracted with acetonitrile and partitioned between hexane and the acetonitrile extract, which was diluted with water. The hexane phase was back-washed with water, dried, and cleaned in a florisil column packed with activated magnesium silicate.

A Varian 1400 gas chromatograph equipped with a tritium-foil electron-capture detector was used to identify and quantify pesticide residues on the sample extracts. Operating parameters were as follow:

Column: DC-200 5 percent on Aeropak 30
 Temperatures: detector, 200°C ; injector, 240°C ; column, 185°C
 Carrier gas: nitrogen 40 ml/min

Recoveries of DDT, DDD, DDE, and dieldrin from samples fortified with $1\ \mu\text{g}$ of each compound were 98, 93, 96, and 83 percent, respectively. Blank runs on solvents and reagents allowed a lower limit of reliable

estimation to be set at 0.005 ppm. All data reported are corrected for recovery.

For confirmation of peak identity, the extract was concentrated to a low volume and a thin-layer chromatogram was run and compared with standards treated in a similar manner. At the levels under consideration, visualization of the spots was not possible and components were identified by scraping zones from the plate, extracting with hexane/ether, and injecting the extract into the gas chromatograph.

TABLE 1. Australian sampling sites, land use, and population of catchment areas from which oysters were collected for monitoring, 1970-72

STATION 1	
Site:	adjacent to small boat harbor. Samples from rock wall.
Industry:	dairy farming.
Population:	low-density rural, with small holiday settlement.
STATION 2	
Site:	rocky headland adjacent to estuarine area of bay. Samples from rock.
Industry:	sugar-cane farming, dairy farming, sugar mill, distillery.
Population:	predominantly rural; one town, Beenleigh.
STATION 3	
Site:	adjacent to small boat harbor. Samples from rocks.
Industry:	fruit and vegetable farming.
Population:	intensive rural; some outer-city suburbs.
STATION 4	
Site:	rocky headland near small boat harbor. Samples from rocks.
Industry:	principally suburban residential.
Population:	medium- to high-density urban.
STATION 5	
Site:	rock wall on river's edge near oil refinery. Samples from rocks.
Industry:	dairying and intensive agriculture in upper reaches of river. Industrial, commercial and high-density urban in lower reaches.
Population:	high density; major city, Brisbane.
STATION 6	
Site:	rocky headland adjacent to small boat harbor. Samples from rocks.
Industry:	residential and light industry.
Population:	high density.
STATION 7	
Site:	rocky headland. Samples from rocks.
Industry:	outer city residential, paper mill, pine forests, and some agriculture upstream.
Population:	medium density.
STATION 8	
Site:	mangrove trees in sandy silt. Samples from mangrove roots.
Industry:	dairying, pine forests.
Population:	medium- to low-density rural; one town, Caboolture, upstream.

Results and Discussion

Residue levels of DDT, DDD, DDE, and dieldrin calculated on a whole oyster-meat basis from eight samplings at each station are given in Table 2. DDT and dieldrin averages for the period of the survey are shown in graphic form in Figure 2.

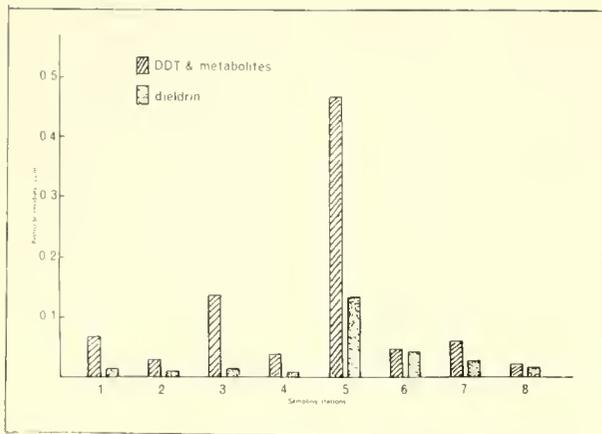


FIGURE 2. Average pesticide residue levels at Australian oyster sampling stations 1-8, 1970-72

Highest individual residues, 0.94 ppm DDT, 0.51 ppm DDD, 0.20 ppm DDE, and 0.34 ppm dieldrin, were obtained in July 1970 at the Brisbane River Station, in whose catchment area lies the city of Brisbane, population 700,000. Second-highest levels were from station 3, which adjoins an area of land used intensively for vegetable and fruit production. Most other stations lie downstream from regions with considerably lower levels of human activity.

Stations 2 and 7 had levels which were somewhat unexpectedly low. The river adjoining station 2 passes through a cane-growing area where dieldrin is used to control root pests. Station 7 lies at the mouth of a stream on which a paper mill and pine forests are located.

Residue levels varied with the seasons. Two factors most likely to influence these variations are temperature and rainfall. Mean shade temperatures in this region range from about 26°C in December and January to about 16°C in June and July. A decrease in the pumping rate of the oyster in winter months would tend to lower both the rate of intake of material from the water and the rate of its elimination. Whether this would result in a net loss or gain in chlorinated hydrocarbons is not certain.

Reports commenting on seasonal variations do so mainly in terms of rainfall changes (1-3). In the region where this survey was conducted, the wet season occurs in the summer, December to March, although the winter is comparatively dry. Figures 3 and 4 show variation in rainfall and the fluctuation in total DDT group levels for stations 3 and 5. It is clear that residue maxima do not coincide with nor immediately follow periods of high rainfall. Other stations, while exhibiting irregularities in some cases, follow this general pattern.

This phase difference between rainfall maximum and residue level maximum may be explained in several

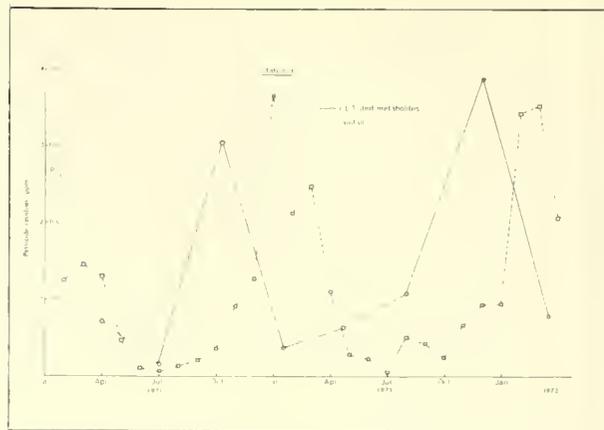


FIGURE 3. Rainfall and total DDT levels at Australian oyster sampling station 3, 1970-72

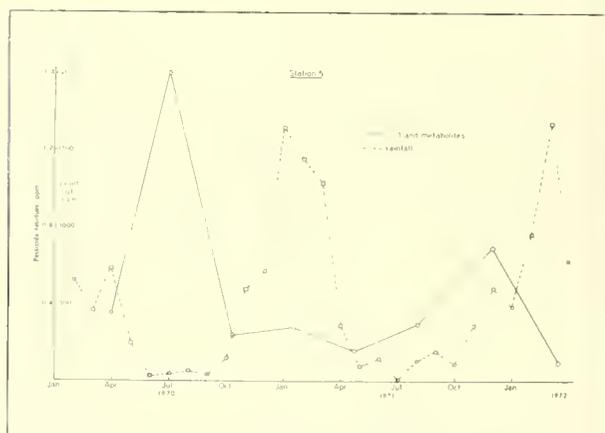


FIGURE 4. Rainfall and total DDT levels at Australian oyster sampling station 5, 1970-72

ways. Rowe et al. interpret an increase in estuarine oysters near New Orleans as a result of an immediately preceding increase in runoff following heavy rains (3). In the present survey the rainfall maximum preceded the residue maximum by 5 to 11 months, generally with a dry period in between. Thus it is difficult to reconcile these data with the interpretation given below.

A general similarity in the pattern of residue variations found at most sampling stations suggests an alternative explanation. It is possible that the main source of residues in the region under investigation is the Brisbane River (station 5), and that distribution throughout the bay is effected by tidal diffusion.

However, this interpretation runs into at least two difficulties. The greatest similarity in the pattern of residue variations exists between station 5 and the streams to the south (stations 1-4); yet water from the Brisbane River flows predominantly northward. A second prob-

TABLE 2. Chlorinated hydrocarbon levels in oysters (*Crassostrea commercialis*), Moreton Bay, Queensland, Australia

Sampling Station	Sampling Date	Residues, ppm			
		DDE	DDD	DDT	Dieldrin
1 Coomera River	4-2-70	0.007	0.006	0.006	0.007
	7-2-70	—	—	—	—
	10-8-70	0.039	0.023	0.046	—
	1-14-71	0.008	0.007	—	0.022
	4-22-71	0.014	0.007	0.038	0.047
	8-3-71	0.023	—	0.161	—
	11-29-71	0.011	0.007	0.068	0.005
2 Logan River	3-9-72	0.007	0.008	0.036	0.013
	4-2-70	0.007	—	—	—
	7-2-70	0.055	—	—	—
	10-8-70	0.020	—	0.055	—
	1-14-71	0.006	0.007	—	0.027
	4-22-71	0.009	0.007	—	0.012
	8-3-71	0.014	—	0.022	—
3 Redland Bay	11-29-71	0.007	0.007	0.005	—
	3-9-72	—	—	—	0.010
	4-2-70	0.022	0.020	0.029	0.009
	7-2-70	0.035	—	0.011	—
	10-8-70	0.035	0.010	0.26	—
	1-14-71	0.010	0.010	0.017	0.025
	4-22-71	0.016	0.014	0.034	0.032
4 Tingalpa Creek	8-3-71	0.028	0.009	0.071	—
	11-29-71	0.046	0.025	0.318	0.006
	3-9-72	0.018	0.012	0.049	0.015
	4-2-70	0.007	—	0.016	—
	7-2-70	—	—	—	—
	10-8-70	0.017	—	0.073	—
	1-14-71	—	—	—	—
5 Brisbane River	4-22-71	0.010	0.007	0.019	0.022
	8-3-71	0.014	—	—	—
	11-29-71	0.018	0.013	0.061	—
	3-9-72	0.008	0.005	0.014	0.016
	4-2-70	0.037	0.116	0.203	0.094
	7-2-70	0.20	0.51	0.94	0.34
	10-8-70	0.033	0.107	0.094	0.083
6 Cabbage Tree Creek	1-14-71	0.072	0.057	0.150	0.069
	4-22-71	0.026	0.034	0.097	0.071
	8-3-71	0.045	0.085	0.168	0.116
	11-29-71	0.146	0.119	0.427	0.150
	3-9-72	0.026	0.019	0.054	0.111
	4-2-70	0.009	—	0.013	0.020
	7-2-70	—	—	—	0.058
7 Pine Rivers	10-8-70	0.020	0.014	—	0.057
	1-14-71 ¹	—	—	—	—
	4-22-71	0.039	0.022	0.022	0.058
	8-3-71	0.023	0.011	0.051	0.033
	11-29-71	0.028	—	0.046	0.027
	3-9-72	—	—	0.006	0.023
	4-2-70	0.009	0.023	0.012	0.023
8 Caboolture River	7-2-70	0.016	—	—	—
	10-8-70	0.021	0.017	0.040	0.051
	1-14-71	0.035	0.027	0.035	0.010
	4-22-71	0.021	0.009	0.014	0.032
	8-3-71	0.023	0.007	0.095	0.020
	11-29-71	0.005	—	0.030	0.014
	3-9-72	—	—	0.012	0.044
Caboolture River	4-2-70	0.009	—	0.007	0.018
	7-2-70	0.059	—	—	—
	10-8-70 ¹	—	—	—	—
	1-14-71	0.008	—	—	—
	4-22-71	0.009	—	—	0.013
	8-3-71	0.009	—	—	0.016
	11-29-71	0.006	—	0.006	0.012
3-9-72	—	0.006	0.010	0.035	

NOTE: — = < 0.005 ppm

¹ Large interfering peaks prevented analysis.

lem with this interpretation is that separation between the residue maximum and the rainfall maximum for each station would be expected to change to reflect increasing distance between a particular station and station 5. No such clear trend is observable.

A third hypothesis might also explain the data. If it is assumed that the amount of pesticide entering streams via sewerage outflows, industrial waste discharge, and irrigation systems does not vary greatly throughout the year, then the concentration in the water at the mouth

of the stream will be inversely related to the volume of fresh water flowing in that stream. Therefore one would expect the level of pesticide in the indicator organism to be highest during or shortly after the period when the flow is least, i.e., when the concentration of pesticide in the water is greatest.

Data for the DDT group totals at stations 1-5 fit this hypothesis satisfactorily; data for stations 6-8 moderately correlate. Dieldrin levels at station 5 also conform to this pattern.

Marked changes in the levels of DDT in oysters collected by Butler in 1966 in Tres Palacios Bay, Tex., were explained in this manner (1).

Ockham's razor notwithstanding, data for station 3, an area of intensive vegetable and tropical fruit cultivation, may also be interpreted in terms of the high seasonal rate of application of pesticides in the spring months of September and October.

Clearly, no single causative factor will adequately explain environmental data of this kind because the possibility of accidental spillages and intermittent high usage levels may and almost certainly do contribute to the distortion of otherwise regular patterns. Nevertheless it seems worthwhile to eliminate facile explanations and to try to attribute the data to some reasonable set of circumstances, thus providing a basis for comment and further investigation.

Overall levels obtained in this survey might usefully be compared with several published reports (1-6). In

the major survey carried out by Butler's group in which data were collected over 5 years from 170 stations on the Atlantic, Gulf, and Pacific coasts of the United States, DDT and metabolites were usually less than 0.5 ppm even near intensively farmed areas, and only rarely greater than 1.0 ppm (2,4). The highest level found was 5.4 ppm; this was the result of a single incident of gross pollution. In other surveys, levels were generally of the same order of magnitude as those reported in this paper (3,5,6).

It would appear, then, that levels in this region were generally not atypical, although two samplings at station 5 could only be described as rare, in terms of the Butler survey.

LITERATURE CITED

- (1) Butler, P. A. 1971. Influence of pesticides on marine ecosystems. *Proc. Roy. Soc. London* 177:321-329.
- (2) Butler, P. A. 1969. Monitoring pesticide pollution. *Bio-science* 19:889-891.
- (3) Rowe, D. R., L. W. Canter, and J. W. Mason. 1970. Contamination of oysters by pesticides. *J. Sanit. Eng. Div. Amer. Soc. Civil Eng.* 96 (5A5) 1221-1234.
- (4) Butler, P. A. 1973. Organochlorine residues in estuarine mollusks, 1965-72—National Pesticides Monitoring Program. *Pestic. Monit. J.* 6(4):238-362.
- (5) Fay, Roger R., and Leo W. Newland. 1972. Organochlorine insecticide residues in water, sediment, and organisms, Aransas Bay, Texas—September 1969-June 1970. *Pestic. Monit. J.* 6(2):97-102.
- (6) Foehrenbach, Jack, Ghulam Mahmood, and Dennis Sullivan. 1971. Chlorinated hydrocarbon residues in shellfish (*Pelecypoda*) from estuaries of Long Island, New York. *Pestic. Monit. J.* 5(3):242-247.

DDT and Dieldrin Residues in Selected Biota from San Antonio Bay, Texas—1972¹

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ABSTRACT

A total of 240 samples of 10 species of selected biota from San Antonio Bay, Tex., were collected and analyzed by electron-capture/gas-liquid chromatography for residues of the organochlorine insecticides DDT and its metabolites, and dieldrin. The most common residue detected was p,p'-DDE, which was the only member of the DDT group found in most samples. Results indicated that the DDT/dieldrin load in the biota sampled was relatively low; the greatest concentration was 106 ppb DDE in an oyster. Blue crabs had the greatest incidence of contamination, especially by DDE. Incidence of dieldrin contamination in blue crabs, oysters, and clams was similar. Of the major groups sampled, shrimp had the lowest incidence of DDT/dieldrin residues.

Introduction

The widespread occurrence of the organochlorine insecticides DDT and dieldrin as environmental pollutants has been well documented for all major terrestrial, freshwater, and marine environments. The presence of DDT and dieldrin in the water, sediments, and biota of Texas bays has been reported by Ahr (1), Butler (2), Childress (3,4), Fay and Newland (5), Flickinger and Meeker (6), Flickinger and King (7), and Petrocelli et al. (8). Although most of the former uses of DDT are now banned, there are still sufficient residues in the environment to warrant consideration of its effects (9). The significance of dieldrin as a pollutant in the environment has been well demonstrated: it has been the most common insecticide in all U.S. river basins since 1958 (10,11); it is more toxic than DDT to a number

of organisms including salmonid fish (12,13), American oyster larvae (14), and wildlife (15); and it is extremely persistent in the environment (16). Dieldrin, an insecticide in its own right, also results from the oxidative breakdown (epoxidation) of aldrin, a closely related insecticide (17). Both DDT and dieldrin are accumulated by aquatic organisms (18-21) and biologically magnified in food chains (22-27).

The San Antonio Bay system is located just south of the geographic center of the Texas Gulf Coast (Fig. 1) between 28°00' and 28°30' N latitude and 96°30' and 97°00' W longitude in Calhoun and Refugio Counties. The Aransas National Wildlife Refuge is on the west side of the bay (Fig. 2). San Antonio Bay is a commercial fisheries area with significant landings of penaeid shrimp, American oysters, blue crabs, and a wide variety of fin fish.

Sample Collecting

March clams (*Rangia cuneata*) were collected at a depth of 2-3 feet along the shoreline just above Grassy Point in Hynes Bay; eastern oysters (*Crassostrea virginica*) were from Panther Point reef; blue crabs (*Callinectes sapidus*) were collected in traps in the mouth of Hynes Bay off McDowell Point and from trawls taken in various parts of San Antonio Bay; brown shrimp (*Penaeus aztecus*) were also taken from trawls. Miscellaneous samples, which included two species of fish: Bay anchovies (*Anchoa mitchilli*) and southern flounders (*Paralichthys lethostigma*); bivalved molluscs (*Mercenaria campechiensis*, *Tagelus plebeius*, and *Macoma constricta*); and marsh grass (*Spartina spartinae*), were from areas along the Aransas National Wildlife Refuge shore and islands along the Intracoastal Waterway. All samples were placed on ice in appropriate containers immediately after collection until returned to the laboratory where they were analyzed or frozen at -15° C until analysis.

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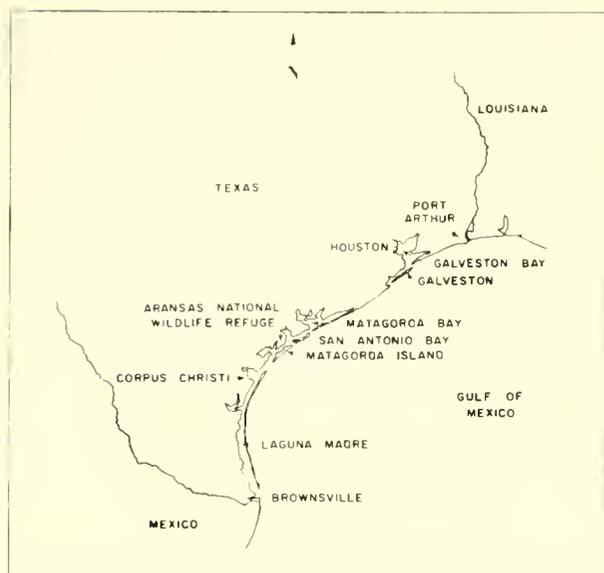


FIGURE 1. Texas coast, Gulf of Mexico, with San Antonio Bay system indicated

Analytical Procedures

Samples were analyzed for DDT and dieldrin residues by a modification of the procedures of the U.S. Department of Health, Education, and Welfare, Food and Drug Administration, as described in the *Pesticide Analytical Manual* (28). Insecticide residues were extracted from tissues by blending with Mallinckrodt nanograde acetonitrile for 5 minutes at high speed. The resulting mixture was filtered through sharkskin filter paper. The filter paper and tissue residue were re-extracted with acetonitrile and filtered as before. Filtrates were combined and 200 ml were partitioned in 100 ml nanograde petroleum ether in a separatory funnel. The aqueous layer was discarded and the solvent layer washed twice with a 2 percent sodium sulfate solution and dried by the addition of anhydrous sodium sulfate.

The dried extract was concentrated to a volume of 10 ml on a steam bath and placed on a florisil column for cleanup. The amount of florisil used was determined by lauric acid titration (28). Residues were eluted individually from the florisil column by 6, 15, and 50 percent solutions of diethyl and petroleum ether. Residue analyses were performed on a Barber-Colman Selecta-System Series 5000 gas-liquid chromatograph (GLC) fitted with an electron-capture detector. The column was a 2m-by-4mm-ID Pyrex glass coil, packed with 80/100 mesh Gas Chrom Q support on which the liquid phase of 3 percent OV-1 was distributed. The carrier gas was prepurified nitrogen and the operating temperatures

were: injector, 200°C; column, 180°C; and detector, 210°C. Minimum detectable level for these organochlorine compounds was 0.001 ppm.

Residue peaks were qualified by retention time relative to a standard, and quantification was performed by peak height measurements. Confirmations of random sample residues were performed on a second GLC column (DC-200) and by p-values (28). Multiple peaks characteristic of polychlorinated biphenyls (PCB's) were not detected in any samples. Residue concentrations are expressed as parts per billion (ppb, $\mu\text{g}/\text{kg}$) on a wet-weight, whole-animal basis. Recoveries of pesticide standards obtained from Shell Chemical Company carried through the analytical procedure were consistently over 85 percent and often over 90 percent. No corrections for percent recovery have been made in reporting these data.

Results and Discussion

Results of analyses indicated a relatively low DDT/dieldrin load in biota of San Antonio Bay (Tables 1-3). Of 240 samples analyzed, 159 (66 percent) contained residues of ΣDDT , which were almost exclusively *p,p'*-DDE; 70 (29 percent) contained dieldrin residues, and 47 (20 percent) contained residues of ΣDDT and dieldrin (Table 3). The greatest incidence of ΣDDT and dieldrin was in blue crabs: 94 percent contained residues of ΣDDT and 32 percent contained residues of dieldrin. Oysters and clams, the two major bivalved mollusc groups sampled, had a similar incidence of dieldrin residues: 25 percent of the oysters and 31 percent of the clams had detectable residues. Compared with blue crabs, however, the bivalves' incidence of total DDT was much lower: 60 percent of the oysters and 68 percent of the clams contained these residues. In 1973 Butler reported detecting residues of DDE without residues of DDT or TDE in oysters collected the preceding year from San Antonio Bay (2); the present study revealed similar findings in oysters. This predominance of DDE residues in tissues may reflect decreasing DDT input over the years; conversion of DDT to its common metabolite, DDE, which occurs in many aquatic species (17); and the biocycling of these residues. Shrimp had a comparatively low incidence of DDT/dieldrin residues.

High incidence of ΣDDT in blue crabs may be caused by their omnivorous or opportunistic feeding habits. Blue crabs, which scavenge on dead fish, also eat a wide variety of living organisms: fish; benthic invertebrates such as *Rangia* clams, oysters, and snails; and vascular plants and organic detritus (29). Therefore high incidence of ΣDDT in blue crabs may result from their ingestion of a wide variety of insecticide-contaminated materials. Bivalves, on the other hand, are more selective, feeding on suspended detritus, protozoans, and plankton for at least 70 percent of their

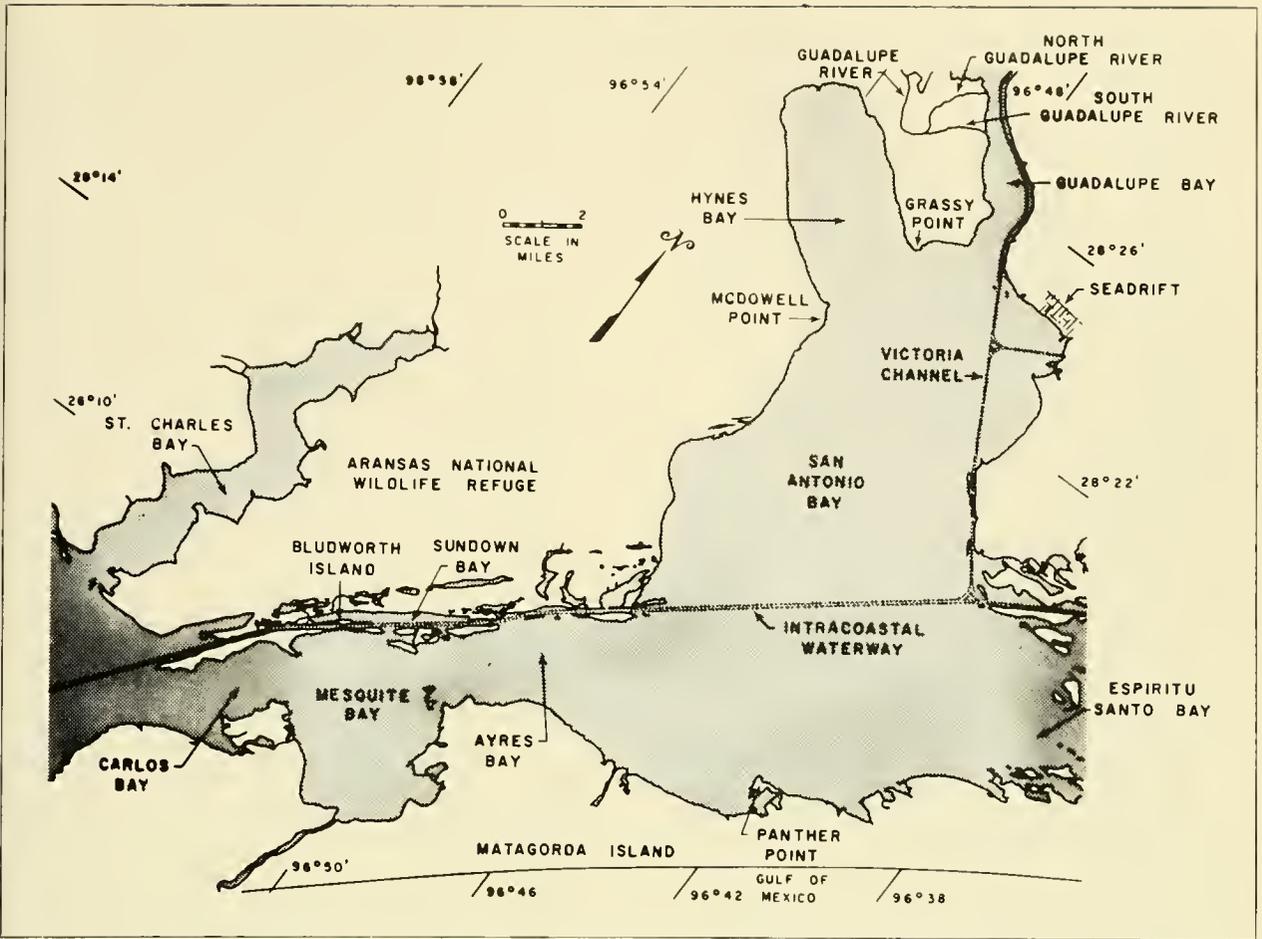


FIGURE 2. San Antonio Bay system and Aransas National Wildlife Refuge

nourishment (29). Hence they have less overall exposure to insecticide residues than have blue crabs, in spite of the bivalves' well-known ability to concentrate insecticides from water into their tissues. Furthermore, because blue crabs may undertake migrations, they have many more opportunities to be exposed than have bivalves.

LITERATURE CITED

- (1) Ahr, W. M. 1972. The DDT profile of some South Texas coastal-zone sediments: a study of the mechanisms of pollution dispersal and accumulation in nature. TAMU-Environmental Quality Note 05: 32 pp.
- (2) Butler, P. A. 1973. Organochlorine residues in estuarine mollusks, 1965-72—National Pesticide Monitoring Program. *Pestic. Monit. J.* 6(4):238-362.
- (3) Childress, R. 1968. Levels of concentration and incidence of various pesticide toxicants in some species from selected bay areas. Coastal Fisheries Project Reports 1968. Texas Parks and Wildlife Department. John H. Reagan State Bldg., Austin, Tex. 1-21.
- (4) Childress, R. 1971. Levels of concentration and incidence of various pesticide residues in Texas (Unpublished report). 58 pp.
- (5) Fay, R. R., and L. W. Newland. 1972. Organochlorine insecticide residues in water, sediment, and organisms,

- Aransas Bay, Texas—September 1969—June 1970. *Pestic. Monit. J.* 6(2):97-102.
- (6) Flickinger, E. L., and D. L. Meeker. 1972. Pesticide mortality of young white-faced ibis in Texas. *Bull. Environ. Contam. Toxicol.* 8(3):165-168.
- (7) Flickinger, E. L., and K. A. King. 1972. Some effects of aldrin-treated rice on Gulf Coast wildlife. *J. Wildl. Manage.* 36(3):706-727.
- (8) Petrocelli, S. R., J. W. Anderson, and A. R. Hanks. 1974. Seasonal fluctuations of dieldrin residues in the tissues of the marsh clam, *Rangia cuneata*, from a Texas estuary. *Tex. J. Sci.* 26(1) (in press).
- (9) National Science Foundation. 1972. Baseline studies of pollutants in the marine environment and research recommendations. The IDOE Baseline Conference, May 24-26, 1972. New York. 54 pp.
- (10) Breidenbach, A. W., and J. J. Lichtenberg. 1963. DDT and dieldrin in rivers: a report on the National Water Quality Network. *Science* 141(3584):899-900.
- (11) Weaver, L., C. G. Gummerson, A. W. Breidenbach, and J. J. Lichtenberg. 1965. Chlorinated hydrocarbon pesticides in major U.S. river basins. U.S. Department of Health, Education, and Welfare. Public Health Service Report 80(6):481-493.
- (12) Henderson, C., Q. H. Pickering, and C. M. Tarzwell. 1959. Relative toxicity of ten chlorinated hydrocarbon insecticides to four species of ten fish. *Trans. Amer. Fish. Soc.* 88(1):23-32.

- (13) Katz, M. 1961. Acute toxicity of some organic insecticides to three species of salmonids and to the three-spined stickleback. *Trans. Amer. Fish. Soc.* 90(3): 264-268.
- (14) Davis, H. C., and H. Hidu. 1969. Effects of pesticides on embryonic development of clams and oysters and on survival and growth of the larvae. *Fish. Bull.* 67(2):393-404.
- (15) Tucker, R. K., and D. G. Crabtree. 1970. Handbook of Toxicity of Pesticides to Wildlife. U.S. Department of the Interior—Fish and Wildlife Service. Bur. Sport Fish. Wildl. Resources Publication No. 84. 131 pp.
- (16) Nash, R. G., and E. A. Woolson. 1967. Persistence of chlorinated hydrocarbon insecticides in soil. *Science* 157(3791):924-927.
- (17) Menzie, C. M. 1969. Metabolism of pesticides. U.S. Department of the Interior—Fish and Wildlife Service. Bur. Sport Fish. Wildl. Spec. Sci. Report—Wildlife No. 127. 487 pp.
- (18) Butler, P. A. 1969. The significance of DDT residues in estuarine fauna. In M. W. Miller and G. G. Berg, eds., *Chemical Fallout. Current Research on Persistent Pesticides.* Charles C. Thomas Publisher, Springfield, Ill. 205-220.
- (19) Nimmo, D. R., A. J. Wilson, Jr., and R. R. Blackman. 1970. Localization of DDT in the body organs of pink and white shrimp. *Bull. Environ. Contam. Toxicol.* 5(4):333-340.
- (20) Odum, W. E., G. M. Woodwell, and C. F. Wurster. 1969. DDT residues absorbed from organic detritus by fiddler crabs. *Science* 164(3879):576-577.
- (21) Petrocelli, S. R., A. R. Hanks, and J. W. Anderson. 1973. Uptake and accumulation of an organochlorine insecticide (dieldrin) by an estuarine mollusc, *Rangia cuneata*. *Bull. Environ. Contam. Toxicol.* 10(5):315-320.
- (22) Jensen, S., A. G. Johnels, M. Olsson, and G. Otterlind. 1969. DDT and PCB in marine animals from Swedish waters. *Nature* 224(5216):247-250.
- (23) Johnson, B. T., C. R. Saunders, H. O. Sanders, and R. S. Campbell. 1971. Biological magnification and degradation of DDT and aldrin by freshwater invertebrates. *J. Fish. Res. Bd. Can.* 28(5):705-709.
- (24) Metcalf, R. L., G. K. Sangha, and I. P. Kapoor. 1971. Model ecosystem for the evaluation of pesticide biodegradability and ecological magnification. *Environ. Sci. Technol.* 5(8):709-713.
- (25) Petrocelli, S. R., J. W. Anderson, and A. R. Hanks. Biological magnification of dieldrin in a two-part food chain. Paper presented at the 65th Annual Meeting of the National Shellfisheries Assoc., June 24-28, 1973, New Orleans, La.
- (26) Reinert, R. E. 1972. Accumulation of dieldrin in an alga (*Scenedesmus obliquus*), *Daphnia magna*, and the guppy (*Poecilia reticulata*). *J. Fish. Res. Bd. Can.* 29(10):1413-1418.
- (27) Woodwell, G. M., C. F. Wurster, and P. A. Isaacson. 1967. DDT residues in an east coast estuary: a case of biological concentration of a persistent insecticide. *Science* 156(3776):821-824.
- (28) U.S. Department of Health, Education, and Welfare—Food and Drug Administration. 1969. Pesticide analytical manual. Vol. 1.
- (29) Darnell, R. M. 1968. Food habits of fishes and larger invertebrates of Lake Pontchartrain. Louisiana, an estuarine community. *Publ. Inst. Mar. Sci. Univ. Tex.* 5:353-416.

TABLE 1. Baseline residues ($\mu\text{g}/\text{kg}$) of DDT and dieldrin in blue crabs, oysters, clams, and brown shrimp, San Antonio Bay System, Tex.—1972

SAMPLE No. ¹	WET WEIGHT, G	p,p'-DDE	DIELDRIN	MONTH OF COLLECTION
BLUE CRABS				
219	98.24	9.47	1.44	April
220	144.86	9.73	ND	April
225 ^a	77.28	28.32	4.22	April
226	147.53	22.13	1.38	April
227	113.41	11.14	1.97	April
228	103.91	29.50	6.16	April
229	161.85	20.20	3.27	April
230	94.64	19.40	3.56	April
231	193.84	18.54	3.22	April
303	159.96	13.80	2.76	June
304	137.81	10.80	TR	June
306	48.75	22.80	ND	June
307	66.54	17.60	2.12	June
308	17.39	40.30	ND	June
309	75.32	12.20	TR	June
310	79.63	9.95	ND	June
311	29.51	25.80	3.47	June
312	11.30	28.00	ND	June
313	68.85	19.00	2.96	June
314	54.50	13.10	TR	June
330	91.39	16.30	20.70	June
331	31.53	16.30	ND	June
332	29.62	51.20	5.41	June
333	62.22	13.70	2.69	June
366	41.24	23.90	ND	July
367	27.03	18.10	2.75	July
368	5.95	ND	ND	July
369	9.68	ND	ND	July
370	40.37	19.30	3.50	July
371	23.82	ND	5.76	July
372	10.68	14.90	ND	July
373	11.93	13.10	ND	July
374	22.26	27.70	44.60	July
375	37.61	ND	2.64	July
376	29.68	ND	4.41	July
383	146.91	11.70	1.30	July
384	100.62	11.40	1.01	July
385	126.48	8.77	ND	July
386	117.72	9.66	ND	July
387	65.13	16.30	ND	July
395	148.89	68.20	ND	July
396 ^b	296.38	29.80	ND	July
397	116.94	3.13	ND	July
398	44.39	21.60	ND	July
410	396.90	4.43	ND	July
411	168.17	12.10	ND	July
412	196.48	10.00	ND	July
413	163.05	6.54	ND	July
518	87.69	13.60	ND	October
519	74.28	6.20	ND	October
520	59.01	13.40	ND	October
521	77.06	5.90	ND	October
522	93.74	18.70	ND	October
523	75.53	15.80	ND	October
584 ^c	64.95	15.00	ND	October
585 ^d	53.88	6.20	ND	October
586 ^e	56.74	6.30	ND	October
587 ^f	58.58	55.00	ND	October
588 ^g	93.78	5.20	ND	October
589 ^h	62.77	4.30	ND	October
590 ⁱ	51.85	15.00	ND	October
591 ^j	63.76	8.10	ND	October
OYSTERS				
213	10.85	29.85	9.28	April
214	5.17	46.59	19.62	April
215	4.16	28.18	22.91	April
216	9.31	27.11	13.38	April
234	7.70	51.87	27.11	April
235	14.10	29.76	13.14	April
236	2.90	72.25	31.90	April
237	2.12	70.17	36.08	April
294 ^k	28.81	ND	ND	June
295 ^l	131.73	3.74	ND	June
405	3.48	28.50	ND	June
406	2.73	28.90	ND	June
407	7.14	28.80	ND	June
408	9.15	28.40	ND	June
409	3.96	37.30	ND	June
551	8.39	27.00	ND	July

(Continued next page)

TABLE 1 (cont'd). Baseline residues ($\mu\text{g}/\text{kg}$) of DDT and dieldrin in blue crabs, oysters, clams, and brown shrimp, San Antonio Bay System, Tex.—1972

SAMPLE No. ¹	WET WEIGHT, G	p,p'-DDE	DIELDRIN	MONTH OF COLLECTION	SAMPLE No. ¹	WET WEIGHT, G	p,p'-DDE	DIELDRIN	MONTH OF COLLECTION
OYSTERS, cont'd					CLAMS, cont'd				
552	7.01	ND	22.20	July	564	6.22	43.00	ND	April
553	7.38	106.00	20.60	July	565 ¹³	7.83	15.00	ND	April
554	8.57	24.40	24.20	July	566	7.52	ND	ND	April
555	7.73	ND	ND	July	567	6.99	10.00	ND	April
556	5.56	ND	ND	July	568	9.20	ND	ND	April
557	7.08	ND	ND	July	569	7.83	ND	ND	April
558	2.55	ND	ND	July	570	7.02	ND	5.10	April
559	3.26	ND	ND	July	571 ¹⁴	18.67	ND	2.00	April
560	4.14	ND	ND	July	598	6.30	ND	ND	October
592	2.42	ND	26.00	October	599	4.71	18.00	ND	October
593	3.21	23.00	ND	October	600	4.58	ND	18.00	October
594	5.51	25.00	ND	October	601	3.65	ND	ND	October
595	5.60	48.00	ND	October	602	2.82	79.00	ND	October
596	7.53	ND	ND	October	603	9.74	20.00	ND	October
					605	8.12	ND	ND	October
CLAMS									
221	10.89	18.42	13.73	April	606 ¹⁵	5.92	16.00	ND	October
222	13.64	22.86	ND	April	607	12.33	16.00	ND	October
296 ¹⁰	33.81	21.90	ND	June	BROWN SHRIMP				
297 ¹¹	56.27	18.40	ND	June	240	6.48	ND	6.70	April
339	21.51	25.40	ND	June	241	7.82	ND	4.51	April
340	23.18	37.00	6.65	June	242	8.16	ND	4.38	April
341	16.42	36.70	ND	June	249	6.71	ND	8.71	April
342	18.68	32.90	3.73	June	250	9.44	ND	ND	April
343	18.25	42.40	3.75	June	251	5.64	ND	6.50	April
344	20.62	38.70	3.16	June	252	10.15	ND	ND	April
346	11.75	42.80	9.34	June	254	5.73	ND	11.36	April
347	9.06	59.90	1.07	June	256	8.87	ND	ND	April
348	10.69	50.20	12.40	June	257	6.59	ND	ND	April
349	6.28	ND	13.90	June	258	12.40	ND	ND	April
356	10.85	34.70	3.53	June	259	6.74	ND	ND	April
357	5.36	ND	ND	June	266	4.23	ND	ND	May
358	11.63	54.80	2.50	June	267	3.80	ND	ND	May
359	10.96	35.80	ND	June	268	6.20	ND	ND	May
360	10.18	ND	ND	June	269	4.81	ND	ND	May
541 ¹²	3.20	ND	ND	September	270	3.53	ND	ND	May
542	3.91	ND	ND	September	271	5.98	ND	ND	May
543	4.63	ND	ND	September	272	5.08	ND	ND	May
544	7.80	ND	ND	September	273	10.65	ND	ND	May
561	6.50	36.00	14.00	April	402	5.60	15.70	ND	July
562	7.55	30.00	12.00	April	403	5.52	14.70	ND	July
563	6.36	ND	ND	April	404	5.58	13.70	ND	July

NOTE: Residue totals and averages listed in Table 3.

ND = not detected.

TR = trace ($< 1.0 \mu\text{g}/\text{kg}$).

¹ Samples represent individual specimens unless indicated otherwise.

² Sample taken from Bludworth Island.

³ Sample contained $18.60 \mu\text{g}$ kg p,p'-DDE.

⁴ Composite of two crabs.

⁵ Composite of six crabs.

⁶ Composite of four crabs.

⁷ Composite of three crabs.

⁸ Composite of ten small oysters.

⁹ Composite of ten large oysters.

¹⁰ Composite of ten small clams.

¹¹ Composite of ten large clams.

¹² Sample taken from Sundown Bay.

¹³ Sample contained $33.00 \mu\text{g}$ kg p,p'-DDE.

¹⁴ Composite of five clams.

¹⁵ Sample contained $47.00 \mu\text{g}$ kg p,p'-DDE.

TABLE 2. Baseline residues ($\mu\text{g}/\text{kg}$) of DDT and dieldrin in miscellaneous species, San Antonio Bay System, Tex.—1972

SAMPLE No.	ORGANISM ¹	LOCATION ²	WET WEIGHT, G	<i>p,p'</i> -DDE	DIELDRIN	MONTH OF COLLECTION
223	<i>Anchoa mitchilli</i>	Bludworth Island	32.80	52.61	5.38	April
224	<i>Tagelus plebeius</i>	Bludworth Island	29.84	5.67	2.68	April
238	<i>Paralichthys lethostigma</i>	Refuge	14.72	13.32	ND	April
239	<i>Paralichthys lethostigma</i>	Refuge	14.78	14.21	ND	April
435	<i>Mercenaria campechiensis</i>	Hynes Bay	75.95	ND	ND	July
436	<i>Mercenaria campechiensis</i>	Hynes Bay	34.28	ND	ND	July
437	<i>Mercenaria campechiensis</i>	Hynes Bay	55.66	ND	ND	July
438	<i>Mercenaria campechiensis</i>	Hynes Bay	25.41	ND	ND	July
439	<i>Mercenaria campechiensis</i>	Hynes Bay	42.58	ND	ND	July
450	<i>Tagelus plebeius</i>	Refuge	4.75	ND	ND	July
451	<i>Tagelus plebeius</i>	Refuge	8.07	ND	ND	July
452	<i>Macoma constricta</i>	Refuge	2.83	ND	ND	July
526	<i>Spartina spartinae</i>	Dunham Bay	57.43	2.20	ND	August
527	<i>Spartina spartinae</i>	Mustang Lake	57.25	ND	ND	August
528	<i>Spartina spartinae</i>	Dunham Bay	49.11	ND	ND	August
533	<i>Mercenaria campechiensis</i>	Hynes Bay	95.26	ND	1.30	October
534	<i>Mercenaria campechiensis</i>	Hynes Bay	135.69	ND	1.20	October
535	<i>Mercenaria campechiensis</i>	Hynes Bay	109.45	ND	1.40	October
536	<i>Mercenaria campechiensis</i>	Hynes Bay	155.47	ND	1.00	October
537	<i>Mercenaria campechiensis</i>	Hynes Bay	20.43	ND	ND	October
538	<i>Mercenaria campechiensis</i>	Hynes Bay	11.52	ND	ND	October
539	<i>Mercenaria campechiensis</i>	Hynes Bay	17.95	ND	ND	October
540	<i>Tagelus plebeius</i>	Sundown Bay	4.24	ND	ND	September

¹ See text for common names.

² Compare map, Fig. 2.

TABLE 3. Summary of insecticide residues detected in biological samples, San Antonio Bay System, Tex.—1972

SPECIES	NO. ORGANISMS ANALYZED	NO. ORGANISMS CONTAINING INSECTICIDE RESIDUES AND PERCENT TOTAL ANALYZED		
		<i>p,p'</i> -DDE	DIELDRIN	BOTH
Blue crabs	81	76 (94%)	26 (32%)	23 (28%)
Oysters	48	29 (60%)	12 (25%)	10 (21%)
Clams	65	44 (68%)	20 (31%)	12 (18%)
Shrimp	23	3 (13%)	6 (26%)	0 (0%)
Miscellaneous	23	7 (30%)	6 (26%)	2 (9%)
Total	240	159 (66%)	70 (29%)	47 (20%)

Residues of 2,4-D in Pond Waters, Mud, and Fish, 1971^{1,2}

Donald P. Schultz and Paul D. Harman

ABSTRACT

Nine ponds in Florida, Georgia, and Missouri were treated in 1971 with the dimethylamine salt of 2,4-Dichlorophenoxyacetic acid (DMA-2,4-D) to determine residue levels of the herbicide in water, bottom mud, and fish as a function of application rate, time, substrate, and geographic location. The acid equivalent of 2,4-D was applied at treatment rates of 2.24, 4.48, or 8.96 kg/ha. Samples were taken up to 147 days after treatment.

Residues of 2,4-D in pond waters declined from a maximum of 0.345 and 0.692 mg/liter in Florida and Georgia, respectively, to less than 0.005 mg/liter 28 days after treatment, and from 0.630 mg/liter to less than 0.005 mg/liter 56 days after treatment in Missouri pond waters.

Residues in mud from the Florida and Georgia ponds never exceeded 0.05 mg/kg and had declined to trace or non-detectable levels 56 days after treatment. The highest residue found was 0.170 mg/kg from the first- and third-day samples of mud in the most heavily treated Missouri pond. In mud from one Missouri pond, residues were detected as late as 28 days after treatment; no residues occurred in any ponds after that.

No evidence of fish kill was found in any ponds treated with DMA-2,4-D. Of 307 fish samples analyzed, 45 contained detectable residues of 2,4-D. Residue levels ranged from slightly more than 1.0 mg/kg to less than 0.010 mg/kg.

Introduction

Proliferation of obnoxious aquatic plants is presently controlled by mechanical, physical, biological, or chemical means, or by combinations of these methods. Formulations of 2,4-D are used most widely to control plants such as the waterhyacinth (*Eichornia crassipes*) and eurasian watermilfoil (*Myriophyllum spicatum*).

In 1966 the Tennessee Valley Authority applied 888 tons of the butoxyethanol ester of 2,4-D to 8,000 acres of watermilfoil in several reservoirs (1). Over 18,000 surface acres of Nickajack and Guntersville Reservoirs on the Tennessee River were treated with about 170,000 gallons of the dimethylamine salt of 2,4-D (DMA-2,4-D) April—June 1969, to control watermilfoil (2).

Objectives of the present study conducted in 1971 were to determine the residue levels and rate of dissipation of DMA-2,4-D in fish, water, and bottom mud. These data are required to register the product for use in aquatic plant control and to assist in establishing residue tolerances for DMA-2,4-D in fish and domestic water. Also, by using ponds in Florida, Georgia, and Missouri, authors hoped to determine whether different physical and chemical characteristics of the aquatic environment affect the uptake and dissipation of the herbicide. A third objective was to assess the efficacy of the herbicide on minor infestations of waterhyacinth in Florida and Georgia ponds.

Methods and Materials

SITE SELECTION

Three ponds were located near Crystal River, Fla. Willow Pond contained some aquatic plants including *Hydrocotyle* sp., cattail (*Typha* sp.), waterlettuce (*Pistia stratiotes*), widgeongrass (*Ruppia maritima*), and *Sagittaria* sp. in about 5 percent of its total area. One bank was heavily covered with willow (*Salix* sp.). Shelter Pond contained a dense stand of *Chara* sp., which covered about one-third of the bottom, and *Hydrilla verticillata*, which covered about 50 percent of the pond area at the beginning of the experiment. The third pond, designated 11-T, contained small amounts of widgeongrass, *Sagittaria* sp., and *Hydrocotyle* sp. Initially, about 30 percent of its area contained

¹ Southeastern Fish Control Laboratory, Fish and Wildlife Service, U.S. Department of the Interior, Warm Springs, Ga. 31830.

² Supported in part by the U.S. Army Corps of Engineers.

Hydrilla sp. All three ponds were treated with rotenone in May 1971 and restocked in June 1971 with largemouth bass (*Micropterus salmoides*), channel catfish (*Ictalurus punctatus*), bluegill (*Lepomis macrochirus*), and redear sunfish (*Lepomis microlophus*). One month prior to treatment the three ponds were stocked with waterhyacinth so that it would cover 5-10 percent of surface area of each pond at the time of treatment.

A second study area of four ponds was located within a 10-mile radius of Warm Springs, Ga., on the Piedmont Plateau and was comprised of four ponds which contained little, if any, submersed vegetation. Several of the ponds had small stands (less than 5 percent coverage) of cattail. Because the ponds contained established fish populations of the desired species, only enough fish were added to ensure an adequate number for the experiment. Waterhyacinths were transported from Florida to stock the ponds; their total coverage did not exceed 5 percent of the surface area of each pond. The ponds were designated 0, 2, 4, and 8 in accordance with the amount of herbicide applied.

Four ponds representing a third ecological and geographical type were located at the USDI Fish and Wildlife Service, Fish-Pesticide Research Laboratory, Columbia, Mo. Pond 9 contained no emersed or submersed macrophytes because of its prior use as a crayfish holding pond. Pond 15, the control, contained a common grass (*Avena* sp.) which had established itself when the pond was dry. About 5 percent of the surface area of Pond 28 contained cattails. There was also a 20-30 percent infestation of an unidentified filamentous alga. About 10 percent of the surface area of Pond 26 contained smartweed (*Polygonum* sp.). Physical characteristics of the ponds used in the experiment are listed in Table 1.

TABLE 1. Physical characteristics of ponds in Florida, Georgia, and Missouri, and initial 2,4-D concentrations, 1971

POND	SURFACE AREA, ACRES	VOLUME, ACRE-FT	DEPTH, FT		2,4-D, MG/L
			AVERAGE	MAXIMUM	
Fla-Willow	0.60	2.54	4.23	7.0	0.174
Fla-Shelter	0.43	1.45	3.37	6.0	0.436
Fla-11-T	0.80	3.12	3.90	8.0	0.801
Ga-0	1.30	7.30	5.60	11.0	0.000
Ga-2	0.60	2.65	4.40	8.0	0.166
Ga-4	0.90	2.70	3.00	7.0	0.490
Ga-8	0.86	2.95	3.40	7.0	0.857
Mo-15	0.073	0.166	2.26	4.5	0.000
Mo-9	0.073	0.166	2.26	4.5	0.444
Mo-28	0.162	0.368	2.26	4.0	1.002
Mo-26	0.140	0.451	3.20	4.5	1.631

NOTE: Florida ponds had sandy bottoms covered with a muck layer 1-3 inches deep, Georgia ponds had red clay bottoms characteristic of the Piedmont Plateau, and Missouri ponds had bottoms of heavy colloidal clay.

TREATMENT

DMA-2,4-D was applied to nine ponds at 2.24, 4.48, or 8.96 kg per hectare (kg/ha.) (2, 4, or 8 lb/acre) using a commercial formulation of herbicide (Weedar 64, Amchem Products, Ambler, Pa.) which contained 4 lb 2,4-D acid equivalent (a.e.) per gallon. All dilutions were made with water and no adjuvants were used. The Florida ponds were sprayed July 12, 1971, and the Georgia and Missouri ponds were sprayed July 26, 1971.

SAMPLING

Samples of fish, water, and mud were taken at 0, 1, 3, 7, 14, 28, 56, 84 or 86, 112, and 140 or 147 days after treatment. Fish were placed in live-cages in the Florida ponds for first- and third-day samples. Thereafter, fish were collected by hook and line, seine, or setline; they were weighed, measured, wrapped in aluminum foil, bagged, and frozen on dry ice. Water samples were taken with a 2-liter Kemmerer water bottle; they were composites of samples from areas whose depths varied from shallow (1 foot) to medium (2-3 feet) to deep (4 feet or more). The pH of water samples was determined either colorimetrically or with a pH meter. Water for residue analysis was placed in quart jars and acidified to a pH of less than 2 with concentrated sulfuric acid. Jars were capped with aluminum foil and sealed with screw caps.

Mud samples were taken with an Ekman dredge from shallow, medium, and deep sites. The three samples were composited for residue analysis, placed in plastic bags, and frozen on dry ice until analysis.

Analytical Procedures

Acidified water samples were extracted with chloroform which was subsequently evaporated. The 2,4-D residues were derivatized with diazomethane (3) for quantification by gas-liquid chromatography (GLC). Mud samples were acidified and extracted in a blender with a mixture of acetone, petroleum ether, and diethyl ether. The slurry was filtered and extracted twice with base (4). The basic solution was acidified and extracted with chloroform and the chloroform solution was treated as above. Fish samples were ground with dry ice (5) and the resultant powder was packed in a column and extracted with acidified methanol (6). The methanol eluate was added to water, the pH was adjusted to 1.5, and the solution was extracted with diethyl ether. The diethyl ether extract was treated as described earlier for chloroform extracts. Esterified 2,4-D residues were cleaned up on a column of silica gel. The gas chromatograph used to quantify 2,4-D residues was equipped with an electrolytic conductivity detector (7). Recovery values from spiked water, mud, and fish samples were 97.5 ± 2.5 , 90 ± 2.5 , and 90 ± 2.5 , respectively.

All solvents used for extractions were glass-distilled (Burdick and Jackson, Muskegon, Mich.). All other chemicals used were analytical reagent grade. Residue levels are given in terms of the methyl ester of 2,4-D and were not corrected for percent recovery.

The detection limit of the 2,4-D methyl ester was 1.25 ng; 15 ng registered a 50 percent deflection on the recorder. Detection limits were 0.01 mg/kg, 0.005 mg/kg, and 0.001 mg/liter for fish, mud, and water samples, respectively.

Confirmatory analyses of the 2,4-D methyl ester standard, spiked samples, and periodic samples were conducted by electron-capture detection on a Beckman GC-4 gas chromatograph.

Detailed procedures for extraction of 2,4-D residues from water, mud, and fish samples, as well as the derivatization and gas chromatographic procedures, have been described by Schultz and Whitney (7).

WATER

In five of the nine treated ponds, highest residue levels were detected the third day after treatment. Presumably it took this length of time for the herbicide to be thoroughly dispersed in the water. The highest level of 2,4-D residues in Florida pond water was 0.345 mg/liter; it was found 3 days after herbicide application to Pond 11-T, which was treated at 8.96 kg/ha. (8 lb/acre). Residue levels of 2,4-D in Florida ponds decreased to no more than 0.005 mg/liter within 14 days after treatment. Thereafter, only trace amounts (less than 0.005 mg/liter) or no residues were detected (Table 2).

In Georgia pond water the highest detectable residue was 0.692 mg/liter found in Pond 8 three days after treatment at 8.96 kg/ha. Residue levels of 2,4-D in these waters decreased to trace amounts (less than 0.005 mg/liter) within 28 days after treatment; no residues were detected thereafter (Table 2).

TABLE 2. Residues of DMA-2,4-D in water (mg/L) and mud (mg/kg) samples from ponds treated with 2,4-D, 1971

TREATMENT, POND, AND SAMPLE	DAYS AFTER TREATMENT									
	0	1	3	7	14	28	56	84/86 ¹	112	140/147 ²
FLORIDA										
2.24 kg/ha. (Willow Pond)										
water	ND	0.125	0.025	TR	TR	TR	TR	TR	ND	ND
mud	ND	TR	TR	0.005	TR	ND	ND	ND	ND	ND
4.48 kg/ha. (Shelter Pond)										
water	ND	0.155	0.172	0.048	0.005	TR	ND	TR	ND	ND
mud	ND	0.014	0.014	0.010	0.010	0.007	ND	TR	ND	ND
8.96 kg/ha. (11-T)										
water	ND	0.312	0.345	0.025	0.005	TR	ND	TR	ND	ND
mud	ND	0.033	0.046	0.008	0.013	ND	TR	TR	TR	ND
GEORGIA										
No herbicide (Pond 0)										
water	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
mud	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
2.24 kg/ha. (Pond 2)										
water	ND	0.025	0.087	0.059	0.027	TR	ND	ND	ND	ND
mud	ND	0.018	0.008	0.010	0.006	TR	ND	ND	ND	ND
4.48 kg/ha. (Pond 4)										
water	ND	0.233	0.390	0.400	0.050	TR	ND	ND	ND	ND
mud	ND	0.024	0.018	0.003	TR	ND	ND	ND	TR	ND
8.96 kg/ha. (Pond 8)										
water	ND	0.617	0.692	0.395	0.008	TR	ND	ND	ND	ND
mud	ND	0.026	0.040	0.042	TR	ND	ND	ND	ND	ND
MISSOURI										
No herbicide (Pond 15)										
water	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
mud	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
2.24 kg/ha. (Pond 9)										
water	ND	0.104	0.108	0.102	0.050	0.017	ND	ND	ND	ND
mud	ND	ND	TR	0.009	ND	ND	ND	ND	ND	ND
4.48 kg/ha. (Pond 28)										
water	ND	0.160	0.256	0.250	0.480	0.150	ND	ND	ND	ND
mud	*	0.011	0.012	0.005	TR	ND	ND	ND	ND	ND
8.96 kg/ha. (Pond 26)										
water	ND	0.580	0.420	0.326	0.630	0.135	ND	ND	ND	ND
mud	*	0.170	0.170	0.091	0.068	0.005	ND	ND	ND	ND

NOTE: ND = not detectable; TR = trace (less than 0.005 mg/L or kg).

¹ In Florida and Georgia the seventh posttreatment sampling was made 84 days after application; in Missouri it was made 86 days after application.

² In Florida and Georgia the last sampling was made 140 days after application; in Missouri it was made 147 days after application.

* Sample was lost.

The most persistent residues were found in the two most heavily treated Missouri ponds which contained more than 0.1 mg/liter of 2,4-D 28 days after treatment (Table 2). However, no herbicide was detected 56 days after treatment or thereafter.

MUD

Highest 2,4-D residues in mud were consistently found in the ponds which had received the heaviest herbicide treatment. The largest 2,4-D residue detected in mud from Florida ponds was 0.046 mg/kg found in Pond 11-T three days after treatment (Table 2). Trace amounts were found in the same pond up to 112 days after treatment. In the Georgia ponds the highest residue found was 0.042 mg/kg in Pond 8 seven days after treatment (Table 2). A residue level of 0.170 mg/kg from Missouri Pond 26 was found at the first- and third-day samplings; no residues were detected in any other Missouri pond 56 days after treatment or thereafter (Table 2).

FISH

Highest residues found in fish were from the first-day harvest of Willow and Shelter Ponds in Florida (Table 3). These fish were kept in live-cages during and after treatment to facilitate sampling; hence they were unable to escape from the applied herbicide (8). No residues were detected in fish from Florida ponds during the third- or seventh-day harvests; however, residues were detected 14 days after treatment. This may have been caused by release of the herbicide from decaying vegetation. Only one fish from the Florida ponds contained a detectable residue after 14 days. It was one of two largemouth bass from Pond 11-T, which had been treated at 8.96 kg/ha.; the residue was a trace amount (0.005 mg/kg).

The highest 2,4-D residue found in fish from the Georgia ponds was 0.075 mg/kg in one of three bluegills harvested 14 days after pesticide application at 8.96 kg/ha. (Table 3). No detectable residues were found in any fish from the Georgia ponds at the third- or seventh-day harvests; this parallels results of Florida pond samples. With one exception, the last detectable residues were found 28 days after treatment. The exception was a bluegill from Pond 8: it contained less than 0.005 mg/kg 84 days after treatment.

No residues of 2,4-D were detected in fish from the Missouri ponds until 28 days after treatment (Table 3). At that time all five bluegills sampled and one of five largemouth bass sampled had less than 0.005 mg/kg. No other fish from the Missouri ponds contained detectable residues of 2,4-D.

None of the fish from control ponds contained detectable residues of 2,4-D. The four highest residues

were in fish from the first-day harvest which had been held in live-cages in the Florida ponds. The 2,4-D residues found in the exposed fish were well below the levels of the dimethylamine salt formulation found to be toxic to fish (9-11).

WATERHYACINTH CONTROL

The effect of the 2,4-D application on waterhyacinth in the Florida and Georgia ponds was assessed by visual observation. Nearly all the waterhyacinth was brown and decomposing 7 days after spraying. Approximately 98 percent of the plants had been killed by the herbicide application; no difference in kill was noted among the different treatment levels. Spot retreatment was needed in some areas of all ponds to prevent reinfestation from the estimated 2 percent of the waterhyacinth which survived the initial application.

TABLE 3. Residues of DMA-2,4-D in fish from ponds treated with 2,4-D, 1971

SPECIES AND FISH NUMBER	DAYS AFTER TREATMENT	RESIDUES (MG/KG) IN FISH TREATED AT—			
		0 kg/ha.	2.24 kg/ha.	4.48 kg/ha.	8.96 kg/ha.
FLORIDA					
LMB-1	0	ND			
LMB-2	0	ND			
CCF	0	ND			
LMB-1	1		0.080	0.048	TR
LMB-2	1				ND
LMB-3	1				0.008
CCF-1	1		1.075	0.340	ND
CCF-2	1				ND
CCF-3	1				ND
BLG-1	1		0.024	0.420	0.010
BLG-2	1				TR
BLG-3	1				0.012
LMB	3		ND	ND	ND
CCF	3		ND	ND	ND
BLG	3		ND	TR	ND
LMB	7	ND	ND	ND	ND
CCF	7	ND	ND	ND	ND
BLG	7	ND	ND	ND	ND
LMB-1	14	ND	0.036	ND	0.043
LMB-2	14		0.031		ND
LMB-3	14		TR		
CCF-1	14		0.029	0.050	0.024
CCF-2	14		0.032	0.012	0.102
CCF-3	14		0.012	0.039	0.094
BLG-1	14	ND	ND	0.018	ND
BLG-2	14	ND	ND	0.008	ND
LMB-1	28		ND	ND	ND
LMB-2	28		ND	ND	TR
LMB-3	28			ND	
CCF-1	28		ND		ND
CCF-2	28		ND	ND	ND
CCF-3	28		ND	ND	ND
BLG	28		ND	ND	ND
LMB	56		ND	ND	ND
CCF	56		ND	ND	ND
BLG	56		ND	ND	ND
LMB	84		ND	ND	
CCF	84		ND		ND
BLG	84		ND	ND	
LMB	112				ND
CCF	112		ND	ND	ND
BLG	112		ND	ND	ND
LMB	140		ND	ND	ND
CCF	140		ND		ND
BLG	140		ND		ND

(Continued next page)

TABLE 3 (cont'd). Residues of DMA-2,4-D in fish from ponds treated with 2,4-D, 1971

SPECIES AND FISH NUMBER	DAYS AFTER TREATMENT	RESIDUES (MG/KG) IN FISH TREATED AT—			
		0 kg/ha.	2.24 kg ha.	4.48 kg/ha.	8.96 kg/ha.
GEORGIA					
LMB	0	ND			
CCF-1	0	ND			
CCF-2	0	ND			
BLG	0	ND			
LMB	1		ND	0.014	0.022
CCF	1	ND	ND	0.043	0.008
BLG	1	ND	ND	0.024	0.044
LMB-1	3	ND	ND	ND	ND
LMB-2	3			ND	ND
LMB-3	3			ND	ND
CCF-1	3	ND	ND	ND	ND
CCF-2	3	ND	ND	ND	ND
BLG	3			ND	ND
LMB-1	7	ND	ND	ND	ND
LMB-2	7			ND	ND
LMB-3	7			ND	ND
CCF-1	7	ND	ND	ND	ND
CCF-2	7			ND	ND
BLG	7	ND	ND	ND	ND
LMB-1	14	ND		ND	ND
LMB-2	14			ND	ND
LMB-3	14			ND	ND
CCF-1	14	ND		ND	0.012
CCF-2	14			ND	ND
CCF-3	14			ND	ND
BLG-1	14	ND		ND	0.075
BLG-2	14			ND	ND
BLG-3	14			ND	ND
LMB-1	28	ND	ND	ND	0.010
LMB-2	28	ND	ND	ND	0.005
LMB-3	28	ND	ND		
LMB-4	28	ND	ND		
CCF-1	28	ND	ND	ND	ND
CCF-2	28			ND	ND
CCF-3	28			ND	ND
BLG	28	ND	ND	ND	ND
LMB-1	56	ND	ND	ND	ND
LMB-2	56	ND	ND	ND	ND
CCF	56	ND	ND	ND	ND
BLG	56	ND	ND	ND	ND
LMB	84	ND	ND	ND	ND
CCF	84	ND	ND	ND	ND
BLG-1	84			ND	ND
BLG-2	84			ND	TR
LMB-1	112	ND	ND	ND	ND
LMB-2	112			ND	ND
CCF	112	ND	ND	ND	ND
BLG	112	ND	ND	ND	ND
LMB-1	140	ND	ND	ND	ND
LMB-2	140	ND	ND		
LMB-3	140			ND	
LMB-4	140			ND	
LMB-5	140			ND	
CCF-1	140		ND	ND	ND
CCF-2	140		ND	ND	
BLG-1	140		ND	ND	ND
BLG-2	140			ND	
BLG-3	140			ND	
BLG-4	140				ND
BLG-5	140				ND

MISSOURI					
CCF	1			ND	ND
BLG	1			ND	ND
LMB	1			ND	ND
CCF	7			ND	ND
BLG	7			ND	ND
LMB	7			ND	ND
CCF	14			ND	ND
BLG	14			ND	ND
LMB	14			ND	ND
CCF-1	14		ND		
CCF-2	14		ND		
CCF-3	14		ND		
CCF-4	14		ND		
CCF-5	14		ND		
BLG-1	14		ND		
BLG-2	14		ND		
BLG-3	14		ND		

SPECIES AND FISH NUMBER	DAYS AFTER TREATMENT	RESIDUES (MG/KG) IN FISH TREATED AT—			
		0 kg/ha.	2.24 kg ha.	4.48 kg/ha.	8.96 kg/ha.
MISSOURI, cont'd					
BLG-4	14			ND	
BLG-5	14			ND	
LMB-1	14			ND	
LMB-2	14			ND	
LMB-3	14			ND	
LMB-4	14			ND	
LMB-5	14			ND	
CCF	28				ND
BLG	28				ND
LMB	28				ND
CCF-1	28				ND
CCF-2	28				ND
CCF-3	28				ND
CCF-4	28				ND
CCF-5	28				ND
BLG-1	28				TR
BLG-2	28				TR
BLG-3	28				TR
BLG-4	28				TR
BLG-5	28				TR
LMB-1	28				ND
LMB-2	28				TR
LMB-3	28				ND
LMB-4	28				ND
LMB-5	28				ND
CCF	56				ND
BLG	56				ND
LMB	56				ND

NOTE: LMB = largemouth bass, CCF = channel catfish, BLG = bluegills. ND = not detectable. TR = trace (less than 0.005 mg/kg). Blank = no sample analyzed.

Discussion

WATER

Residues in Missouri pond waters were more persistent than were Florida and Georgia residues. This may have been caused partly by cooler water temperatures in the Missouri ponds which may have slowed the biological decomposition. For example, the median water temperature (shallow, medium, deep) in the three Missouri ponds averaged 26.6°C from the day of treatment to 28 days thereafter, whereas average temperatures in the Georgia and Florida ponds were 28.0°C and 30.9°C, respectively. Also, the Missouri ponds had been sprayed on the assumption that they were either 0.1 or 0.25 acres in area. However, when morphometric measurements were made, it was found that their areas in acres were as follow: Pond 9, 0.073; Pond 28, 0.162; and Pond 26, 0.140. Hence the initial concentration of 2,4-D (mg 2,4-D/liter water) in Missouri ponds was almost twice that in Florida and Georgia ponds (Table 1).

Residual persistence of the herbicide in Missouri ponds may also be attributed to direct application of the herbicide to the water surface. Because no waterhyacinth was present, there was little surface biomass to absorb or adsorb and degrade the chemical.

Wojtalik et al. (2) reported residues greater than 0.02 mg/liter at only 2 of 19 stations 4 weeks after treatment at 20 or 40 lb a.e./acre DMA-2,4-D. Aly and Faust (12) reported a photodecomposition loss of 50 percent of a sodium salt of 2,4-D in 50 minutes at pH 7. Hence the disappearance of DMA-2,4-D from water is rapid compared to the herbicide dichlobenil, 2,6-Dichlorobenzonitrile, which had a reported residue of 0.05 mg/liter 85 days after treatment at 0.55 mg/liter, and the herbicide fenac, 2,3,6-Trichlorophenylacetic acid, which had a reported residue of 0.77 mg/liter 85 days after treatment at 1.56 mg/liter (13).

MUD

The dissipation of 2,4-D from mud was quite rapid compared to dissipation of fenac and dichlobenil, which have been reported at 0.06 and 0.12 mg/kg, respectively, 160 days after treatment (13). Presumably, the dissipation of 2,4-D from mud was caused in great measure by microbiological degradation. At least 11 species of bacteria and two actinomycetes are known to degrade 2,4-D (14).

FISH

Chemicals can impart an off-taste or even toxicity to fish consumed by humans; hence it is imperative that residue levels in fish of any pesticide applied to aquatic environments be as low as possible. At this writing, no tolerance levels have been set for residues of DMA-2,4-D in fish.

Only 7 percent of the fish analyzed 28 days or more after treatment contained detectable 2,4-D residues and only 1 percent (one fish) of those analyzed 56 days or more after treatment contained detectable residues (Table 3). Thus if tolerance levels are based on the level of parent compound only, it would appear that fish could be consumed 1 month after treatment. However, degradation products were present in fish for as long as 84 days after treatment in plastic pools (11). Hence the presence of these unidentified products also should be considered.

Little, if anything, is presently known about the direct effects of herbicides on fish reproduction. However, reproduction of bluegills occurred in two Florida ponds, Willow and 11-T, during the experiment. Growth and development of the fry appeared to be normal. At no time was there any evidence of fish mortality caused by the herbicidal application.

Pesticides usually biomagnify through the food chain. Authors found that fish absorbed little 2,4-D when fed radio-labelled herbicide (11). Also, Wojtalik et al. (2) reported no harmful effects or accumulation in zooplankton, phytoplankton, or macroinvertebrates in water treated at 20 or 40 lb a.e./acre. Hence there is little danger of biomagnification of 2,4-D in contrast to the chlorinated hydrocarbon pesticides (15). How-

ever, when fish were exposed to ¹⁴C-DMA-2,4-D in water, radioactive compounds were ubiquitous in all tissues examined (11). Therefore, the identity and potential toxicity of these compounds must not be overlooked. It also has been reported that although fish absorbed more 2,4-D at pH 6 than at pH 9, they retained more of the parent compound at a basic pH (11). Thus, aquatic applications of 2,4-D probably should be avoided under conditions of high pH.

Although fish can be killed by high concentrations of DMA-2,4-D, the reported TL_m at 96 hours (11) is high enough that even a tenfold error in application rate would not decimate a fish population. In the same study, death of fish from the herbicide was found not to result from a single, specific factor such as a carcinogenic effect; it undoubtedly resulted from a plethora of effects on carbohydrate metabolism. On the basis of this study, then, waterhyacinth can be controlled by judicious application of DMA-2,4-D at recommended rates without concomitantly high residue levels in fish, water, or hydrosol.

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LITERATURE CITED

- (1) Smith, G. E., and B. G. Isom. 1967. Investigations of effects of large-scale applications of 2,4-D on aquatic fauna and water quality. *Pestic. Monit. J.* 1(1):16-21.
- (2) Wojtalik, T. A., T. F. Hall, and L. L. Hill. 1971. Monitoring ecological conditions associated with wide-scale applications of DMA-2,4-D to aquatic environments. *Pestic. Monit. J.* 4(4):184-203.
- (3) Howard, S. F., and G. Yip. 1971. Diazomethane methylation of a mixture of chlorophenoxy acids and dinitrophenols. *J. Ass. Offic. Anal. Chem.* 54(4):970-974.
- (4) Woodham, D. W., W. G. Mitchell, C. D. Loftis, and C. W. Collier. 1971. An improved gas chromatographic method for the analysis of 2,4-D free acid in soil. *J. Agr. Food Chem.* 19(1):186-188.
- (5) Benville, P. E., and R. C. Tindle. 1970. Dry ice homogenization procedure for fish samples in pesticide residue analysis. *J. Agr. Food Chem.* 18(5):948-949.
- (6) Hesselberg, R. J., and J. L. Johnson. 1972. Column extraction of pesticides from fish, fish food and mud. *Bull. Environ. Contam. Toxicol.* 7(2/3):115-120.
- (7) Schultz, D. P., and E. W. Whitney. 1973. Monitoring 2,4-D residues at Loxahatchee National Wildlife Refuge. *Pestic. Monit. J.* 7(3/4):146-152.
- (8) Hansen, D. J. 1969. Avoidance of pesticides by untrained sheepshead minnows. *Trans. Amer. Fish. Soc.* 98(3):426-429.
- (9) Davis, J. T., and W. S. Hardcastle. 1959. Biological assay of herbicides for fish toxicity. *Weeds* 7(4):397-404.
- (10) Hughes, J. S., and J. T. Davis. 1963. Variations in toxicity to bluegill sunfish of phenoxy herbicides. *Weeds* 11(1):50-53.

- (11) *Shultz, D. P.* 1973. Dynamics of a salt of (2,4-dichlorophenoxy) acetic acid in fish, water, and hydrosol. *J. Agr. Food Chem.* 21(2):186-192.
- (12) *Aly, O. M., and S. D. Faust.* 1964. Studies on the fate of 2,4-D and ester derivatives in natural surface water. *J. Agr. Food Chem.* 12(6):541-546.
- (13) *Frank, P. A., and R. D. Comes.* 1967. Herbicidal residues in pond water and hydrosol. *Weeds* 15:210-213.
- (14) *Loos, M. A.* 1969. Phenoxyalkanoic acids, pp. 1-50. In P. C. Kearney and D. D. Kaufman, ed. *Degradation of Herbicides*. Marcel Dekker, Inc. New York.
- (15) *Hunt, E. G.* 1966. Biological magnification of pesticides. *Scientific Aspects of Pest Control*, pp. 251-262. *Nat. Acad. Sci., Washington, D.C.* 470 pp.

RESIDUES IN FOOD AND FEED

Chlorinated Hydrocarbon Insecticide Residues in Feed and Carcasses of Feedlot Cattle, Texas—1972¹

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ABSTRACT

Residues of several chlorinated insecticides in fat samples from calves that had been on controlled feed for 112 days were compared with residues in their feed. Both feed and fat samples contained lindane, dieldrin, DDT, DDE, and DDD. Except for dieldrin, each insecticide was found in higher levels in fat than in feed. Addition of ammonium sulfate and ammonium chloride as sources of nonprotein-nitrogen did not affect accumulation of residues. Average residue levels found in composite feed samples were: lindane, 0.002 ppm; DDE, 0.022 ppm; dieldrin, 0.029 ppm; DDD, 0.032 ppm; and DDT, 0.083 ppm. Average residue levels found in the fat were: lindane, 0.026; DDE, 0.261 ppm; dieldrin, 0.030 ppm; DDD, 0.101 ppm; and DDT, 0.292 ppm.

Introduction

The trend in beef production toward large feedlot operations has increased tremendously; the total number of cattle and calves in feedlots in the United States increased from about 7 million head in 1971 to 8.8 million head in May 1972 (1). In response to demands of large feedlot operations, the feed grain industry utilizes the services of professional livestock nutritionists and computer analysis to formulate rations on the basis of least-cost. Thus, ration components and amounts may change according to price but the ration remains constant in nutritional value. Rations are generally composed of high-energy, low-roughage sorghum grain with supplements of alfalfa meal, corn chops, or rice hulls for roughage. Premixed supplements containing a number of essential ingredients such as calcium, phosphorus, salt, trace minerals, antibiotics, and vitamins are also included. The complete ration is mixed and fed,

free choice, to the cattle. Little or no information is provided about the origin of the feed components and there is very little pesticide residue monitoring of either the components or the mixed feed.

Many reports dealing with pesticide residues in specific forage crops have been published (2-7). Annual reports are made by Government regulatory agencies on pesticide residues in total human diet samples, individual items of food or crops at their origin, and meat and poultry samples taken at numerous slaughterhouses throughout the Nation (8). Present investigations were undertaken to determine occurrence and concentration of chlorinated insecticide residues in composite samples of a commercial feedlot ration as it was offered to animals, and occurrence and residue levels of these insecticides in visceral fat of animals at slaughter.

Parallel studies on the use of two levels of both ammonium sulfate and ammonium chloride as sources of supplemental nitrogen were conducted. Ammonium chloride acts as a diuretic and urine acidifier and controls urinary calculi in sheep and cattle (9,10). Studies were undertaken to determine whether the diuretic effect, under practical feedlot conditions, would result in increased excretion and thus decreased pesticide residues in fat samples.

Materials and Methods

The feedlot used in our 1972 study was located near Midland, Tex. Diets of experimental feed were mixed in a mill located on the premises, then distributed by truck to feed bunkers arranged on the periphery of each pen. Feed was mixed and animals were maintained under standard feedlot conditions.

Some 450 calves, purchased commercially and weighing approximately 280 kg (600 lb) each, were used in

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these studies. So far as authors know, none of the calves had been exposed to pesticides either before purchase or in the feedlot, except for possible residues incidental in their feed. Cattle were separated into five groups, examined to insure good health, identified, and kept in separate pens. Calves were randomly and evenly allotted to test groups; weights and feed consumption were recorded monthly (11).

The control diet (group I) was essentially the same as that used by the feedlot, but ammonium salts were excluded. In keeping with existing clearances for ammonium chloride set by the Food and Drug Administration (FDA), U.S. Department of Health, Education, and Welfare, no tetracyclines or growth hormones were included in the ration. Test diets for all five groups had equal levels of crude protein equivalent from nonprotein-nitrogen, and equal caloric values. Group II animals were fed approximately 20 g ammonium chloride per head per day; this is the level used to control calculi formation in the renal system of cattle (9). The group III ration supplied approximately 85 g ammonium chloride per head per day. Animals in groups IV and V were provided diets supplying approximately 25 and 100 g ammonium sulfate per animal per day. These dosages were established to provide the same amount of supplemental nitrogen as was provided groups I and II by ammonium chloride.

Samples of feed were taken after distribution to feed pens. Each day's mix was considered separately; thus random samples were taken twice weekly throughout the study. At each sampling, a cup of mixed feed was removed from both ends and the middle of each trough and the three cupfuls were combined to form a composite sample. The composite samples of each test group were combined and thoroughly mixed, and aliquots were taken for analysis.

Cattle were on feed for 112 days. They were then marketed and slaughtered in a commercial packing plant operating under the inspection of the U.S. Department of Agriculture (USDA). Lot integrity was maintained until final disposition of carcasses. After inspection of carcasses and viscera, samples of omental fat were taken from 50 animals, 10 randomly selected from each of the 5 lots. Samples were immediately frozen for later analysis.

Chlorinated insecticide residues were determined by electron-capture/gas-liquid chromatography (EC/GLC). Samples were prepared for analysis using a modified method of the procedures developed by Kadoum (12,13). Fat and feed samples were extracted by homogenization with hexane in a VirTis-23 homogenizer. Fat samples of 250 mg were cut into small cubes and placed in 5-ml homogenizing flasks; then 4.0 ml pesticide-quality hexane and about 1.5 g anhydrous sodium sulfate were added. Contents of the flasks were then

homogenized for 10 minutes at medium speed. Feed samples of 0.5 to 2.0 g were similarly extracted with 10-20 ml hexane.

Sample cleanup was accomplished on silica gel elution columns. Prior to use, the absorbent, Woelm Activity Grade I silica gel was washed sequentially with methanol, benzene, and hexane; it was dried, first in air, then overnight in a 250° C oven. This process was necessary to eliminate the appearance of gas chromatographic background peaks. Hexane-washed distilled water was added to the dried silica gel for deactivation to a water content of 4.6 percent. Deactivated silica gel was stored in a glass-stoppered bottle until elution columns were prepared just before use. Glass columns 200 by 6 mm were plugged at the bottom with glass wool; 10 cm deactivated silica gel and 1 cm anhydrous sodium sulfate were placed in the column. The absorbent was wetted with 10 ml hexane just before addition of the sample. As soon as the hexane had percolated into the column, aliquots of either 1 ml fat extract or 2 ml feed extract were added. Pesticides were eluted with 1:1 benzene:hexane until a volume of 15 ml of the eluate had been collected. The solvent was removed by evaporation to 0.5 ml at 40° C under a gentle stream of dry nitrogen. The volume was then brought up to 1.0 ml with hexane. Appropriate aliquots were taken for GLC analysis.

Conditions and operating parameters for GLC analysis were as follows:

Instrument: Varian 2100-40 gas chromatograph
Detector: Ni-63; 225°C
Column: 6-ft.-by-¼-in. glass column packed with 1.5 percent OV-17 + 1.9 percent QF-1 on Supelco HD, 80/100 mesh; 195°C
Injector temperature: 225°C
Carrier gas: prepurified nitrogen, 18 ml/min at 50 psi
Attenuation: 4
Range: 1×10^{-10} amps/mv
Sensitivity: 15 percent full-scale (1 mv) response to 5 pg aldrin
Retention: aldrin—2.77 minutes

Insecticide peaks were identified by comparing their retention times and peak geometry with those resulting from addition of known amounts of insecticides to control fat extracts. Additional confirmatory tests were not conducted.

Known amounts of insecticides were added to control samples before extraction in order to determine analytical efficiency.

Results and Discussion

The extraction procedure employed in this study gave satisfactory recoveries from fat tissue of each of the chlorinated insecticides and derivatives studied (Table 1). Gas chromatograms from extracts of control samples were free from interfering peaks at retention times of insecticides in question.

TABLE 1. Recovery of chlorinated insecticides from fortified fat samples

	LINDANE		HEPTACHLOR EPOXIDE		DIELDRIN		<i>p,p'</i> -DDE		<i>p,p'</i> -DDD		<i>p,p'</i> -DDT	
Quantity, ppm Added	0.020	0.040	0.200	0.400	0.040	0.080	0.400	0.800	0.040	0.080	0.400	0.800
Recovered	0.019	0.036	0.184	0.356	0.039	0.066	0.040	0.672	0.038	0.073	0.376	0.800
Percent recovery	97	90	92	89	98	83	100	84	95	92	94	100

NOTE: All recoveries are average of two replications. i Single sample.

TABLE 2. Chlorinated insecticide residues in commercial feed and fat of feedlot cattle after consumption of feed with and without ammonium salts added, Texas—1972

INSECTICIDE	RESIDUES, CATTLE FAT				
	GROUP I UNTREATED CONTROLS	GROUP II NH ₄ Cl 20 G/DAY/ ANIMAL	GROUP III NH ₄ Cl 85 G/DAY/ ANIMAL	GROUP IV (NH ₄) ₂ SO ₄ 25 G/HEAD/ DAY	GROUP V (NH ₄) ₂ SO ₄ 100 G/HEAD/ DAY
Lindane	0.029 ± 0.007	0.025 ± 0.004	0.028 ± 0.009	0.032 ± 0.005	0.014 ± 0.010 ¹
DDE	0.244 ± 0.037	0.274 ± 0.146	0.227 ± 0.076	0.295 ± 0.110	0.236 ± 0.094
Dieldrin	0.033 ± 0.017	0.022 ± 0.027	0.033 ± 0.027	0.044 ± 0.052	0.030 ± 0.023
DDD	0.095 ± 0.040	0.121 ± 0.093	0.099 ± 0.033	0.139 ± 0.051	0.086 ± 0.054
DDT	0.340 ± 0.096	0.324 ± 0.256	0.430 ± 0.106	0.518 ± 0.104	0.352 ± 0.212

NOTE: All residues reported in ppm. Values reported as mean ± standard deviation. Each group represents 10 animals. ¹ Significant, *p* = 0.05

Gas chromatographic analysis indicated that lindane, dieldrin, DDE, DDD, and DDT were present in both feed samples and fat from slaughtered animals (Table 2). Average residues in fat were lindane, 0.026 ppm; DDE, 0.261 ppm; dieldrin, 0.030 ppm; DDD, 0.101 ppm; and DDT, 0.292 ppm. Heptachlor epoxide residues were not detected in any samples analyzed. Values in Table 2 represent means and standard deviations (uncorrected for recovery) calculated from 10 fat samples and 5 feed samples in each group. Residues reported herein are based on adipose tissue as removed from the animals. Such tissue contains 80-85 percent extractable fat.

No evidence of toxicity was observed in any of the cattle; this was expected, considering the very low levels of pesticide consumed. However, observations were made during the test for possible enhancement of toxicity from the addition of ammonium salts to the diet. All animals gained weight normally during the test and showed no evidence of toxic conditions at slaughter.

With the exception of the insecticide dieldrin, all residues found in fat samples were much higher than residues observed in feed. Magnification of this type is well documented and is to be expected. Dieldrin residues present in the fat of each of the animal groups very closely approximate levels found in the diet. The Duncan Multiple Range Test (14), used to determine significance of differences in residues resulting from the test diets, indicated that with the exception of lindane residues in the fat of animals receiving high ammonium sulfate levels, pesticide residue levels were not affected by addition of either ammonium chloride or ammonium sulfate to the diet. Fat samples from animals receiving 100 g/head/day ammonium sulfate had lindane residues significantly lower than those from other treated animals or from control animals.

Conclusions

Low residue levels of five chlorinated insecticides, lindane, dieldrin, DDE, DDD, and DDT, were found in feed and fat of west Texas feedlot cattle. Levels in feed were less than 0.1 ppm; those in fat were less than 0.5 ppm.

Except for decreased lindane residues in cattle receiving 100 g ammonium sulfate daily, chlorinated pesticide residues were not affected by ammonium chloride or ammonium sulfate when ammonium compounds were used as nitrogen supplements.

No ill effects resulting from interaction of pesticides and ammonium compounds were observed in any of the groups.

The analytical method was sensitive and efficient for analysis of fat samples for low levels of multiple chlorinated insecticide residues.

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LITERATURE CITED

- (1) *Santa Fe Crop Report*. June 1972.
- (2) Moubry, R. J., G. R. Myrdol, and H. P. Jensen. 1967. Chlorinated hydrocarbon residues in or on alfalfa grown in soil with a previous history of aldrin and heptachlor application. *Pestic. Monit. J.* 1(2):13-14.
- (3) Marth, E. H. 1965. Residues and some effects of chlorinated hydrocarbon insecticides in biological material. *Residue Rev.* 9:1-89.
- (4) Finlayson, D. G., and H. R. McCarthy. 1965. The movement and persistence of insecticides in plant tissue. *Residue Rev.* 9:114-152.
- (5) Bruce, W. N., G. C. Decker, and J. G. Wilson. 1966. Relationship of the levels of insecticide contamination of crop seed to their fat content and soil concentrations of aldrin, heptachlor and their epoxides. *J. Econ. Entomol.* 59:179-181.
- (6) Newsom, L. D. 1967. Consequences of insecticide use on nontarget organisms. *Annu. Rev. Entomol.* 12:257-286.
- (7) Daniels, N. E. 1968. Insecticidal residues in soil and grain sorghum. *Tex. Agr. Exp. Sta. Bull.* PR-2531.
- (8) Duggan, R. E., and H. R. Cook. 1971. National food and feed monitoring program. *Pestic. Monit. J.* 5(1):37-43.
- (9) Crookshank, H. R., F. E. Keating, Earl Burnett, J. H. Jones, and R. D. Davis. 1960. Effect of chemical and enzymatic agents on the formation of urinary calculi in fattening steers. *J. Anim. Sci.* 19:595-600.
- (10) Crookshank, H. R. 1970. Effect of ammonium salts on the production of ovine urinary calculi. *J. Anim. Sci.* 30:1002-1004.
- (11) Crookshank, H. R., H. E. Smalley, Dale Furr, and George F. Ellis. 1973. Ammonium chloride and ammonium sulfate in cattle feedlot finishing ration. *J. Anim. Sci.* 36:1007-1009.
- (12) Kadoum, A. M. 1967. A rapid micromethod of sample cleanup for gas chromatographic analysis of insecticidal residues in plant, animal, soil, and surface and ground water extracts. *Bull. Environ. Contam. Toxicol.* 2(5):264-273.
- (13) Kadoum, A. M. 1968. Application of the rapid micromethod of sample cleanup for gas chromatographic analyses of common organic pesticides in ground water, soil, plant and animal extracts. *Bull. Environ. Contam. Toxicol.* 3:65-70.
- (14) Duncan, D. B. 1955. New Multiple Range Test. *Biometrics* 11:1-42.

GENERAL

DDT and Dieldrin in Watersheds Draining the Tobacco Belt of Southern Ontario

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ABSTRACT

Production of flue-cured tobacco in Ontario is concentrated mainly in four watersheds adjacent to Norfolk County on the north shore of Lake Erie, where tobacco is raised on a sandy loam soil using a 2- to 3-year rotation with cereals and corn. In 1961-69 an average amount of 4.4 kg/ha. DDT was used to control soil and foliar insects attacking tobacco. In 1970-71, DDT was restricted to the control of soil insects only; applications averaged 1.7 kg/ha. Residue data from soil samples collected in 1971 indicated total levels of 325,000 kg Σ DDT and 14,000 kg dieldrin in the entire tobacco-growing area. These residues represented 37 percent of the total DDT application to the area since 1961, and were calculated to agree with the half-life disappearance of 3-4 years.

Residue analysis of the tobacco crop in 1971 (42 million kg cured leaf) revealed that 52.6 kg Σ DDT and 1.97 kg dieldrin had been removed from the soil. This represents 0.18 percent of the DDT applied in 1971 or 0.03 percent of the Σ DDT and dieldrin resident in the soil the same year. Corn silage and hay were calculated to contain 38.3 kg DDT and 0.76 kg dieldrin, but these residues remained in the watershed because the crops were used as feed for livestock. Animal products leaving the watershed in 1971 amounted to 54 million kg milk and 6 million kg meat which contained only 0.95 kg Σ DDT and 156 g dieldrin.

Total water discharging into Lake Erie from the four watersheds was calculated to carry 12.6 kg Σ DDT and 0.86 kg dieldrin in the water and on suspended sediments, representing 0.002 percent and 0.003 percent, respectively, of the Σ DDT and dieldrin resident in the four watershed soils.

Fish species caught in Big and Dedrich Creeks contained residues 4 to 15 times higher than those of species from Long Point Bay and Lake Erie, reflecting the rapid dilution of the creek waters within 3 miles of the mouths of these creeks. Lowest pesticide concentrations in fish were about the same as the concentrations in water-suspended sediments. Magnification observed from water to the highest concentrations in large fish was approximately 10^5 ; however, the tissue residue did not exceed the 5 ppm tolerance established in fish.

Residues in air appeared to be the result of either spray drift or airborne soil particles rather than volatilization from the soil.

Introduction

Production of flue-cured tobacco in Ontario is concentrated in a few counties along the north shore of Lake Erie. Forty-six percent of this cropping area is located in the four watersheds of Big Creek, Big Otter Creek, Dedrich Creek, and Nanticoke Creek, which are centered around Norfolk County (Fig. 1). The total area of these four watersheds is 190,340 hectares (ha.) (Table 1). The land is flat or gently undulating and the soil is a deep sandy loam derived from alluvial deposits. Agricultural production occupies 80 percent (152,610 ha.) of the watershed area and tobacco production occupies 10-15 percent of this agricultural land (1). Corn and grain, especially rye, are alternated with tobacco in a 2- to 3-year crop rotation.

The dark-sided cutworm (*Euxoma messoria*) has been a serious pest to tobacco production of the area since 1961. This species has shown a high tolerance to cyclo-diene insecticides (2); thus DDT has been used, instead, as an effective early-spring treatment applied to the rye cover crop before plow-down or to soil before planting tobacco (3,4). DDT has also been used to control leaf-eating insects during the season. As a result

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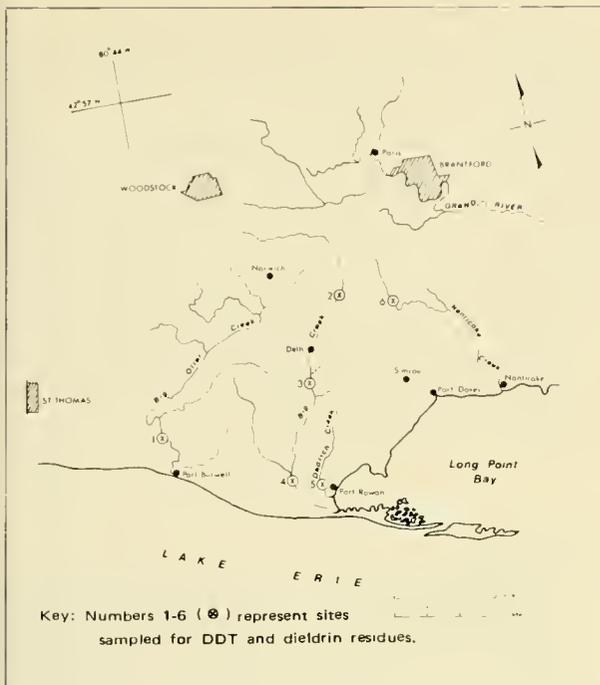


FIGURE 1. Four watersheds draining tobacco belt of southern Ontario, Canada

of these treatments, Harris and Sans have reported residues between 3 and 4.5 ppm Σ DDT in tobacco soils of Ontario (5). Residues increased from 3.1 ppm in 1964 to 4.6 ppm in 1966, and declined slightly in 1969 to 3.4 ppm.

The pathway of DDT and its metabolites into the aquatic environment on soil particles is well documented for many parts of the world. Residues found in the water, sediment, and fish in this area have been reported by Miles and Harris, and Frank et al. According to Miles and Harris, highest concentrations were 67 parts per trillion (ppt) in water, 441 parts per billion (ppb) in mud, and 1.0 parts per million (ppm) in fish (6). Frank et al. reported a mean of 91 ppb Σ DDT in sediments and a residue range of 0.03 to 3.86 ppm in fish depending on the species and its position in the aquatic food chain (7).

Miles and Harris noted a correlation between rainfall and the concentration of insecticides in Big Creek, and reported that this creek carried 50 g DDT per week into Lake Erie in 1970 (6). Although the largest quantity of DDT was used in this area, residues in river sediment were no higher than those in recreational areas where only small quantities were used for spraying mosquitoes (7). This was especially evident on the Precambrian Shield where rock was bare or only thinly covered with soil, and DDT readily found its way to lakes and streams following rain.

Joint action by the Ontario Ministries of the Environment and of Agriculture and Food restricted DDT to three permit uses in 1970. Included was a use for cut-worm control on tobacco which permitted application of 1.7 kg/ha. to a rye cover crop at plow-down or a soil treatment before planting. Between 85 and 90 percent of the DDT applied under permit in Ontario was used in tobacco production and about 40 percent, 28,970 kg, was used in the study area (Table 1).

Most of this study was carried out in 1971 within the boundary of the specified watersheds with the intention of drawing up a balance sheet on the use and dispersal of DDT. Samples were collected from the physical environment, agricultural products, and aquatic biota.

Field Procedures

PHYSICAL ENVIRONMENT

Authors selected six sites on the four watersheds drained by Big Creek, Big Otter Creek, Dedrich Creek, and Nanticoke Creek for regular sampling; four of these, 1, 4, 5, and 6, were so located that 96, 87, 100, and 81 percent of the tobacco acreage, respectively, were upstream from the site.

Sample sites 1, 4, and 5 on Big Otter, Big, and Dedrich Creeks, respectively, were only a short distance upstream from flow gauge meters; they were located on sections of each creek where no major inflow of water occurred between any two creeks. Site 6 on Nanticoke Creek was in the tobacco belt; the flow meter was located downstream at the town of Nanticoke. Water passing the gauge was collected occasionally during the season and compared with water from site 6.

TABLE 1. Land acreage, water discharge, and DDT use by watershed, southern Ontario—1971

WATERWAY	WATERSHED AREA, ha.	WATER DISCHARGE ($\times 10^6$ m ³)	AGRICULTURAL AREA, ha.	TOBACCO, ha.	DDT PURCHASED, ¹ kg
Big Otter Creek	79,965	165.0	71,430	6,156	11,175
Big Creek	81,815	143.0	57,830	8,562	15,288
Dedrich Creek	8,650	12.9	6,190	512	927
Nanticoke Creek	19,910	33.4	17,160	870	1,580
TOTAL	190,340	354.3	152,610	16,100	28,970

¹ DDT purchased by permit.

Creek water samples of 4.5 liters were collected weekly throughout the season from all six sites. Samples were taken from the center of the streams between the surface and the water-sediment interphase. Although most waters were clear, all were filtered through Whatman No. 1 filter paper to remove suspended material. Water was quite clear and colorless following this procedure; deposits were too small to analyze.

Creek sediment samples weighing 450 g were collected weekly from the same locations by scraping along the creekbed and skimming up surface and mobile sediments. Water and sediments were also collected off the mouths of Big and Dedrich Creeks and from Inner Long Point Bay during the spring and late summer.

Soils were collected during the spring and fall from one woodlot and several rye and tobacco fields on six to eight farms around each of the six sites. Rye and tobacco soils were sampled from surface to plow-depth.

An air monitor was set up in the middle of the tobacco belt close to site 3 on Big Creek; airborne organics were extracted into acetonitrile on 33 days (24-hr periods) between May 13 and August 31, 1971. Between 3,540 and 3,960 liters of air were passed through the acetonitrile in a 24-hour period.

AGRICULTURAL PRODUCTS

Flue-cured tobacco was sampled at the end of the 1971 season from 20 farms in the four watersheds. Composites of 500 g were obtained from each of the five primings by sampling several bales on each farm. Composite milk samples of 1.1 liters were obtained from 26 bulk transporters that collected the total volume of milk produced in the four watersheds. Samples were taken directly from the tanker following mechanical mixing. Collections were made over a 2-week period in early summer 1971. Composite beef fat samples of 100 g were collected from abattoirs where animals were known to have come from the study area. A 1-inch cube of fat was removed from the backs of up to 10 carcasses to procure one sample.

Samples of corn silage, hay, drinking water, milk, and beef were collected from farms around the six creek sites in October 1971. Silage samples of 25 kg were taken during the normal course of unloading and feeding; composite hay samples of 10 kg were obtained from a minimum of 10 bales in storage; water samples of 1 liter were collected from farm ponds and wells; and milk samples of 0.6 liter were taken from holding tanks on farms where silage or hay was obtained. Beef fat was obtained from farms where animals were going for slaughter.

AQUATIC BIOTA

A total of 289 fish of 24 species were caught either by net or line between 1969 and 1972. Researchers caught eight species predominantly in the creeks and ten in the bay or the lake; six species were common to both creeks and the lake (Table 2). The majority of the fish caught in the creeks were from Big Creek or its tributaries; only a few were obtained from the Big Otter. Those from Dedrich and Nanticoke Creeks were caught close to the mouths and were common to Long Point Bay. All fish were weighed and measured before evisceration. Analyses were conducted on the puree produced by homogenizing the eviscerated fish. Individual fish which were analyzed weighed over 25 g.

Analytical Procedures

EXTRACTIONS

Researchers partitioned 1 liter of filtered water twice by shaking it vigorously for 60 seconds with 50 ml dichloromethane. Extracts of dichloromethane were dried by passing them through anhydrous sodium sulfate and evaporating just to dryness with rotary vacuum at 45° C. Residues were redissolved in 10 ml hexane. Soil and sediment samples were air dried and ground to a fine consistency. A 25-g sample was moistened with 4 ml water and allowed to stand for 12 hours. Soil was extracted with 250 ml 1:1 acetone:hexane (v/v) by shaking briskly on a wrist-action shaker for 2 hours. A 100-ml aliquot was removed by filtering and shaking with 300 ml 2 percent aqueous sodium chloride for 60 seconds. The hexane extract was dried by passage through anhydrous sodium sulfate; it was evaporated to 5-10 ml by rotary vacuum at 45° C.

The acetonitrile solution from the air impinger was reduced to approximately 100 ml by rotary vacuum at 75° C. The solution was partitioned by shaking vigorously, first with 100 ml hexane for 60 seconds, then with 500 ml 2 percent aqueous sodium chloride for 30 seconds. The hexane extract was dried by filtration through anhydrous sodium sulfate; it was reduced to 5-10 ml by rotary vacuum at 45° C.

Hay and silage samples of 25 g dry weight were extracted by blending them with 250 ml 2:1 acetonitrile:water. A 100-ml aliquot was filtered off and partitioned into 100 ml hexane. The extract was concentrated to 5-10 ml by rotary vacuum. Moisture content of the silage and hay was determined by drying at 80° C.

Butterfat was separated from milk samples with a detergent reagent which had been prepared from 200 g sodium tetrphosphate and 24 ml Triton X-100 in 1 liter distilled water. Butterfat was separated in a water bath at 95°-100° C with 100 ml milk and 100 ml detergent.

TABLE 2. Accumulations of DDT, its metabolites, and dieldrin in several fish species by weight class

SPECIES	LOCATION	WEIGHT CLASS, g	No. FISH ANALYZED	AVERAGE WEIGHT, g	ΣDDT			DIELDRIN		
					TISSUE, ppm	FAT, ppm	FISH, μg	TISSUE, ppm	FAT, ppm	FISH, μg
WATERSHED CREEKS AND LAKE ERIE										
<i>Clupeiformes</i>										
<i>Cyprinidae</i>										
Carp (<i>Cyprinus carpio</i>)	Creek	All	1	2460	0.45	5.47	1107	0.04	0.49	98.4
	Lake	All	1	577	0.05	3.13	28.9	0.005	0.31	2.89
<i>Perciformes</i>										
<i>Centrarchidae</i>										
Rock bass (<i>Ambloplites rupestris</i>)	Creek	All	5	90	0.76	20.8	82.9	0.04	1.05	3.38
	Lake	All	13	147	0.076	4.15	11.8	0.003	0.16	0.25
Bluegill (<i>Lepomis macrochirus</i>)	Creek	All	2	180	0.075	1.98	12.2	0.005	0.186	1.15
	Lake	All	4	209	0.021	4.07	3.33	0.001	0.138	0.126
Pumpkinseed (<i>Lepomis gibbosus</i>)	Creek	All	7	82	0.60	13.0	23.2	0.024	0.48	1.32
	Lake	All	5	98	0.041	3.15	4.02	0.005	0.37	0.48
<i>Siluriformes</i>										
<i>Ictaluridae</i>										
Brown bullhead (<i>Ictalurus nebulosus</i>)	Creek	All	3	301	0.430	60.0	86.3	0.018	2.68	3.16
	Lake	All	3	137	0.039	16.4	4.17	0.002	0.72	0.23
<i>Amiiformes</i>										
<i>Amiidae</i>										
Bowfin (<i>Amia calva</i>)	Mouth	All	1	765	0.03	2.24	24.5	0.004	0.28	3.06
WATERSHED CREEKS										
<i>Cypriniformes</i>										
<i>Catostomidae</i>										
White sucker (<i>Catostomus commersoni</i>)		0-100	2	6	0.010	18.5	0.07	0.004	6.00	0.02
		101-200	4	153	0.405	14.9	25.3	0.019	2.19	2.87
		over 200	2	472	0.050	51.2	30.4	0.004	1.06	1.89
<i>Cyprinidae</i>										
Creek chub (<i>Semotilus atromaculatus</i>)		All	5	72	0.678	16.0	33.9	0.036	1.17	1.96
Blacknose dace (<i>Rhinichthys atratulus</i>)		All	16	2.2	1.07	13.8	1.50	0.080	1.23	0.12
Spottail shiners (<i>Notropis hudsonius</i>)		All	10	5.2	0.382	10.4	3.03	0.018	0.43	0.07
<i>Perciformes</i>										
<i>Centrarchidae</i>										
Largemouth bass (<i>Micropterus salmoides</i>)		All	2	153	3.86	51.2	740.0	0.190	4.92	34.9
<i>Salmoniformes</i>										
<i>Salmonidae</i>										
Brown trout (<i>Salmo trutta</i>)		All	6	122	1.44	30.7	164	0.047	1.02	5.9
Rainbow trout (<i>Salmo gairdneri</i>)		0-1000	4	270	1.43	38.6	229	0.050	1.44	7.6
		1001-2000	2	1415	1.08	18.1	1518	0.100	1.68	137
		2001-3000	2	2750	1.03	18.3	2828	0.070	1.24	193
		over 3000	1	6400	1.35	25.1	8640	0.070	1.30	448
<i>Umbridae</i>										
Central mudminnows (<i>Umbra limi</i>)		All	3	3.7	0.81	27.1	3.0	0.050	1.67	0.19
LONG POINT BAY AND LAKE ERIE										
<i>Clupeiformes</i>										
<i>Clupeidae</i>										
Alewife (<i>Alosa pseudoharengus</i>)		All	8	102	0.25	1.13	26.2	ND	ND	ND
<i>Cypriniformes</i>										
<i>Catostomidae</i>										
Northern redhorse (<i>Moxostoma macrolepidotum</i>)		All	3	742	0.162	10.8	119	0.009	0.585	6.06
<i>Perciformes</i>										
<i>Centrarchidae</i>										
Smallmouth bass (<i>Micropterus dolomieu</i>)		0-150	9	87	0.12	5.3	10.3	0.005	0.24	0.47
		150-300	11	220	0.48	30.8	104.4	0.005	0.33	1.21
		300-450	8	373	0.54	26.4	194	0.012	0.40	4.66
		450-600	6	486	1.04	34.1	485	0.020	0.59	9.63
		over 600	3	1192	0.88	13.3	1241	0.013	0.25	11.6
Black crappie (<i>Pomoxis nigromaculatus</i>)		0-100	5	75	0.117	7.82	8.71	0.019	1.02	1.12
		100-200	2	152	0.174	15.6	26.3	0.006	0.50	0.85
Green sunfish (<i>Lepomis cyanellus</i>)		All	4	199	0.050	2.18	11.0	ND	ND	ND
<i>Percidae</i>										
Yellow perch (<i>Perca flavescens</i>)		0-50	6	47	0.102	3.33	4.69	0.024	0.87	1.12
		51-100	18	79	0.063	3.16	3.70	0.009	0.54	0.70
		101-150	15	126	0.081	7.84	10.13	0.003	0.29	0.36
		over 150	3	174	0.043	3.75	7.56	0.008	0.67	1.38
<i>Sciaenidae</i>										
Freshwater drum (<i>Aplodinotus grunniens</i>)		0-200	7	171	0.047	0.71	7.90	ND	ND	ND
		201-400	7	316	0.071	0.81	27.0	ND	ND	ND
		over 400	6	513	0.245	3.24	128	0.007	0.031	3.45
<i>Serranidae</i>										
White bass (<i>Morone chrysops</i>)		50-100	9	82	0.101	5.82	7.81	0.004	0.29	0.27
		101-150	19	118	0.122	5.70	14.9	0.007	0.44	0.90
		151-200	10	180	0.153	3.87	27.8	0.009	0.29	1.69
		over 200	4	394	0.470	5.69	229	0.013	0.16	6.52
<i>Salmoniformes</i>										
<i>Osmeridae</i>										
American smelt (<i>Osmerus mordax</i>)		0-20	4	16	0.13	7.4	2.0	0.009	0.52	0.14
		20-40	9	28	0.19	8.4	5.3	0.013	0.55	0.34
<i>Salmonidae</i>										
Coho salmon (<i>Oncorhynchus kisutch</i>)		0-1000	7	622	1.14	18.0	829	0.016	0.24	10.2
		over 1000	2	2883	2.38	41.5	6652	0.004	0.07	11.5

Beef or beef fat containing significant amounts of connective tissue was extracted by soxhlet as described for fish tissues.

Eviscerated fish were ground into a puree and 10 g were mixed thoroughly with sodium sulfate and Ottawa sand. The mixture was exhaustively extracted by soxhlet over a period of 6 hours with 300 ml hexane. Solvent was removed by rotary-vacuum evaporation and the amount of lipids was determined gravimetrically.

COLUMN CLEANUP

Water, air, soil, sediment, hay, and silage extracts and up to a maximum of 1 g extractible fat or oil from milk, meat, and fish were quantitatively mixed with 25 g florisil (60/100 mesh) previously deactivated by equilibration with 5 percent water. A second 25-g portion of similarly deactivated florisil was first added to a chromatographic column, and the florisil, plus extract, was then added to form the upper half of the cleanup column. Columns were eluted with 300 ml 1:4 dichloromethane:hexane (v/v) at a rate of approximately 5 ml/min. (8). The eluate was evaporated just to dryness with rotary vacuum at 45° C and redissolved in hexane. Polychlorinated biphenyls (PCB's) were separated from the samples on a charcoal column before gas-liquid chromatographic determinations. PCB results will appear in a later report.

GAS CHROMATOGRAPHY

Qualitative and quantitative gas chromatographic determinations were carried out using the following parameters:

- Columns: 152-cm-by-3.2-mm-OD Pyrex containing 4 percent SE-30 + 6 percent QF-1 on 80/100 Chromosorb W-AW preconditioned 72 hr at 225° C.
- Detector: Electron capture, either tritium or Ni-63.
- Temperatures: Injection block 225° C.
Column 175° C isothermal.
Detectors 200° C (tritium), 275° C (Ni-63).
- Carrier Gas: Nitrogen at 40 ml/min.

Limits of detection for all ingredients except DDT were 0.001 ppb in water, 0.001 ppm in soil, sediment, and plant tissue, and 0.005 ppm in extractible fat of milk, meat, and fish. For DDT the limit of detection was twice these levels.

CONFIRMATORY PROCEDURES

When concentrations permitted, qualitative DDT confirmations were carried out by thin-layer chromatography (TLC) using a 250- μ layer of silica gel developed with 1 percent chloroform in n-heptane and visualized with alkaline silver nitrate. Additional confirmation was achieved by removing the appropriate section of the TLC adsorbent and eluting it with a polar solvent for reexamination by gas chromatography. To form the respective dehydrochlorinated derivatives which were measured by gas chromatography (9), *p,p'*-DDT and *p,p'*-TDE were confirmed by treatment with alcoholic potassium hydroxide.

RECOVERY STUDIES

Recoveries of pesticides were checked periodically by direct fortification into the substrate with an acetone solution followed by extraction and cleanup as described above. Fortified milk samples were allowed to stand 24 hours prior to separation of butterfat; soil and sediment samples stood 1 week before extraction. The efficiency of the air sampler could not be practically determined. Recoveries from air samples are indicative only of the acetonitrile partitioning and cleanup operations.

Averaged percent recoveries were as follow:

	WATER	SOIL AND SEDIMENT	MILK, BEEF, AND FISH FAT
<i>p,p'</i> -DDE	98	91	96
<i>p,p'</i> -TDE	96	89	92
<i>p,p'</i> -DDT	94	87	91
<i>o,p'</i> -DDT	94	91	93
Dieldrin	96	86	89

Residues were determined on the basis of dried soil, sediment, silage, hay, tobacco, and the extractible fat of milk, meat, and fish. Moisture and fat contents were used in calculating quantities resident in animal populations of the watersheds. Results were not adjusted to include recovery percentages.

Results

DDT USE

Between 1961 and 1969 about 821,400 kg DDT were used on 183,200 ha. tobacco. Annual acreage varied from a high of 23,850 ha. in 1967 to a low of 13,680 ha. in 1964 (Table 3). Following the DDT restrictions of January 1, 1970, rates per hectare were reduced from about 4.4 to 1.7 kg/ha. and purchase was restricted to permitholders. In 1970 and 1971, 61,330 kg were applied to 33,280 ha. tobacco. Thus, over the 11-year period of 1961 through 1971, a total of 882,730 kg DDT was applied to 216,480 ha. tobacco in the four watersheds (Table 3).

SOILS

In the four watersheds 40,455 ha. of land is devoted to tobacco production in a 2- to 3-year rotation involving rye, corn, and wheat (Table 4). In 1971 about 16,100 ha. were devoted to tobacco; 24,355 ha. were cultivated for grain.

Rye fields sampled in April and May 1971 had not been cropped with tobacco since 1968 or 1969, but were to be planted late in May 1971. Mean Σ DDT concentrations in soil by watershed varied from 2.33 to 3.44 ppm (Table 4); dieldrin concentrations varied from 0.10 to 0.19 ppm. Authors calculated that a minimum of 173,700 kg DDT and 8,780 kg dieldrin could be resident in these soils.

TABLE 3. Quantities of tobacco grown and DDT used, southern Ontario—1961-71

YEAR	TOBACCO HARVESTED, ha. ¹	DDT APPLIED, kg
1961	22,760	102,100
1962	21,700	97,300
1963	18,530	83,100
1964	13,680	61,300
1965	16,170	72,500
1966	21,880	98,100
1967	23,850	106,900
1968	22,730	101,900
1969	21,900	98,200
1961-69 (subtotal)	183,200	821,400
1970	17,180	32,360
1971	16,100	28,970
1970-71 (subtotal)	33,280	61,330
TOTAL	216,480	882,730

¹ Agricultural Statistics for Ontario, 1971. (Refer to Literature Cited, reference 1.)

TABLE 4. Σ DDT and dieldrin in soils of tobacco fields and adjoining woodlots of four watersheds, southern Ontario—1961-71

WATERSHED	AREA, ha.	NO. SAMPLES	CONCENTRATION IN SOIL			RESIDUES IN SOIL, kg	
			Σ DDT, ppm	DDE/TDE, %	DIELDRIN, ppm	Σ DDT	DIELDRIN
SOIL: RYE, WHEAT, AND CORN FIELDS ¹							
Big Otter Creek	9,235	10	2.96	19.7	0.19	61,278	3,934
Big Creek	12,845	30	3.44	22.0	0.14	99,051	4,031
Dedrich Creek	765	10	3.20	18.0	0.10	5,487	171
Nanticoke Creek	1,510	10	2.33	21.8	0.19	7,884	643
Total	24,355	60				173,700	8,779
Mean			2.98	20.4 ²	0.16		
SOIL: TOBACCO FIELDS ³							
Big Otter Creek	6,156	12	3.98	19.2	0.19	54,921	2,622
Big Creek	8,562	20	4.36	19.0	0.14	83,683	2,687
Dedrich Creek	512	8	3.95	19.3	0.19	4,522	218
Nanticoke Creek	870	10	3.88	24.8	0.10	7,571	195
Total	16,100	50				150,697	5,722
Mean			4.04	20.6 ²	0.16		
Total acreage in tobacco	40,455						
SOIL: WOODLOTS							
Big Otter Creek	478	3	0.307	13.0	Trace	329	4.3
Big Creek	882	5	0.048	50.0	Trace	95	7.9
Dedrich Creek	61	2	0.074	73.0	Trace	10	0.5
Nanticoke Creek	101	2	0.024	33.0	Trace	5.4	0.9
Total	1,522	12				439.4	13.6
Mean			0.113	42.0 ²	Trace		
Grand Total	41,977	122				324,840	14,515

¹ Residue at end of rotation before planting tobacco.

² DDE represented 17.3 and 17.5 percent Σ DDT and TDE represented 3.1 percent Σ DDT; hence DDT represented 79.6 and 79.4 percent Σ DDT.

³ Residue in soil after tobacco was harvested.

Tobacco fields were sampled in early October 1971, shortly after the crop had been harvested and stalks had been disked under. DDT had been applied in May at plow-down of the rye cover crop or just before planting tobacco. Concentrations of Σ DDT ranged from 3.88 to 4.36 ppm with a mean of 4.04 ppm (Table 4). Because the same fields were involved in rye and tobacco, increase in soil residues suggested that at least 2.35 kg/ha. DDT had been added during the growing season for the two crops. The amount of DDT resident in soil cropped with tobacco in 1971 was calculated at 150,700 kg. Dieldrin residues in soil remained unchanged from rye to tobacco fields and about 5,700 kg was calculated to be present in the tobacco acreage.

Composition of the Σ DDT in soil collected from rye and tobacco fields showed little difference. In both cases

almost 80 percent was present as *o,p'*- and *p,p'*-DDT and only 20.4 and 20.6 percent was present as the two metabolites, DDE (17.1-17.3 percent) and TDE (3.1 percent).

A total of 1,522 ha. (0.8 percent of the four watersheds) is devoted to woodlots. Many of these woodlots are adjacent to or part of tobacco farms. Samples of woodlot soils were taken in both spring and fall. Because no woodlot had actually been sprayed, the mean residue of 0.113 ppm (Table 4) represents drift from either aircraft or ground applications, or else the accumulation of deposits from wind erosion. It was calculated that 440 kg Σ DDT and 14 kg dieldrin were resident in these woodlots. Composition of Σ DDT in these soils varied greatly from as little as 27 percent to as much as 87 percent *o,p'*- and *p,p'*-DDT.

A total of 324,840 kg Σ DDT was calculated to be present in the 41,977 ha. of land, including woodlots, involved in tobacco production. This amount represented almost 37 percent of the total estimated application of 882,730 kg over the 11-year period. Assuming a half-life of 3 and 4 years for Σ DDT, the predicted residue falls between 297,000 and 386,000 kg. These calculations support a half-life of 3 to 4 years for DDT in the light sandy loams observed in this study.

Total dieldrin residue amounted to 14,515 kg in 41,977 ha. of land; no estimate of use over the 11-year period was available. Use of aldrin and dieldrin in the 5 years preceding this study had been slight, largely because of the increasing preponderance of the dark-sided cutworm which exhibited a high tolerance to cyclodiene insecticides (2).

TOBACCO

The largest exported crop which removed organochlorine residues from the soil of the four watersheds was tobacco (Tables 4,5). The residue level of Σ DDT in cured tobacco leaf varied from farm to farm; mean residues declined from 2.52 ppm in sand leaves to 0.66 ppm in tips. The major portion of this Σ DDT was *o,p'*- and *p,p'*-DDT; 21-30 percent was DDE, and 4-9.5 percent was TDE. The amount of Σ DDT in the 1971 crop was calculated at 52.6 kg. If it were all derived from the 1971 application, this would represent 0.18 percent

of the 28,970 kg applied. If it were derived from Σ DDT resident in tobacco soils during the growing season, it would represent only 0.035 percent.

Dieldrin residues were insignificant, declining from 0.09 ppm in the sand leaves to 0.02 ppm in the tips. The amount of dieldrin calculated to be present in the crop was 1.97 kg, representing 0.035 percent of that resident in the planted tobacco acreage.

SILAGE

Silage in the four watersheds is produced largely from corn which is often inserted in the tobacco-grain rotation in place of wheat for feeding dairy or beef cattle. In the four watersheds approximately 6,028 ha. corn produced 172.7×10^6 kg silage during 1971 (Table 6). The weighted mean of this silage crop contained 0.339 ppm Σ DDT and 0.005 ppm dieldrin on a dry-weight basis. Total quantity of Σ DDT in the whole crop was calculated at 34.2 kg and 536 g dieldrin.

Composition of DDT in the silage varied greatly from a high of 74 percent to a low of only 21 percent *o,p'*- and *p,p'*-DDT. Likewise, the *p,p'*-DDE content ranged from 22 to 77 percent; TDE content ranged from 2 to 6 percent. These findings suggest that residues resulted from spray drift where *o,p'*- and *p,p'*-DDT were high, and from soil uptake or soil contamination where DDE was high.

TABLE 5. Σ DDT and dieldrin in cured tobacco leaf of four watersheds, southern Ontario—1971

PRIMING (LEAVES)	CURED LEAF ¹ PRODUCTION ($\times 1000$ kg)	CONTENT IN DRIED CURED LEAF, ppm		DDT METABOLITES, %		RESIDUES IN CROP, kg	
		Σ DDT	DIELDRLIN	DDE	TDE	Σ DDT	DIELDRLIN
1 Sand	4,211	2.52	0.09	21.4	9.5	10.61	0.38
2 Seconds	5,894	2.08	0.07	23.1	7.7	12.26	0.41
3 Thirds	8,000	1.18	0.07	24.6	5.9	9.44	0.56
4 Fourths	13,893	0.98	0.03	29.6	4.1	13.62	0.42
5 Tips	10,104	0.66	0.02	28.8	4.5	6.67	0.20
Total	42,102					52.60	1.97
Mean		1.25	0.05	26.7	5.6		

¹Records of Ontario Flue-Cured Tobacco Marketing Board, 1971. (Refer to Literature Cited, reference 15.)

TABLE 6. Σ DDT in corn silage and hay of four watersheds, southern Ontario—1971

WATERSHED	CROP ACREAGE, ha.	CROP PRODUCTION ($\times 1000$ kg)	MOISTURE, %	RESIDUES IN DRIED FEED		RESIDUES IN TOTAL FEED	
				Σ DDT, ppm	DIELDRLIN, ppm	Σ DDT, kg	DIELDRLIN, g
CORN SILAGE							
Big Otter Creek	3,938	114,020	42.0	0.343	0.004	22.68	265
Big Creek	1,772	49,990	40.5	0.353	0.008	10.50	238
Dedrich Creek	61	1,670	38.5	0.260	0.004	0.27	4
Nanticoke Creek	257	7,030	41.8	0.185	0.007	0.26	29
Total	6,028	172,710				34.21	536
Mean				0.339 ¹	0.005		
HAY ²							
Total	11,792	61,600	10.1			4.10	222
Mean				0.074 ³	0.004		

¹ Σ DDT residue consisted of 21-74 percent DDT, 22-77 percent DDE, and 2-6 percent TDE.

²Hay samples were scarcer than silage samples; hence individual watersheds are not listed.

³ Σ DDT residue on hay by watershed ranged from 0.05 to 0.09 ppm present mainly as actual DDT (75 percent).

TABLE 7. Σ DDT and dieldrin in milk and beef of four watersheds, southern Ontario—1971

WATERSHED	ANNUAL PRODUCTION ($\times 1000$ kg)	Σ DDT IN EXTRACTIBLE FAT, ¹ ppm	COMPOSITION OF DDE AND TDE, %	DIELDRIN IN EXTRACTIBLE FAT, ppm	RESIDUES IN ANNUAL SUPPLY, g Σ DDT	DIELDRIN
MILK PRODUCTION ²						
Big Otter Creek	32,060	0.183	79.1	0.031	234.7	39.8
Big Creek	9,716	0.234	82.9	0.050	90.9	19.4
Dedrich Creek	70	0.230	80.1	0.045	0.6	0.1
Nanticoke Creek	11,716	0.258	86.0	0.057	120.9	26.7
Total	53,562				447.1	86.0
Mean		0.188	81.0	0.035		
BEEF PRODUCTION ³						
Big Otter Creek	4,182	0.340	82.4	0.042	355.5	43.9
Big Creek	1,468	0.325	81.5	0.051	119.3	18.7
Dedrich Creek	57	0.298	80.9	0.030	4.2	0.4
Nanticoke Creek	275	0.267	85.0	0.052	18.4	3.6
Total	5,982				497.4	66.6
Mean		0.333	82.3	0.045		

¹ Average butterfat content: 4%; average beef content: 25%.

² Reference Records, Ontario Milk Marketing Board, Toronto. (Refer to Literature Cited, reference 16.)

³ Annual Livestock Market Review, 1971, Canada Department of Agriculture. (Refer to Literature Cited, reference 17.)

HAY

Hay samples of limited quantity were obtained from fields in the four watersheds but not from tobacco farms. Residues of Σ DDT varied from 0.05 to 0.09 ppm with a mean composition of 75 percent actual DDT. This suggested that the deposition of DDT was recent, possibly resulting from spray drift. Total hay production in the four watersheds was 61.6×10^6 kg in 1971; this contained 4.1 kg Σ DDT and 0.22 kg dieldrin (Table 6).

MILK

Milk produced in the four watersheds totalled 53.6×10^6 kg a year (Table 7). The weighted mean residue of Σ DDT in the butterfat from the four watersheds was 0.188 ppm. Where dairy and tobacco production occurred close together, residues ranged from 0.183 to 0.258 ppm. On three farms that raised tobacco and maintained sizable dairy herds, Σ DDT residues in butterfat were 0.39 ppm; average butterfat in the milk was 4.1 percent. These residues were considerably higher than the provincial average of 0.134 ppm reported by Frank et al. (10). Composition of Σ DDT in the general milk supply ranged from 79 to 86 percent DDE and TDE.

All milk except that from Big Otter Creek watershed had residues of dieldrin above the 1967-69 provincial average of 0.031 ppm (10). A total of 447 g Σ DDT and 86 g dieldrin were present in the annual milk supply of the four watersheds (Table 7). The 447 g DDT present in milk represented only 1.2 percent of the DDT found in hay (4.1 kg) and corn silage (34.1 kg); the 86 g dieldrin in the milk represented 11 percent of that in hay (222 g) and corn silage (536 g).

BEEF

Almost 6 million kg meat a year are produced in the four watersheds (Table 7). Concentrations of Σ DDT ranged from 0.267 to 0.340 ppm with a weighted mean

of 0.333 ppm. Over 80 percent of the Σ DDT was present as the two metabolites DDE and TDE. Beef contained a mean of 25 percent fat; the calculated amount of Σ DDT in the meat supply was about 500 g, a quantity slightly greater than that found in the annual milk supply, but representing only 1.3 percent of that present in the corn silage (34.1 kg) and hay (4.1 kg) produced in the area.

Dieldrin residues in beef fat ranged from 0.030 to 0.052 ppm with a weighted mean of 0.045 ppm. Total dieldrin present in the annual production of beef was less than 70 g, slightly lower than the amount found in the milk supply; this represented about 9.3 percent of the dieldrin present in corn silage (536 g) and hay (222 g) (Table 7).

LIVESTOCK WATER SUPPLIES

Water from shallow wells and from spring- and surface-fed farm ponds was collected to determine contamination of livestock water supplies. Of 14 wells, 3 had waters containing residues of 4, 40, and 50 ppt Σ DDT, respectively, but none contained dieldrin. In 11 wells neither Σ DDT nor dieldrin could be detected.

Six spring-fed and nine surface-fed farm ponds were sampled (Table 8); Σ DDT was detected in two spring-fed ponds at 1 and 50 ppt, and in four surface-fed ponds at 9, 35, 60, and 80 ppt. Dieldrin was found in only two surface-fed ponds at 5 and 8 ppt.

These data give mean residues of 6.7 ppt Σ DDT in 14 wells, 8.5 ppt Σ DDT in 6 spring-fed ponds, and 20 ppt Σ DDT and 1.4 ppt dieldrin in 9 surface-fed ponds.

AIR

On 35 days (24-hr periods) between May 1 and August 31, 1971, air was sampled for DDT. Residues occurred on 19 of the 35 days (Table 9). Highest mean concentrations occurred in May (74 ng/m^3); lowest

concentrations occurred in June (2.3 ng/m³). On 10 of the 19 days only *o,p'*- and *p,p'*-DDT were detected; on 2 other days when *o,p'*- and *p,p'*-DDT were high, TDE was also detected. When found, TDE represented 4.3 percent of the Σ DDT, a normal percent component in the formulated product. Hence these residues were considered to have been the result of spray drift. Spraying operations appeared to have occurred on 12 days: 2 in May, 5 in June, 4 in July, and 1 in August. Mean concentration in air on these spray-days was 46.7 ng/m³ air. On 9 of the 12 days, the concentration in air was less than 10 ng/m³, but on the other 3 days Σ DDT concentrations were 15, 48, and 469 ng/m³.

For 7 days, DDE and TDE were present at 21 percent and 14 percent, respectively, of the Σ DDT (Table 9). The presence of these metabolites suggested that residues were derived from either airborne dust particles or volatiles. The fact that the ratio of DDE + TDE/DDT was 1:2 and fairly constant for the 7 days suggested that these residues were derived from airborne particles rather than from volatiles. Mean concentration on these 7 days was 34.5 ng/m³ Σ DDT. Mean residue in air for the 35 days was 27.4 ng/m³. No dieldrin was detected on any sampling days.

Snow samples were collected in late winter from three main areas in the Big Creek watershed in order to

measure DDT fallout. Samples were divided into upper and lower levels to represent early-winter and late-winter snowfalls. Water from the early snowfalls contained an average of 43 ppt Σ DDT with a high of 205 ppt. Late-winter snow contained only 4 ppt (Table 10). Dieldrin was also highest in early-winter snow with a mean of 10 ppt as opposed to 0.7 ppt in late-winter snow. Composition of the Σ DDT suggested that these residues were derived from airborne particles and not volatiles.

It is assumed that residues detected in air and snow might explain the movement of DDT, its metabolites, and dieldrin from the tobacco crop to other crops such as hay and silage that are not sprayed and often are not grown on soil in which tobacco has been produced.

CREEK AND BAY WATER

Big Otter, Big, Dedrich, and Nanticoke Creeks discharged 165, 143, 12.9, and 33.4 million m³ water, respectively, into Lake Erie during 1971 (11). Monitoring of waters for organochlorine insecticides was extended on Big Creek from February to October, a period that accounted for 81 percent of the discharge. On the other three creeks, monitoring extended from March to October and accounted for 60 to 69 percent of the discharge (Table 11).

TABLE 8. Residues of Σ DDT and dieldrin in surface-fed and spring-fed ponds and farm wells, southern Ontario—1971

SOURCE OF WATER	NO. SOURCES SAMPLED	NO. RESIDUES DETECTED		RESIDUES DETECTED, ppt	
		Σ DDT	DIELDRIN	Σ DDT	DIELDRIN
Surface-fed farm ponds	9	5	7	9, 35, 60, 80	5, 8
Spring-fed farm ponds	6	4	6	1, 50	ND
Farm wells	14	11	4	4, 40, 50	ND

NOTE: ND = not detectable.

TABLE 9. DDT and its metabolites in air from Big Creek watershed, southern Ontario—1971

MONTH OF SAMPLING	NO. DAYS IN OPERATION	NO. DAYS RESIDUES DETECTED	Σ DDT	DDT COMPOSITION, %		
			MEAN RESIDUE IN AIR, ng/m ³	DDE	TDE	DDT
May	9	4	73.9	5.2	6.0	88.8
June	12	4	2.32	0	0	100
July	5	5	23.8	4.0	2.0	94.0
August	9	6	8.11	9.4	13.6	77.0
May-August	35	19	27.4	5.2	6.1	88.7
Suspected sprayings		12	46.7	0	4.3	93.7
Suspected soil or dust		7	34.5	20.8	14.2	65.0

TABLE 10. Σ DDT and dieldrin in snow from Big Creek watershed, southern Ontario—1971

SNOW LAYER	NO. SAMPLES	NO. DAYS RESIDUES DETECTED	MEAN RESIDUE IN WATER, ppt ¹		Σ DDT COMPOSITION, %		
			Σ DDT	DIELDRIN	DDE	TDE	DDT
Upper level	6	4	4	0.7	12	0	68
Lower level	6	4	43	10.0	14	10	76

¹Ppt = parts per trillion.

TABLE 11. Concentration and amount of Σ DDT and dieldrin in creeks, southern Ontario—1971

MONTH	WATERFLOW ¹ ($\times 10^6$ m ³)	CONCENTRATIONS IN WATER, ppt ²		COMPOSITION, %			RESIDUES, g	
		Σ DDT	DIELDRIN	DDE	TDE	DDT	Σ DDT	DIELDRIN
BIG OTTER CREEK								
March	28,659	15.2	1.8	18	48	34	436.0	51.6
April	31,406	18.0	3.0	22	33	45	565.0	94.2
May	14,240	21.4	0.4	13	35	52	305.0	5.70
June	7,214	14.6	0.9	46	14	40	105.0	6.49
July	8,169	9.7	0.8	32	48	40	79.2	6.54
August	4,910	5.7	0.1	32	28	40	28.0	0.49
September	5,486	4.8	0.0	30	50	20	26.3	0.00
October	7,901	4.7	0.1	19	60	21	37.1	0.79
Mar.-Oct.	107,985	14.6	1.5				1,581.6	165.31
% Total	65.4						76.9	87.9
Jan., Feb., Nov., Dec.	57,118	4.7	0.1				268.0	5.71
Annual total	165,103						1,849.6	171.52
Annual mean		11.2	1.0					
BIG CREEK								
February	13,628	5.5	0.2	17	61	21	75.0	2.73
March	37,408	30.0	0.8	18	50	32	1,122.0	29.9
April	24,062	43.0	3.0	15	50	35	1,035.0	72.2
May	11,383	16.8	1.0	17	26	57	191.0	11.4
June	7,776	11.8	0.2	51	17	32	91.8	1.56
July	4,910	8.8	1.5	30	28	42	43.2	7.37
August	4,910	6.9	0.1	26	29	45	33.9	0.49
September	5,875	11.0	0.1	16	29	55	64.6	0.59
October	6,250	7.1	0.1	17	45	38	44.4	0.63
Feb.-Oct.	116,202	23.2	1.1				2,700.9	126.87
% Total	81.1						94.0	96.9
Jan., Nov., Dec.	27,100	6.3	0.1				171.0	2.71
Annual total	143,302						2,871.9	129.58
Annual mean		20.0	0.9					
DEDRICH CREEK								
March	554	23.1	2.5	15	58	27	12.3	1.39
April	3,339	20.0	3.0	15	50	35	66.8	10.0
May	1,629	18.1	0.4	14	41	45	29.5	0.65
June	890	45.1	0.4	9	46	45	40.1	0.36
July	281	8.1	0.8	28	36	36	2.28	0.22
August	250	8.1	0.4	28	36	36	2.03	0.10
September	337	7.4	0.3	27	41	32	2.49	0.10
October	379	6.5	0.2	25	47	28	2.46	0.03
Mar.-Oct.	7,659	20.7	1.7				158.46	12.90
% Total	59.5						82.4	92.5
Jan., Feb., Nov., Dec.	5,215	6.5	0.2				33.9	1.04
Annual total	12,874						192.36	13.94
Annual mean		14.9	1.1					
NANTICOKE CREEK								
March	12,812	11.1	1.2	15	57	28	142.2	15.37
April	4,882	16.0	2.0	25	48	37	78.1	9.76
May	1,821	23.9	1.3	18	31	51	43.5	2.37
June	2,497	18.9	2.5	34	15	51	47.2	6.24
July	241	11.2	1.5	25	35	40	2.70	0.36
August	76	5.5	0.1	25	35	40	0.42	0.01
September	242	7.0	1.0	14	29	57	1.69	0.24
October	455	6.2	0.5	15	48	37	2.32	0.23
Mar.-Oct.	23,026	13.8	1.5				318.63	34.53
% Total	68.9						77.9	80.6
Jan., Feb., Nov., Dec.	10,371	6.2	0.5				64.3	5.19
Annual total	33,397						382.93	39.77
Annual mean		11.5	1.2					
FOUR WATERSHEDS								
Annual total	354,676						5,296.8	354.81
Annual mean		14.8	1.0					
INNER LONG POINT BAY								
Mouths of Big and Dedrich Creeks	89,106 ⁴	12.5	0.3	45	22	33	409.9	8.91
Middle of bay (3 miles)		1.3	ND	100	0	0		
Edge of Inner and Outer Long Point Bay		Trace	ND	—	—	—		

¹ Water Flow Data, Environment Canada. (Refer to Literature Cited, reference 11.)

² Ppt = parts per trillion.

³ Berst and McCrimmon. (Refer to Literature Cited, reference 12.)

The highest concentration of Σ DDT in the waters of these four creeks occurred during the spring months, March to May, when discharge volumes were highest. Concentrations rose to 21, 43, 45, and 24 ppt, respectively, in Big Otter, Big, Dedrich, and Nanticoke Creeks coincident with spring thaw and runoff, cultivation of land, and spraying of the rye cover crop for cutworm control. Concentrations in water declined in midsummer to 5-8 ppt in spite of rainfall that was heavier in the period from July to September (Table 12). Σ DDT in water in Long Point Bay just off the creek mouths contained lower concentrations (12.5 ppt) than either the waters from Big Creek (20 ppt) or Dedrich Creek (14.9 ppt), indicating mixing and dilution as water enters the bay.

Three miles off the mouths of these creeks in the middle of the Inner Bay, residues had declined to 1.3 ppt Σ DDT and were all present as DDE (Table 11). Water collected at the juncture of Inner and Outer Bays contained only traces of DDT. It is estimated that Inner Bay contained 89,106 thousand m^3 water (12) which could contain 410 g Σ DDT and 8.9 g dieldrin.

During the months of February, March, and April, the largest fraction of Σ DDT was present as TDE (Table 11, Fig. 2). The parent compound DDT was lowest in February and increased to become greater than TDE in May; the DDE fraction remained small and unchanged. In the period of May to September, DDT comprised the greatest fraction as it rose to a peak; it then declined in October. The TDE fraction declined to its lowest level in June, but increased again in July. The DDE fraction almost doubled during June to August to 30 percent. By October TDE again became the predominant fraction; DDE and DDT declined and remained in roughly equal proportions. Increase in DDT coincided with its use on rye and the cultivation of the soil for planting the tobacco crop.

The largest resident load of Σ DDT discharged by the four creeks occurred between March and April when

the water discharge volumes were at their highest; this was over 1000 g Σ DDT in the case of Big Creek during March and April (Fig. 3). Big Otter Creek, which discharged a greater volume of water than Big Creek, delivered only half the quantity of DDT to Lake Erie during these peak months. Dedrich, a small creek, discharged only 67 g in April.

Site 6, the main sampling site on Nanticoke Creek, was located in the tobacco belt; the flow meter was downstream. Water at site 6, which was sampled regularly, contained a peak of 24 ppt in May and a low of 5.5 ppt in August. The six water samples collected at the flow meter near the town of Nanticoke had a peak of 35 ppt in May and 4 ppt in August. It was not clear where the additional DDT between the two sites originated because the volume of water almost trebled. Because the residue data at site 6 were more complete than at the flow meter, these site data were used to estimate residue loads. Nanticoke Creek appeared to carry its largest load of DDT, 142 g, in March.

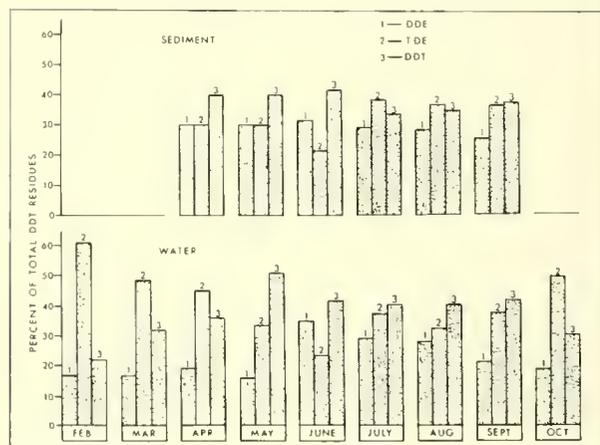


FIGURE 2. Monthly composition of Σ DDT in water and sediment of creeks in study area, 1971

TABLE 12. Frequency and amount of rainfall, 1971¹

MONTH	FREQUENCY OF RAINFALL, DAYS				RAINFALL, cm^2
	RANGE, cm				
	0.01-1.00	1.01-2.00	2.01-3.00	Over 3.01	
January	10	0	0	0	4.72
February	10	3	0	0	8.26
March	3	2	0	0	3.68
April	5	2	0	0	3.73
May	8	0	0	1	4.06
June	8	2	0	0	4.27
July	6	1	1	0	5.36
August	6	0	2	1	9.68
September	10	0	1	0	4.55
October	6	1	0	0	3.86
November	9	2	0	0	5.00
December	9	5	0	0	11.63
Total	90	18	4	2	68.80

¹Climatological Station Report, Canada Department of Agriculture, Delhi, Ontario, 1971. (Refer to Literature Cited, reference 18.)

²Of total rainfall, snow comprised 3.05 cm in January, 3.56 cm in February, 2.03 cm in March, 1.27 cm in April, 1.14 cm in November, and 2.06 cm in December.

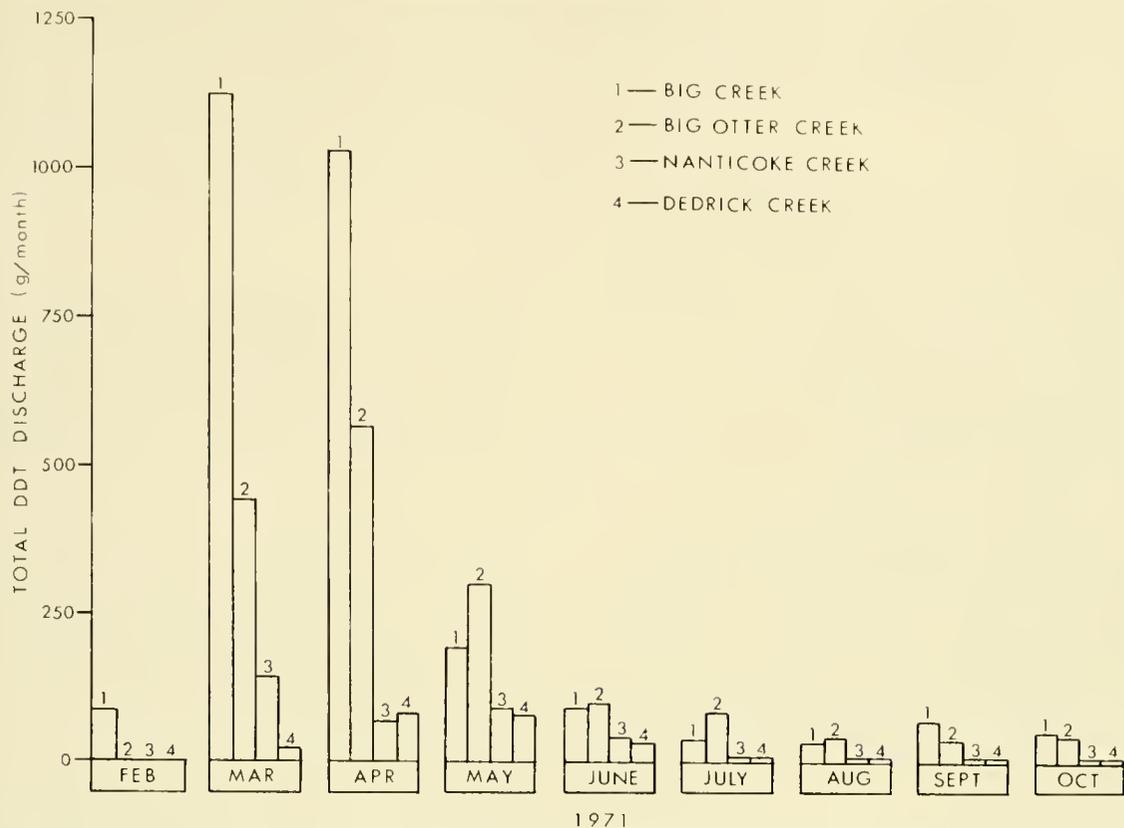


FIGURE 3. Σ DDT residues in discharge water entering Lake Erie from the four creeks in the study area, 1971 (NOTE: no data available on creeks 2, 3, or 4 for February)

Because the concentration of Σ DDT in creek water was highest in the spring and lowest in the fall, an estimate based on lower concentrations was made for quantities of DDT and dieldrin through late fall and early winter. Big Creek carried the greatest annual residue load of Σ DDT which was estimated at 2,872 g. Big Otter Creek carried the second-highest load, 1,850 g, and Nanticoke and DEDRICK CREEKS carried 383 and 192 g, respectively. Collectively, all four watersheds carried a total of 5,297 g/year, an average of 14.5 g/day, into Lake Erie. This represented that portion of DDT and its metabolites that was either dissolved in the water or on particles that passed through Whatman No. 1 filter paper and not that transported on removable suspended sediment.

Concentrations of dieldrin in creek water were also highest in March and April, rising to a level of 2 to 3 ppt. Concentrations declined during the summer and fall to between one-fifth and one-tenth these levels. Dieldrin concentrations represented between one-tenth and one-hundredth the level of Σ DDT. Residues of dieldrin entering Lake Erie were also highest in March and April; the greatest quantity, 94 g, was carried in the

peak month of April by Big Otter Creek. The largest quantity carried by Big Creek, 72 g, occurred in April. Nanticoke and DEDRICK CREEKS carried peak amounts of 15 and 10 g, respectively, in these same months. The annual quantity reaching Lake Erie was 172 g from Big Otter Creek, 130 g from Big Creek, 40 g from Nanticoke Creek, and 14 g from DEDRICK CREEK. Hence the annual discharge of the four watersheds was 354.7 g, almost 1 g/day.

CREEK AND BAY SEDIMENTS

Sediments taken at the interface between creekbed and water showed weekly variations in the concentrations of Σ DDT and dieldrin as they shifted downstream (Table 13). Highest mean Σ DDT residues were observed in sediments from DEDRICK CREEK (141 ppb) but were much lower in Nanticoke Creek (55.6 ppb), Big Otter Creek (41.3 ppb), and the lower reaches of Big Creek (38.7 ppb). Sediments in DEDRICK CREEK contained almost 200 ppb Σ DDT in June; however, this level declined steadily to 93 ppb by September. Greatest residue levels in Big Otter Creek, 58.6-61.0 ppb, were found in August and September. The highest sediment

residues in Nanticoke Creek, 70-95 ppb, were measured between April and June at site 6; these levels declined steadily to 23 ppb by September. At the flow station downstream, sediment residues ranged from 25 to 1 ppt with a mean of 10 ppb, less than one-fifth the residue at site 6.

In Big Creek, highest sediment residues of Σ DDT, 45-51 ppb, were observed on the lower reaches between June and August. In the middle reaches, sediment residues from April to September were relatively uniform (13-21 ppb); in the upper reaches the sediment residue level reached its peak, 42 ppb, in May and declined until August. Sediment collected from Long Point Bay off the mouths of Big and Dedrich Creeks showed Σ DDT residues of 28.7 ppb; they were only 4.3 ppb 3 miles into the bay (Table 13).

Peak concentrations in sediment occurred several months after peak concentrations in water and composition of Σ DDT in sediment differed from that observed in water (Fig. 2). The parent compound DDT predominated in sediments from Big Creek and was generally greater than the DDE fraction in the other three creeks. In Big Creek, DDE was also generally higher than TDE. In early spring and late summer TDE reached its highest percentage, but between these times, in May and June, it declined to its lowest level (Table 13).

Composition of Σ DDT in sediment from Nanticoke Creek differed from that of Big Creek. In the Nanticoke, TDE predominated in samples collected during 4 of the 6 months; DDT and DDE were in approximately equal quantities. Sediments from Dedrich Creek contained predominately DDT during April, May, and June, and predominately TDE during July, August, and September. In Big Otter Creek the composition of Σ DDT showed no definite pattern (Table 13).

In Long Point Bay, TDE predominated in samples collected near the mouths of Dedrich and Big Creeks, but 3 miles out in the bay, TDE and DDE were present in about equal amounts.

Dieldrin residues in sediments from all four creeks were of a similar level; the highest mean residue, 2.1 ppb, was found in Big Otter Creek, and the lowest, 0.7 ppb, was from Dedrich Creek. Residues in sediment in Long Point Bay close to the outlets of Big and Dedrich Creeks contained 0.6 ppb dieldrin although dieldrin could not be detected 3 miles out in the bay. Dieldrin residues in general appeared in quantities between one-twentieth and one-fortieth the levels of Σ DDT.

In 1971 Environment Canada (11) reported that Big Otter Creek carried 54,368,000 kg and Big Creek carried 13,438,000 kg suspended sediments into Lake

Erie. Based on the residues found in sediments in this study, movement into Lake Erie from these two creeks could amount to 1.60 kg Σ DDT and 0.114 kg dieldrin (Table 14); movement from Big Creek could have been 0.39 kg Σ DDT and 0.013 kg dieldrin. These amounts represent a similar quantity of insecticide carried by filtered water in Big Otter but only one-seventh that carried by the filtered water of Big Creek (Tables 11,14).

FISH

A total of 289 individual fish belonging to 24 species were caught for analysis from the creeks, the lake, or the bay. Of these 24 species, eight were caught only in the creeks, ten were caught only in Long Point Bay or in Lake Erie off the mouths of the four creeks, and six were common to the two systems (Table 2).

All species caught in the lake, except coho salmon (*Oncorhynchus kisutch*), had mean tissue residues below 1.0 ppm Σ DDT. Of the eight species caught in the creeks, four had mean tissue residues over 1 ppm; these were brown and rainbow trout (*Salmo trutta* and *S. gairdneri*), largemouth bass (*Micropterus salmoides*), and blacknose dace (*Rhinichthys atratulus*) (Table 2, Fig. 4). The highest tissue residues, 3.86 ppm, were found in largemouth bass.

Of the eight species caught in the creeks, five had mean extractible fat residues over 15 ppm Σ DDT. These included largemouth bass with the highest level, 51 ppm; brown and rainbow trout; creek chub (*Semotilus atromaculatus*); and central mudminnow (*Umbra limi*). Residue levels over 15 ppm Σ DDT in the fat were found in two species caught in the lake; these were smallmouth bass (*Micropterus dolomieu*) and coho salmon. Although the species were not common to the two bodies of water, there was a greater concentration of Σ DDT in these species confined to the creeks. These differences were very apparent in species caught in both systems. Of six species common to the two systems, tissue residues of Σ DDT ranged from 4 to 15 times higher in those members caught in the creeks than in those caught in the lake (Fig. 4).

Dieldrin residues were over 0.1 ppm in the tissues of only one species, largemouth bass. Only one species, blacknose dace, had mean dieldrin residues between 0.05 and 0.1 ppm. Both species were caught in the creeks. Of the 10 species caught in the lake, three had undetectable dieldrin residues and many of the remainder had residues at or below 0.01 ppm. When residues in extractible fat are considered, only one species caught in the lake, black crappie (*Pomoxis nigromaculatus*), had dieldrin residues over 1 ppm. However, seven species caught in the creeks contained residues over 1 ppm and in largemouth bass the residues were almost 5 ppm.

TABLE 13. *Composition and concentration of Σ DDT and dieldrin in sediments of four water courses in four watersheds, southern Ontario—1971*

MONTH	DRIED SEDIMENT, ppb		COMPOSITION, %		
	Σ DDT	DIELDRIN	DDE	DDE	DDT
BIG CREEK—UPPER REACHES; SAND					
April	19.4	ND	26	36	38
May	41.8	0.8	30	17	53
June	17.6	0.6	39	24	37
July	15.5	0.4	54	16	30
August	10.9	0.6	41	26	33
September	11.6	0.4	29	36	35
Mean	19.5	0.5			
BIG CREEK—MIDDLE REACHES; SANDY SILT					
April	20.8	2.0	43	31	26
May	19.0	0.7	36	24	40
June	12.8	0.2	33	20	41
July	19.7	0.4	29	26	45
August	15.7	0.4	22	21	57
September	20.0	0.5	20	26	54
Mean	18.0	0.7			
BIG CREEK—LOWER REACHES; FINE SAND					
April	25.4	0.4	20	25	55
May	30.6	2.0	29	16	55
June	51.4	0.5	34	13	53
July	50.2	2.1	33	26	41
August	44.8	0.4	29	34	37
September	29.7	0.4	28	34	38
Mean	38.7	1.0			
BIG OTTER CREEK; SANDY SILT					
April	24.4	3.0	33	43	24
May	34.6	0.3	38	23	29
June	40.5	1.4	53	21	26
July	28.8	1.3	29	36	35
August	58.6	3.6	27	28	45
September	61.0	3.0	25	36	44
Mean	41.3	2.1			
DEDRICH CREEK; SANDY SILT					
April	162.4	0.1	22	25	53
May	129.6	1.5	24	36	40
June	198.2	0.8	19	38	43
July	138.3	1.3	22	48	30
August	124.4	0.1	20	43	37
September	93.0	0.4	20	45	35
Mean	141.0	0.7			
NANTICOKI CREEK; SANDY SILT					
April	73.0	2.4	45	25	30
May	94.8	0	30	43	27
June	70.3	1.4	23	34	43
July	45.7	2.4	32	46	32
August	26.6	1.4	35	43	22
September	23.0	3.0	30	39	31
Mean	55.6	1.9			
LONG POINT BAY					
Mouth: May-September	28.7	0.6	18	72	10
Middle of bay: 3 miles	4.3	ND	46	48	6

NOTE: ND = not detected.

TABLE 14. *Σ DDT and dieldrin carried on suspended solids by Big Creek and Big Otter Creek to Lake Erie—1971*

CREEK	SUSPENDED SOLIDS, kg/yr	AVERAGE CONCENTRATION, ppb		AMOUNT CARRIED TO LAKE ERIE, kg	
		Σ DDT	DIELDRIN	Σ DDT	DIELDRIN
Big Otter Creek	54,368,000	41.3	2.1	1.60	0.114
Big Creek	13,438,000	38.7	1.0	0.393	0.013
Total	67,806,000			1.993	0.127

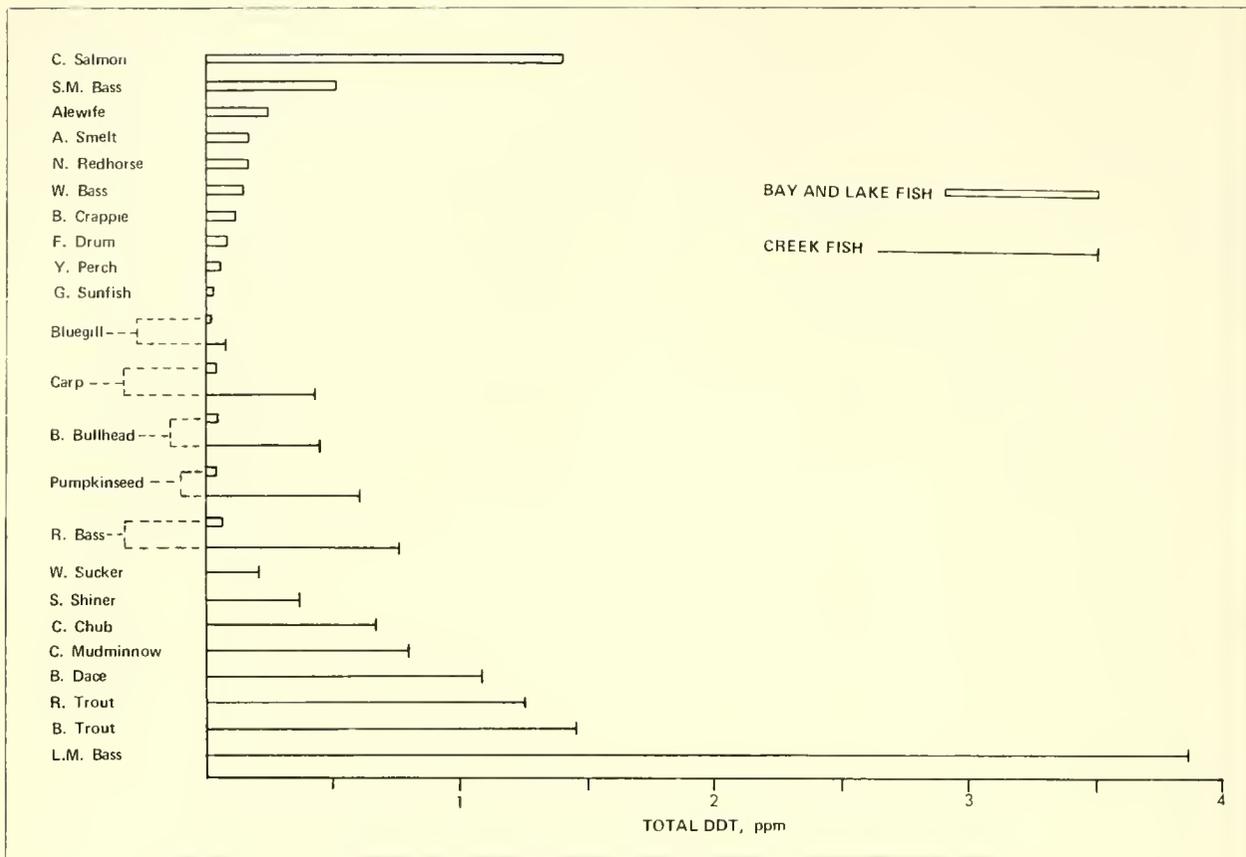


FIGURE 4. Σ DDT concentrations in tissues of 23 fish species caught in creek and lake environments, southern Ontario—1971

Creek Fish

Among the species caught in the creeks, blacknose dace and spottail shiners (*Notropis hudsonius*) were members of the lowest trophic levels. Yet their tissue and fat residues of both Σ DDT and dieldrin were comparatively high. Bottom-feeding white suckers (*Catostomus commersoni*), which have lower fat content in the tissues, had lower residues of DDT and dieldrin than those in dace and shiner; but based on extractible fat their residues were higher. A marked increase in Σ DDT was observed in both extractible fat and total body burdens as the average weight of white suckers increased. Creek chub, an important link in the aquatic food chain, contained almost 0.7 ppm Σ DDT in the tissue and 16 ppm in the extractible fat. Dieldrin levels were 0.04 ppm in the tissue and 1.17 ppm in the fat.

Piscivores caught in the creek included largemouth bass, and brown and rainbow trout. Largemouth bass accumulated the highest residues of Σ DDT and dieldrin in tissue and extractible fat. As the size of the rainbow trout increased, tissue and fat concentrations showed little change although the body load increased rapidly. In fish weighing an average of 6,400 g body load, 8.6 mg Σ DDT and 0.45 mg dieldrin were accumulated.

Body burdens in the creek-caught species increased

from 0.07 μ g Σ DDT in tiny white suckers weighing an average of 6 g to 8,640 μ g in the largest rainbow trout. This represented an accumulation of 1.2×10^5 . With dieldrin, the observed increase was from 0.02 μ g in tiny white suckers (Table 2) to 448 μ g in large rainbow trout, an accumulation of 6.4×10^3 (Table 15).

Lake Fish

Plankton feeders caught in the lake had Σ DDT residues up to 0.25 ppm in the tissue but only trace quantities of dieldrin. The bottom-feeding redhorse (*Moxostoma macrolepidotum*) contained low residues similar to those of the plankton feeders. Black crappies feeding on crustaceans and small fish showed only slightly elevated residues. Among the piscivores, smallmouth bass contained an elevated tissue and fat concentration of Σ DDT and dieldrin and exhibited a buildup in body loads with increasing fish size. Coho salmon contained the highest residue of Σ DDT.

The range from the lowest body load of 2 μ g Σ DDT in American smelt (*Osmerus mordax*) to the highest body load of 6,652 μ g in coho salmon represents an accumulation of 3.3×10^3 . With dieldrin the range was from a nondetectable level in green sunfish (*Lepomis cyanellus*) to 11.6 μ g in smallmouth bass.

TABLE 15. Biomagnification of Σ DDT and dieldrin in the aquatic environment of watershed creeks and Lake Erie, southern Ontario—1971

INSECTICIDE	MATERIAL	RESIDUES IN 1 g	MAGNIFICATION
WATERSHED CREEKS			
Σ DDT	Water	1.5×10^{-11}	
	Sediment	4.1×10^{-8}	2.7×10^3
	White sucker (smallest)	1.2×10^{-9}	8.0×10^2
	Rainbow trout (largest)	1.4×10^{-6}	9.3×10^4
	Largemouth bass (highest residues)	4.8×10^{-6}	3.2×10^5
Dieldrin	Water	1.0×10^{-12}	
	Sediment	1.9×10^{-9}	1.9×10^3
	White sucker (smallest)	3.3×10^{-9}	3.3×10^3
	Rainbow trout (largest)	7.0×10^{-8}	7.0×10^4
	Largemouth bass (highest residues)	2.3×10^{-7}	2.3×10^5
BAY AND LAKE ERIE			
Σ DDT	Water	6.9×10^{-12}	
	Sediment	1.7×10^{-8}	2.5×10^3
	Bluegill (lowest residues)	3.1×10^{-8}	4.5×10^3
	Coho salmon (largest)	2.3×10^{-6}	3.3×10^5
Dieldrin	Water	1.5×10^{-13}	
	Sediment	3.0×10^{-10}	2.0×10^3
	White bass (large)	1.7×10^{-8}	1.1×10^5

Creek and Lake Fish

Among the fish caught in both the creeks and the bay, the plankton-feeders, rock bass (*Ambloplites rupestris*) and pumpkinseed (*Lepomis gibbosus*), had residues 10 to 15 times higher in those members caught in the creek than in those caught in the bay or lake (Fig. 4.5). The bottom-feeders, brown bullhead (*Ictalurus nebulosus*) and carp (*Cyprinus carpio*), contained residues of similar differences in magnitude. The marsh-feeding bowfin (*Amia calya*) had low residues of both DDT and dieldrin. No true piscivore was caught in both the creek and lake waters for comparison.

Discussion

From the data collected it is possible to prepare an inventory of Σ DDT present in the four watersheds and the amount being slowly removed in agricultural produce and by natural processes. The soil that acts as a reservoir was estimated to contain 324,840 kg Σ DDT and 14,515 kg dieldrin in 1971.

Over the past 11 years (1961-71) it was estimated that 882,730 kg DDT was added to the soil. From these data it was proposed that the half-life was between 3 and 4 years. Data compiled by Edwards showed that at

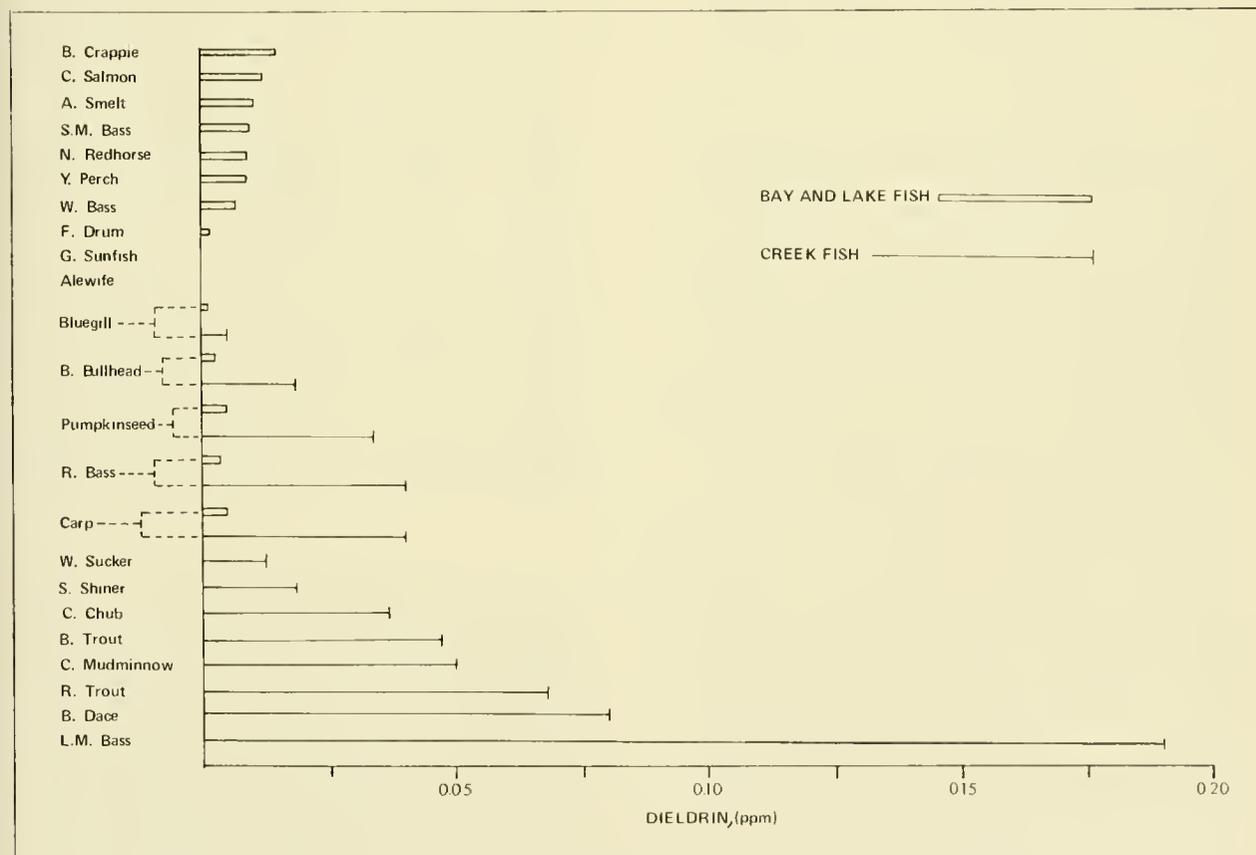


FIGURE 5. Dieldrin concentrations in tissues of 23 fish species caught in creek and lake environments, southern Ontario—1971

dosages between 1.11 and 2.80 kg/ha., disappearance of 95 percent occurred in 4 to 30 years depending on soil, weather, and location (13). In the present study 95 percent disappearance was predicted to occur in 15 to 18 years, well within the span reported by Edwards. The average percent of parent DDT reported by Edwards that remained after 3 years was about 50 percent; however, his range was from 26 to 78 percent. In this study the figure was close to 80 percent.

Mean residues of Σ DDT found in soil agreed closely with the findings of Harris and Sans, in which the averages of four farms taken in 1964, 1966, and 1969 amounted to 3.06, 4.56, and 3.38 ppm Σ DDT, respectively (5). In the present survey, soils recently cropped with tobacco contained mean residues between 3.88 and 4.36 ppm for each of the four watersheds. At the end of a 2- to 3-year rotation the same soils had mean residues ranging from 2.33 to 3.44 ppm. Composition of DDT at the beginning and end of the tobacco/grain rotation showed little change, making it difficult to attribute disappearance to degradation. In woodlots, considerable degradation of DDT to DDE was evident (Table 3) compared to rye and tobacco fields.

Air did not appear to account for volatile losses from the soil. Instead, some samples indicated that most of the DDT was derived from spray drift and others indicated that particulate matter was transported by air.

In the annual marketing of tobacco, milk, and meat from the four watersheds, a total of 53.5 kg Σ DDT and 2.13 kg dieldrin were removed. This represented 0.18 percent of the pesticide applied, assuming it was all from the 1971 application of DDT, which is doubtful. It is significant, however, that both the Σ DDT and the dieldrin removed by tobacco represented 0.035 percent of that resident in the soil used to produce the 1971 crop. Residues in hay and silage appeared to come from either spray drift or the soil and amounted to 38.3 kg Σ DDT and 0.76 kg dieldrin. Amounts found in meat and milk were calculated to be only 0.95 kg Σ DDT and 0.16 kg dieldrin, a fraction of that found in the silage and hay used as animal feed.

The average residue level in milk fat from the four watersheds, 0.188 ppm, was higher than the Provincial average of 0.134 ppm reported by Frank et al. from surveys conducted between 1967 and 1969 (10). The same authors have recently determined residue levels in milk from counties in the Lake Erie watershed (1). In surveys which they conducted in 1968-69 and 1970-71, Frank et al. discovered mean residues of 0.186 and 0.122 ppm Σ DDT and 0.041 and 0.035 ppm dieldrin, respectively (14). Because tobacco production was the only major area of agriculture still using DDT in 1970-71, milk from counties in the tobacco belt, unlike milk from other counties in the Lake Erie watershed, did not show a decline in Σ DDT residues.

Total annual removal of Σ DDT and dieldrin dissolved in water was estimated at 5,297 g Σ DDT and 354.8 g dieldrin. Data collected by the 1971 Water Survey of Canada on Big Otter and Big Creeks determined that the amount of suspended sediment carried into Lake Erie by these two creeks was 54.4 and 13.4 $\times 10^6$ kg/year (11). Bed sediments from Big Otter Creek averaged 41.3 ppb Σ DDT and 2.1 ppb dieldrin; those from the lower reaches of Big Creek averaged 38.7 ppb Σ DDT and 1.0 ppb dieldrin. If it can be assumed that suspended material contained residues similar to those of bed sediments, then it can be estimated that 1,600 g Σ DDT and 114 g dieldrin could have been discharged from Big Otter Creek and 393 g Σ DDT and 13 g dieldrin could have been discharged by Big Creek into Lake Erie on suspended material. In other studies finer sediments tended to contain residues of Σ DDT and dieldrin higher than those of coarser sediments (7); therefore, it might be reasonable to predict that suspended material may carry higher and not lower residues than bed sediments.

Because no data were available on the movement of suspended solids from Nanticoke and Dedrich Creeks, no estimate of sediment residues can be made. Figures from the present study were only slightly higher than those of Miles and Harris (6), showing close agreement. In the case of Nanticoke Creek, sediment at the town of Nanticoke was only 10 ppb; hence the load carried by this creek is probably small. On Dedrich Creek residues in sediment were high. Because the creek is sluggish and the discharge volume is small, the amount of Σ DDT and dieldrin carried on suspended material is probably small also.

Residues leaving the four watersheds in water or on suspended material can be estimated to be 7.3 kg/year Σ DDT and 0.5 kg/year dieldrin. This represents a loss of 38 and 2.6 mg/ha./year for DDT and dieldrin on a total watershed basis. If these losses are confined to the 40,455 ha. tobacco soil in the watersheds, then the amounts lost are 180 and 12 mg/ha./year for DDT and dieldrin, respectively, and represent a loss of 0.002 percent DDT and 0.003 percent dieldrin from the soil reservoir.

In 1971 Miles and Harris reported that for the preceding year the average weekly delivery of organochlorine insecticide from Big Creek into Lake Erie had been 50 g (6). This represents 2,600 g DDT/year. This discharge included suspended matter as well as dissolved pesticide. In the present study conducted in 1971, it was calculated that 2,872 g Σ DDT and 130 g dieldrin were discharged into Lake Erie each year from Big Creek. Riverbed shift and suspended sediments could have carried an additional estimated 393 g Σ DDT and 13 g dieldrin into Lake Erie (Table 14). These figures from the present study are only slightly higher than those from Miles and Harris (6), showing close agreement.

The mean residues in water from Big and Dedrich Creeks were 20.0 and 14.9 ppt Σ DDT and 0.9 and 1.1 ppt dieldrin. In Long Point Bay close to the outlets of these two creeks, residues in water were 12.5 ppt Σ DDT and 0.3 ppt dieldrin. Three miles off the mouth in Long Point Bay Σ DDT residues were 1.3 ppt and dieldrin could not be detected. At the edge of Inner Long Point and Outer Long Point Bays, residues of Σ DDT were down to a trace. A marked dilution of residues occurred in water passing from creek to bay to lake.

Mean residues in sediment were 38.7 and 141 ppb Σ DDT and 1.0 and 0.7 ppb dieldrin from the lower reaches of Big Creek and from Dedrich Creek. Close to shore in Long Point Bay the mean residues were 28.7 ppt Σ DDT and 0.6 ppt dieldrin; in the middle of Long Point Bay sediments contained only 4.3 ppb Σ DDT and no dieldrin. These data also illustrate dilution.

Fish species caught in the creeks had markedly higher residues than those caught in the lake. Tissue levels in 10 species caught in the lake ranged from 0.043 to 2.38 ppm Σ DDT compared to tissue levels of 0.01 to 3.86 ppm Σ DDT in eight species caught in the creeks. Tissue levels of dieldrin ranged from nondetectable to 0.024 ppm in 10 species from the lake and 0.004 to 0.190 ppm for eight species from the creeks. These data emphasized differential accumulation of Σ DDT and dieldrin according to contamination of the location and the species involved. It is significant that of the six species caught in both systems, those members caught in the creeks had much higher residues than those caught in the lake. In both creek and lake, magnifications of Σ DDT and dieldrin from water to the highest concentrations in fish tissue were of the order of 10^5 .

The Σ DDT and dieldrin carried to Lake Erie in the four watersheds represented only 0.003 percent and 0.004 percent of those resident in the soil in 1971. The presence of this amount in the aquatic environment was reflected by the higher residues in fish caught in the creek than in the lake. However, the level of Σ DDT in fish tissue remained below the 5 ppm tolerance permitted in commercial fish.

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LITERATURE CITED

- (1) *Agricultural Statistics for Ontario, 1971*. Publication 20, prepared by the Statistics Section, Economics Branch, Ontario Ministry of Agriculture and Food.
- (2) *Harris, C. R., G. F. Manson, and J. H. Mazurek, 1962*. Development of insecticidal resistance by soil insects in Canada. *J. Econ. Entomol.* 55:777-780.
- (3) *Harris, C. R., and H. J. Svec, 1968*. Toxicological studies on cutworms. I. Laboratory studies on the toxicity of insecticides to the dark-sided cutworm. *J. Econ. Entomol.* 61:788-793.
- (4) *Harris, C. R., H. J. Svec, and W. W. Sans, 1968*. Toxicological studies on cutworms. II. Field studies on the control of the dark-sided cutworm with soil insecticides. *J. Econ. Entomol.* 61:961-965.
- (5) *Harris, C. R., and W. W. Sans, 1971*. Insecticide residues in soils on 16 farms in southwestern Ontario—1964, 1966, and 1969. *Pestic. Monit. J.* 5(3):259-267.
- (6) *Miles, J. R. W., and C. R. Harris, 1971*. Insecticide residues in a stream and a controlled drainage system in agricultural areas of southwestern Ontario, 1970. *Pestic. Monit. J.* 5(3):289-294.
- (7) *Frank, R., A. E. Armstrong, R. G. Boelens, H. E. Braun, and C. W. Douglas, 1974*. Organochlorine insecticide residues in sediment and fish tissue, Ontario, Canada. *Pestic. Monit. J.* 7(3/4):165-180.
- (8) *Langlois, B. E., A. R. Stemp, and B. J. Liska, 1964*. Analysis of animal food products for chlorinated insecticides. *J. Milk Food Tech.* 27:202-204.
- (9) *Hamence, H. H., P. S. Hall, and D. J. Caverley, 1965*. The identification and determination of chlorinated pesticide residues. *Analyst* 90:649-656.
- (10) *Frank, R., H. E. Braun, and J. W. McWade, 1970*. Chlorinated hydrocarbon residues in the milk supply of Ontario, Canada. *Pestic. Monit. J.* 4(1):31-41.
- (11) *Water Survey of Canada, Inland Waters Directorate, Environment Canada, Dec. 31, 1973*. Surface water and sediment data for Canadian rivers, 1965-71.
- (12) *Berst, A. H., and H. R. McCrimmon, 1966*. Comparative summer limnology of Inner Long Point Bay, Lake Erie, and its major tributary. *J. Fish Res. Board Canada* 23:275-291.
- (13) *Edwards, C. A. 1966*. Insecticide residues in soils. *Residue Reviews* 13:83-132.
- (14) *Frank, R., E. H. Smith, H. E. Braun, M. Holdrinet, and J. W. McWade, 1975*. Organochlorine insecticides and industrial pollutants in the milk supply of the Southern Region of Ontario, Canada. *J. Milk Food Technol.* (in press).
- (15) *Annual Report, July 19, 1972*. Ontario Flue-Cured Tobacco Growers Marketing Board, Tillsonburg, Ontario.
- (16) *Unpublished Records, 1971*. Ontario Milk Marketing Board, 50 Maitland Street, Toronto.
- (17) *Annual Livestock Market Review, 1971*. Ontario cattle marketings by counties, 72:43-44. Markets Information Section, Production and Marketing Branch, Agriculture Canada, Ottawa.
- (18) *Climatological Station Report, 1971*. Research Station, Agriculture Canada, Delhi, Ontario.

Persistence and Movement of BHC in a Watershed, Mount Mitchell State Park, North Carolina—1967-72¹

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ABSTRACT

An experimental area in Mount Mitchell State Park, North Carolina, was sprayed with BHC, benzene hexachloride, at an average rate of 11.2 kg/ha. to control the balsam woolly aphid (*Adelges piceae*). Residues were 31 and 585 ppm in soil and litter, respectively, 1 month after spraying. A high percentage of the residue appeared to remain in the treated area; contamination of streams draining the area was minimal. BHC present in surface litter after application slowly moved into surface soil. The residue level in surface soil reached a high of 58 ppm 1.5 years after application. At this time the concentration in litter averaged 134 ppm. Residues in soil and litter were 32 and 27 ppm, respectively, 5 years after application. Concentrations of BHC in animals were unrelated to trapping locations.

Introduction

In North Carolina infestations of balsam woolly aphid (*Adelges piceae*) were first observed in 1957 among stands of Fraser fir (*Abies fraseri*) in the western North Carolina mountains (1). Since that time stands have been severely reduced in many areas; in some areas all mature trees have been killed. Seedlings developing in such areas are also attacked and succumb within 1 to 7 years (2).

Except for commercial plantings for Christmas tree production, the value of Fraser fir is primarily, if not

entirely, aesthetic. The tree occurs naturally in North Carolina only at altitudes above 1200 m.

Both lime sulfur (calcium polysulfides) and BHC (1,2,3,4,5,6-Hexachlorocyclohexane) have been used to control the balsam woolly aphid. Because lime sulfur has no residual activity, retreatment for several years is required for effective control. Therefore, control with lime sulfur is more expensive than it is with BHC. However, the potential for accumulation in nontarget biota is greater with BHC.

Several investigators have studied the depletion of BHC and lindane, the gamma isomer of BHC, from soil. Using electron-capture/gas-liquid chromatography (EC/GLC), Nash and Woolson (3) found an average residue of 10 percent from two BHC applications of 56 and 224 kg/ha. 14 years later. Lichtenstein and Polivka (4) recovered an average of 41 percent by a colorimetric method 11 years after application of 0.3, 2.8, 5.6, and 11 kg/ha. BHC. In another study Lichtenstein et al. (5) detected 0.2 percent lindane, originally applied at rates of 11 and 112 kg/ha., 15 years later.

Although BHC and lindane are less persistent than most other chlorinated hydrocarbon insecticides (3,5), residues remained for several years in soils. Longevity was influenced by soil type, moisture level in soil, evaporation of water from soil, temperature, and other factors (6,7,8). Soil microorganisms appear to be involved in decomposition of lindane (9) and other isomers of BHC (10) in submerged soils. The residual properties of BHC which contribute to its long-term control of the balsam woolly aphid may be undesirable from the standpoint of nontarget biota.

The investigation reported here was undertaken to study the persistence of BHC in a typical Fraser fir stand. In

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conjunction with a spray operation on the north side of the Mount Mitchell peak in 1967, experimental plots and sampling schemes were established for several reasons: to study the deposition and persistence of BHC in surface litter and soil within the sprayed area; to determine residues in water and sediment of small streams within and below the treated area; and to measure residues in small mammals in sprayed and unsprayed areas.

Experimental Procedures

Three 0.04-ha. plots were marked in Mount Mitchell State Park, North Carolina, on the north side of the peak at an elevation of about 1900 m. Plot I contained an intermediate stand of Fraser fir; plot II, a relatively young stand of Fraser fir; and plot III, an old stand of Fraser fir.

BHC was applied to a 13-ha. area on the north side of the mountain June 28—August 30, 1967. Each tree was sprayed individually with a 1:100 dilution of BHC concentrate containing 11.1 percent of the gamma isomer and 16.7-percent of other isomers. The 13-ha. area was sprayed at an average rate of approximately 11.2 kg/ha. BHC. The three experimental plots lay within the sprayed area. Plot III was sprayed June 28, 1967; plots I and II were sprayed July 5 the same year.

Surface litter was defined as the organic material above, but not including, the O2 horizon (11). A sample consisted of litter from 20 random sites (grab subsamples) within each experimental plot. Each plot was sampled twice on each sampling date. Researchers randomly took two 20-core samples of soil, each core 2.5 cm in diameter and 15 cm deep, from all three plots several times during a 5-year period after application.

Because the area treated in 1967 had been sprayed with BHC, control samples of soil and litter were taken from an unsprayed area at Indian Gap in the Great Smoky Mountains.

Water samples were collected several times during a 2-year period from site 1, a small stream immediately below plot II and within the sprayed area. Site 2 was established below the treated area in a small stream which had been formed by drainage from the treated area. Because the streams were very small, the entire cross section of the stream was sampled. On each sampling date, three 3.8-liter samples were taken from each site. The water was stored at 3°-5°C in brown glass jugs. Samples were usually transported to the laboratory on the same day and extracted on the following day. Water was not filtered before extraction.

Grab samples of sediment were taken from the same sites. Each sample was a composite of sediment from five locations 2 to 5 cm deep along an 8-m length of

the stream. Field personnel took three samples at each sampling site.

Small mammals were caught periodically in snap-traps within each plot and outside the treated area during a 3-year period after spraying. During trapping periods, trap lines were run at 12-hour intervals. The type and number of animals were limited; therefore, all trapped animals were sacrificed and analyzed for BHC residues. All samples except water were stored at -18°C until analysis.

The extraction method for water was identical to that used by Bradley et al. (12). Soil and sediment were air-dried and passed through a No. 18 sieve. Sub-samples of 100 g each were extracted by a procedure adapted from one used in the National Soils Monitoring Program (13,14).

Forest litter samples were extracted by the aqueous-acetonitrile method for low-moisture and low-fat samples (15).

Animals of the same species which weighed less than 40 g were grouped by areas. Animals weighing more than 40 g were analyzed separately. The entire animal, including skin and digestive tract, was analyzed. A frozen animal sample was chopped in a Hobart food chopper with sufficient anhydrous sodium sulfate to absorb the moisture. The entire sample was transferred to 500-ml centrifuge bottles. Each bottle was extracted three times with petroleum ether (200, 100, and 100 ml, respectively). The bottles were centrifuged at 1500 rpm for 5 minutes and the solvent layer was decanted through anhydrous sodium sulfate. Extracts were combined, and the solvent was evaporated with a stream of dry air. Fatty materials remained.

A 3-g aliquot of animal fat was subjected to the standard acetonitrile partitioning procedure (15). Extracts from the acetonitrile partitioning of the fat and the litter extract were chromatographed on an activated florasil column; BHC was eluted with 6 percent diethyl ether in petroleum ether (15). Water, soil, and sediment extracts did not require cleanup before gas chromatography.

The alpha, beta, and gamma isomers of BHC were determined with a model MT-220 gas chromatograph equipped with a ⁶³Ni electron-capture detector. A 183-cm-by-0.3-cm, U-shaped, glass column packed with 6 percent QF-1 and 4 percent SE-30 on Gas Chrom Q (60/80 mesh) was used with a nitrogen flow rate of 100 cc/min. Column, injection port, and detector temperatures were 175°, 220°, and 250°C, respectively.

All gas chromatographic measurements were made by the peak height method; amounts present were calculated against standards run daily. Recoveries of added

amounts of BHC from soil, fat, litter, and water are in Table 1.

Results and Discussion

Rainfall and temperature data were taken near the experimental area at the same elevation (Table 2). These data show that the weather was typical for the high mountainous area of the Southeastern United States. Sampling sites received little or no direct sun and the area was cool and damp, even in summer months.

The experimental area had been sprayed with BHC at approximately 11 kg/ha. in 1963. Litter and soil samples collected before the 1967 application contained BHC residues of 67 and 17 ppm, respectively (Tables 3,4).

Initially, the forest litter contained the highest level of BHC. The concentration in the litter averaged 585 ppm about 1 month after application; residues decreased gradually over the next 5 years to 27 ppm.

Because pretreatment BHC levels in soil averaged 17 ppm, the initial deposit in the surface soil from the 1967 spraying was 31 minus 17 ppm, or about 14 ppm; surface soil was usually but not always beneath a layer of litter. BHC residues in soil increased to a peak of 58 ppm 1.5 years after application. Thereafter, the concentration slowly declined to 32 ppm 3.5 years later.

Although no specific weights of soil and litter layers were recorded, authors do know that the 15-cm soil layer weighs several times as much as the overlying litter. Therefore, the increase of BHC concentration in the soil from about 31 ppm at the first sampling date after application to the peak concentration of 58 ppm 1.5 years later may account for 50 percent or more of the BHC lost from the litter (585 ppm to 134 ppm)

during this same period. Extended persistence of the insecticide in this soil probably can be attributed to conditions unfavorable to microbial activity: highly acid soils, cool soil temperatures most of the time, and low intensity of solar radiation within the forest area (3,10).

The present data on persistence of BHC in soil are in general agreement with those of other authors who showed that BHC persisted at least 14 years in soils of a climate more moderate than the mountains of North Carolina (3,5).

Residues in the water from site 2, which drains the entire watershed, were usually below the limit of detection (0.06 ppb; Table 5). On August 30, 1967, after several heavy rains between August 19 and August 27 totaling 18 cm, the stream flow was above normal. Insecticide spraying had been completed by August 30, and the BHC level in samples from the stream averaged 6.3 ppb. April 16, 1969, was the only other sampling date on which there was an appreciable amount of BHC in the stream below the sprayed area. This sampling was made during runoff of melting snow. Water collected from the small stream within the treated area usually contained low concentrations of BHC (Table 5).

Sediment from site 1, the stream within the treated area, contained residues from 0.49 to 3.17 ppm (Table 6). Residues in sediment from site 2, the stream below the treated area, ranged from <0.03 to 0.21 ppm.

Total residues in the fat of animals taken from treated areas ranged from 0.6 to 106 ppm, and those in fat of animals from outside the treated area ranged from 0.1 to 176 ppm (Table 7). There was no relation between BHC residues in animals and the trapping area (treated versus untreated); therefore, no animals were sampled after 1969. Most animals sampled in 1967 and 1968

TABLE 1. Recoveries of BHC isomers from animal fat, forest litter, soil or sediment, and water

TYPE SAMPLE	BHC ISOMER	NO. SAMPLES	AMOUNT ADDED ¹	AVERAGE RECOVERY, %	RECOVERY RANGE, %	SENSITIVITY LEVEL ¹
Animal fat	Alpha	8	0.1-100	92	87- 95	0.02
	Beta	8	0.3-300	92	82- 97	0.06
	Gamma	8	0.1-100	91	84- 95	0.02
Forest litter	Alpha	15	0.2-40.0	99	80-112	0.01
	Beta	15	0.2-200	98	81-110	0.01
	Gamma	15	0.2-200	103	82-142	0.01
Soil or sediment	Alpha	18	0.05-10.0	98	82-127	0.01
	Beta	18	0.05-20.0	94	54-136	0.01
	Gamma	18	0.05-20.0	97	78-126	0.01
Water	Alpha	8	0.02-1.0	80	65- 91	0.02
	Beta	8	0.02-5.6	93	73-148	0.02
	Gamma	14	0.02-2.0	82	70- 90	0.02

NOTE: BHC was added immediately before extraction.

¹ Units are ppm for animal fat, forest litter, soil, and sediment, and ppb for water.

and all those sampled in 1969 were from outside the treated area, although they normally travel across treated and some untreated portions of the area. Attempts to trap animals in the treated area were unsuccessful, and no dead animals were found during routine searches.

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LITERATURE CITED

- (1) Speers, C. F. 1958. The balsam woolly aphid in the southeast. *J. Forest* 56(7):515-516.
- (2) Ciesla, W. M., H. L. Lambert, and R. T. Franklin. 1965. Status of the balsam woolly aphid in North Carolina and Tennessee. 1964. USDA Forest Service, Report 65-1-1. 10 pp.
- (3) Nash, R. G., and E. A. Woolson. 1967. Persistence of chlorinated hydrocarbon insecticides in soils. *Science* 157(3791):924-927.
- (4) Lichtenstein, E. P., and J. B. Polivka. 1959. Persistence of some chlorinated hydrocarbon insecticides in turf soils. *J. Econ. Entomol.* 52(2):289-293.
- (5) Lichtenstein, E. P., T. W. Fuhremann, and Kenneth R. Schulz. 1971. Persistence and vertical distribution of DDT, lindane, and aldrin residues, 10 and 15 years after a single soil application. *J. Agr. Food Chem.* 19(2):718-721.
- (6) Bowman, M. C., M. S. Schechter, and R. L. Carter. 1965. Behavior of chlorinated insecticides in a broad spectrum of soil types. *J. Agr. Food Chem.* 13(4):360-365.
- (7) Lichtenstein, E. P., and K. R. Schulz. 1959. Persistence of some chlorinated hydrocarbon insecticides as influenced by soil types, rate of application and temperature. *J. Econ. Entomol.* 52(1):124-131.
- (8) Yule, W. N., M. Chiba, and H. V. Morley. 1967. Fate of insecticide residues. Decomposition of lindane in soil. *J. Agr. Food Chem.* 15(6):1000-1004.
- (9) Raghu, K., and I. C. MacRae. 1966. Biodegradation of the gamma isomer of benzene hexachloride in submerged soils. *Science* 154(3746):263-264.
- (10) MacRae, I. C., K. Raghu, and T. F. Castro. 1967. Persistence and biodegradation of four common isomers of benzene hexachloride in submerged soils. *J. Agr. Food Chem.* 15(5):911-914.
- (11) Buol, S. W., F. D. Hole, and R. J. McCracken. 1973. Soil genesis and classification. The Iowa State University Press, Ames, Iowa. 360 pp.
- (12) Bradley, J. R., Jr., T. J. Sheets, and M. D. Jackson. 1972. DDT and toxaphene movement in surface water from cotton plots. *J. Environ. Quality* 1(1):102-105.
- (13) Sheets, T. J., M. D. Jackson, W. J. Mistic, and W. V. Campbell. 1969. Residues of DDT and dieldrin in peanuts and tobacco grown on contaminated soil. *Pestic. Monit. J.* 3(2):80-86.
- (14) U.S. Department of Agriculture. 1966. Monitoring agricultural pesticide residues. ARS 81-13. U.S. Government Printing Office, Washington, D.C.
- (15) Burke, J. A., J. A. Gaul, and P. E. Corneliussen. 1971. Pesticide Analytical Manual Vol. 1, U.S. DHEW, Washington, D.C.

TABLE 2. Climatological data near BHC experimental area, North Carolina—1967-72

YEAR	MONTH	TEMPERATURE			RAINFALL, CM
		HIGH (°C)	LOW (°C)	AVG (°C)	
1967	June	21.1	2.8	11.7	28.3
	July	20.0	3.3	11.7	22.7
	Aug.	20.0	2.2	11.1	19.9
	Sept.	18.9	-6.1	6.1	11.2
	Oct.	18.9	-5.6	6.7	12.1
	Nov.	13.3	-17.2	-2.2	10.5
	Dec.	14.4	-16.7	-1.1	19.3
1968	Jan.	12.8	-18.9	-3.3	19.4
	Feb.	10.0	-21.1	-5.6	1.8
	Mar.	17.2	-17.8	-0.6	21.8
	Apr.	20.0	-3.3	8.3	17.0
	May	20.0	-3.3	8.3	14.1
	June	24.4	3.3	13.9	31.7
	July	21.1	2.2	11.7	10.3
	Aug.	22.8	5.6	13.9	12.6
	Sept.	20.0	3.3	11.7	9.4
	Oct.	17.8	-8.9	4.4	32.6
	Nov.	18.3	-14.4	1.7	12.0
	Dec.	18.3	-14.4	1.7	12.7
1969	Jan.	8.9	-21.7	-6.7	13.1
	Feb.	7.8	-17.8	-5.0	22.3
	Mar.	7.8	-17.8	-5.0	19.4
	Apr.	20.0	-7.8	6.1	20.3
	May	21.1	-5.6	7.8	15.3
	June	23.3	0	11.7	19.9
	July	22.8	10.0	16.1	18.0
	Aug.	20.0	6.1	12.8	18.2
	Sept.	17.8	3.3	10.6	12.8
	Oct.	21.1	-7.8	6.7	15.1
	Nov.	13.3	-20.0	-3.3	24.3
	Dec.	8.9	-14.4	-2.8	23.1
1970	Jan.	8.9	-31.1	-11.1	9.6
	Feb.	14.4	-24.4	-5.0	12.0
	Mar.	12.2	-17.8	-2.8	13.0
	Apr.	19.4	-11.1	3.9	15.7
	May	21.1	-1.1	10.0	8.7
	June	21.1	3.3	12.2	12.3
	July	21.1	5.6	13.3	20.9
	Aug.	21.1	7.8	14.4	21.8
	Sept.	22.8	-2.2	10.0	6.3
	Oct.	16.1	-4.4	5.6	45.6
	Nov.	12.2	-22.8	-5.6	14.8
	Dec.	10.0	-20.0	-5.0	10.3
1971	Jan.	10.0	-18.9	-4.4	16.8
	Feb.	11.7	-18.9	-3.9	19.8
	Mar.	13.3	-18.9	-2.8	16.3
	Apr.	17.8	-7.8	5.0	11.5
	May	20.0	-8.9	5.6	14.1
	June	21.1	7.8	14.4	10.9
	July	21.1	4.4	12.8	22.2
	Aug.	20.0	7.2	13.3	24.0
	Sept.	20.0	5.6	12.8	14.2
	Oct.	18.9	-3.3	7.8	34.9
	Nov.	15.6	-14.4	0.6	19.7
	Dec.	15.6	-14.4	0.6	19.6
1972	Jan.	12.2	-12.2	0	21.7
	Feb.	15.0	-17.8	-1.7	12.9
	Mar.	14.4	-14.4	0	20.5
	Apr.	20.0	-12.2	3.9	11.3
	May	15.6	-2.2	6.7	24.9
	June	18.9	-2.2	8.3	33.4
	July	21.1	3.3	12.2	20.2
	Aug.	20.0	8.9	14.4	4.9

TABLE 3. BHC residues in forest litter, North Carolina—1967-72

SAMPLING DATE	PLOT	BHC ISOMER			TOTAL (PPM)
		ALPHA (PPM)	BETA (PPM)	GAMMA (PPM)	
5/18/67	Check ¹	0.04	0.01	0.01	0.06
5/19/67	1 ²	4.68	19.1	9.00	32.78
	2	11.9	75.9	26.4	114.2
	3	4.78	40.4	10.1	55.37
7/7/67	1	146	298	252	696.0
	2	88.6	188	158	434.6
	3	119	302	205	626.0
6/30/67	1	98.2	254	188	540.2
	2	71.2	226	142	439.2
	3	46.0	152	91.4	289.4
8/2/67	1	98.2	254	188	540.2
	2	71.2	226	142	439.2
	3	46.0	152	91.4	289.4
9/1/67	1	66.5	256	142	464.5
	2	44.4	148	95.4	287.8
	3	60.0	210	126	396.0
10/31/67	1	60.3	262	130	452.3
	2	35.8	150	80.8	266.6
	3	47.4	238	106	391.4
5/23/68	1	74.9	236	188	498.9
	2	44.5	170	101	315.5
	3	73.5	286	178	537.5
6/25/68	1	42.6	182	102	326.6
	2	33.8	134	79.4	247.2
	3	22.8	98.7	48	169.5
11/6/68	1	17.2	91.5	41	149.7
	2	13.5	56.2	32.1	101.8
	3	19.2	83.4	47.9	150.5
8/20/69 ³	1	19.6	73.0	41.1	133.6
	2	17.8	58.2	33	109.0
	3	18.7	71.0	40.6	130.3
10/29/70	1	6.46	11.2	39.4	57.06
	2	4.86	9.22	30.4	44.48
	3	8.33	19.2	58	85.53
7/19/72	1	4.07	20.3	7.38	31.75
	2	2.14	10	3.88	16.02
	3	3.62	22.0	7.20	32.82

NOTE: Residues expressed are as received.
 All values are averages of two samples except for those from check plot.
¹ Average of three samples from Indian Gap, Great Smoky Mountains.
² Samples collected May 19, 1967, are pretreatment samples from experimental area.
³ Average of three samples.

TABLE 4. BHC residues in soil, North Carolina—1967-72

SAMPLING DATE	PLOT	BHC ISOMER			TOTAL (PPM)
		ALPHA (PPM)	BETA (PPM)	GAMMA (PPM)	
5/18/67	Check ¹	0.01	0.01	0.08	0.10
5/19/67	1 ²	0.81	3.36	1.82	5.99
	2	1.50	6.36	3.46	11.32
	3	4.72	10.6	17.2	32.52
7/6/67	1	4.15	14.2	8.34	26.69
	2	3.48	13.4	6.72	23.60
6/30/67	3	4.69	27.6	9.79	42.08
8/2/67	1	1.44	4.56	2.80	8.80
	2	4.44	12.9	7.59	24.93
	3	2.89	12.1	6.14	21.12
9/1/67	1	4.82	13.3	8.44	26.56
	2	5.54	16.0	10.8	32.34
	3	5.26	18.2	10.7	34.16
10/31/67	1	4.03	16.4	9.33	29.76
	2	4.18	14.8	7.77	26.75
	3	4.72	17.6	9.40	31.72
5/23/68	1	5.21	15.7	10.6	31.51
	2	3.77	14.6	8.68	27.05
	3	7.34	30.6	16.0	53.94
6/25/68	1	4.50	14.7	8.50	27.70
	2	2.53	10.9	5.92	19.35
	3	6.66	25.4	15.2	47.28
11/6/68	1	10.3	34.6	21.9	66.80
	2	7.58	26.6	21.8	55.98
	3	7.42	25.8	17.6	50.82
8/20/69 ³	1	8.68	17.3	17.7	43.68
	2	3.84	9.43	8.03	21.30
	3	6.09	12.4	13.7	32.19
10/29/70	1	3.72	13.0	11.7	28.42
	2	3.22	12.0	11.7	26.92
	3	8.16	22.6	24.1	54.86
7/19/72	1	2.74	11.1	6.16	20.00
	2	3.42	20.2	7.27	30.89
	3	5.30	28.6	11.7	45.60

NOTE: Residues expressed are oven-dry weight. Values are the average of two samples except as indicated.
¹ Average of three samples from Indian Gap, Great Smoky Mountains.
² Samples collected May 19, 1967, are pretreatment samples from experimental area.
³ Average of three samples.

TABLE 5. BHC residues in water within and below treated area, North Carolina—1967-69

SAMPLING DATE	SITE ¹	BHC ISOMER			TOTAL (PPB)
		ALPHA (PPB)	BETA (PPB)	GAMMA (PPB)	
5/18/67	Control	<0.02	<0.02	<0.02	<0.06
5/19/67	1 ²	0.04	<0.02	0.12	0.17
	2	<0.02	<0.02	0.02	<0.06
7/ 6/67	1	1.14	1.13	2.63	4.90
	2	<0.02	<0.02	0.03	<0.06
7/ 7/67	2 ³	<0.02	<0.02	0.03	<0.06
7/29/67	2 ³	<0.02	<0.02	<0.02	<0.06
8/ 1/67	2 ³	<0.02	<0.02	<0.02	<0.06
8/ 2/67	1	0.86	1.82	2.11	4.79
	2	<0.02	<0.02	<0.02	<0.06
8/22/67	1	3.57	4.18	8.67	16.42
	2	<0.02	0.04	0.03	0.08
8/30/67	1	<0.02	<0.02	<0.02	<0.06
	2	1.15	2.42	2.70	6.27
10/31/67	1	0.06	0.10	0.16	0.32
	2	<0.02	<0.02	<0.02	<0.06
5/23/68	1	0.21	2.75	1.71	4.67
	2	<0.02	<0.02	<0.02	<0.06
6/25/68	1	0.75	5.04	2.28	8.07
	2	<0.02	0.03	<0.02	<0.06
11/ 6/68	1	<0.02	<0.02	<0.02	<0.06
	2	0.92	2.43	2.18	5.52
4/16/69	1	0.19	0.28	0.27	0.74
	2	<0.02	<0.02	<0.02	<0.06

NOTE: Values are averages of three samples analyzed separately except as indicated.
¹ Site 1 is within treated area; site 2 is below.
² Only two samples analyzed.
³ Values are averages of three samples collected during a rainstorm on each date.

TABLE 6. BHC residues in sediment within and below treated area, North Carolina—1967-69

SAMPLING DATE	SITE	BHC ISOMER			TOTAL (PPM)
		ALPHA (PPM)	BETA (PPM)	GAMMA (PPM)	
7/ 6/67	1	0.34	2.00	0.83	3.17
	2	0.01	0.02	0.10	0.13
8/ 2/67	1	0.07	0.71	0.16	0.94
	2	<0.01	0.01	<0.01	<0.03
9/ 1/67	1	0.07	0.46	0.15	0.68
	2	0.01	0.03	0.01	0.05
10/31/67	1	0.01	0.06	0.01	0.08
	2	0.06	0.42	0.16	0.64
5/23/68	1	0.01	0.18	0.02	0.21
	2	0.04	0.34	0.11	0.49
6/25/68	1	0.02	0.05	0.02	0.09
	2	0.02	0.03	<0.01	0.06

NOTE: Residues expressed are oven-dry weight. Values are the average of three samples except as indicated.
¹ Average of two samples.

TABLE 7. BHC residues in animal fat, North Carolina—1967-69

SAMPLING YEAR	LOCATION	NUMBER AND TYPE OF ANIMAL ¹	LIPID, %	BHC ISOMERS			TOTAL (PPM)
				ALPHA (PPM)	BETA (PPM)	GAMMA (PPM)	
1967	Plot I	3 Deer mice	12.6	0.70	1.20	0.30	2.20
		1 Little brown myotis bat	1.4	0.63	2.93	0.86	4.42
		3 Deer mice	7.9	36.4	42.2	27.5	106.1
		1 Boreal redback vole	5.8	0.37	0.55	0.27	1.19
	Plot II	1 Deer mouse	9.7	3.06	6.01	4.85	13.92
		1 Boreal redback vole	7.6	0.15	0.19	0.25	0.59
	Plot III	1 Deer mouse	7.4	0.32	0.60	0.57	1.49
		1 Boreal redback vole	3.3	2.51	3.96	2.58	9.05
	Outside treated area	2 Deer mice	7.0	0.38	0.52	0.24	1.14
		1 Deer mouse	4.1	16.9	17.6	4.58	39.08
		1 Deer mouse	5.9	0.20	0.78	0.31	1.29
		3 Deer mice	8.2	0.51	0.67	0.43	1.61
		1 Boreal redback vole	3.3	0.11	0.45	0.20	0.76
		1 Boreal redback vole	2.9	0.09	0.34	0.18	0.61
		1 Boreal redback vole	5.7	0.07	0.27	0.12	0.46
		1 Boreal redback vole	6.3	0.11	0.18	0.28	0.57
		2 Boreal redback voles	6.3	61.4	29.6	56.8	147.8
		1 Boreal redback vole	2.9	36.0	127.	12.5	175.5
		1 Shorttail shrew	2.4	0.27	0.84	0.51	1.62
		3 Shorttail shrews	8.2	11.9	33.6	13.3	58.8
1 Woodland jumping mouse		3.0	0.23	0.47	0.35	1.05	
1 Woodland jumping mouse	1.4	5.23	24.2	7.10	36.53		
1968	Plot I	3 Deer mice	13.8	1.55	2.98	0.97	5.50
		3 Deer mice	16.2	0.98	1.38	0.71	3.07
		3 Deer mice	19.8	0.69	0.83	0.38	1.90
		1 Boreal redback vole	8.8	9.33	2.94	3.00	15.27
		1 Boreal redback vole	33.4	1.25	1.54	0.69	3.48
	Outside treated area	3 Deer mice	10.2	1.24	1.67	0.90	3.81
		3 Deer mice	13.2	0.10	0.16	0.08	0.34
		3 Deer mice	11.3	0.20	0.25	0.11	0.56
		1 Boreal redback vole	8.1	0.03	0.11	0.03	0.17
		1 Boreal redback vole	15.3	0.02	0.07	0.02	0.11
		1 Boreal redback vole	3.5	3.46	3.91	1.29	8.66
		1 Norway rat	6.5	0.45	0.14	0.20	0.79
		1 Woodchuck	4.8	0.29	0.41	0.19	0.89
1969	Outside treated area	2 Deer mice	11.7	0.09	0.34	0.21	0.64
		2 Deer mice	13.4	<0.02	<0.06	0.02	<0.10
		1 Boreal redback vole	13.0	0.02	0.06	0.02	0.10
		1 Boreal redback vole	19.2	0.05	0.24	0.02	0.31

NOTE: Residues expressed as extractable lipids.

¹ Deer mouse, *Peromyscus maniculatus*; little brown bat, *Myotis lucifugus*; Boreal redback vole, *Clethrionomys gapperi*; short-tailed shrew, *Blarina brevicauda*; woodland jumping mouse, *Napaeozapus insignis*; Norway rat, *Rattus norvegicus*; and woodchuck, *Marmota monax*.

Contribution of Household Dust to the Human Exposure to Pesticides¹

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and Laurence M. Mounce²

ABSTRACT

Preliminary analysis of environmental contributions to pesticide body burden revealed household dust as a major reservoir of pesticides in the environment. A year-long monthly study of the households of pesticide-exposed persons and control households in Weld County, Colo., in 1968 revealed appreciable levels of selected chlorinated pesticides in the exposed group. Exposed subjects varied from entire farm families with high agricultural use of pesticides to households with at least one member who formulated pesticides, either as an employee of a local plant or as a professional applicator who mixed and loaded pesticides for commercial use. In the overall data no quantitative relationships were demonstrated between pesticide levels in household dust and pesticide levels in blood, although circumstantial data from individual households indicate that a certain connection does exist. No correlation could be shown between levels of p,p'-DDT and p,p'-DDE in household dust. Pesticide levels in the dust indicate a probable influence on body burden contributing to total environmental exposure of the individual to pesticides.

Introduction

Pesticide body burden in the general population can be augmented by dust, air (1), water, food, and the nature of the home and working environments. Differences in pesticide levels distinguishing the general population from a pesticide-exposed population may then be attributed to occupational exposure and to pesticides carried into homes on clothing and other items. Surveys of

pesticide content in food, soil, and water have been conducted for many years without attempting to relate levels found to pesticide body burden. The present study was initiated to determine the relationship between pesticide levels in household dust and pesticide levels in human blood sera in Weld County, Colo., which has a high annual usage of pesticide chemicals because it is primarily an agricultural area.

Preliminary analyses of soil, water, and household dusts conducted in 1966 revealed pesticide levels to be higher in household dusts than in soil and water, and indicated some correlation between DDT levels in dust and DDT and DDE levels in sera of householders (2). In order to minimize the variables associated with different sampling times and seasonal peaks in pesticide use, the study was conducted for 1 year. From multiple regression analyses and available data, the following hypothesis was formed: a definable relationship exists between blood serum chlorinated hydrocarbon pesticide levels and household dust levels.

Reviews of published literature revealed no attempt to measure pesticide levels in household dusts. Modifications of other soil assay methods were incorporated in the analytical method for this study to provide sensitivity and specificity needed for accurate analyses of pesticides in household dusts.

Storm dust fall has been analyzed (3) for organochlorine pesticide levels using microcoulometric/gas-liquid chromatography (MC/GLC) in the quantitative step. Pesticide levels in soils have been studied by many researchers who have designed a variety of soil extraction and cleanup techniques for adaptation to current needs (4-6). This paper attempts to report results obtained from a year's study of pesticide levels in both household dusts and blood sera, and, when possible, to demonstrate the relationship of pesticide levels between these two substrates.

¹ Research supported by contract PH-86-65-62 with the Division of Community Studies, Atlanta, Ga. Formerly part of Food and Drug Administration, U.S. Department of Health, Education, and Welfare. Presently under Technical Services Division, Office of Pesticide Programs, U.S. Environmental Protection Agency, Washington, D.C.

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HOUSEHOLD DUST

Household dust from a month's sweepings was collected in disposable vacuum cleaner bags and sifted. Particles passing through a Number 60 mesh screen were taken for analysis. One gram of air-dried dust was Soxhlet-extracted with 1:1 hexane:acetone and column-chromatographed on deactivated aluminum oxide using hexane as the eluent to remove waxes and other extractables. Final separation of chlorinated hydrocarbon pesticides was obtained by Florisil column chromatography. Final concentrations of household dust extracts were 2.0 µg/µl for analysis by electron-capture/gas-liquid chromatography (EC/GLC) and 1.0 mg/µl for analysis by MC/GLC. An arbitrary sensitivity limit of 1.50 parts per million (ppm) was established so that all residues could be qualitatively confirmed by MC/GLC. Organochlorine insecticide recovery data for fortified household dust screenings are given in Table 1. All recoveries were within acceptable analytical ranges. Relatively high standard deviations may have been caused by difficulty in obtaining uniform fortification rather than by the method.

TABLE 1. Recovery of pesticides from fortified household samples, Colorado—1968

COMPOUND	No. SAMPLES	MEAN RECOVERY, %	STANDARD DEVIATION ¹
Lindane	12	87.3	6.99
Heptachlor Epoxide	12	80.6	12.86
Dieldrin	11	86.3	12.89
<i>p,p'</i> -DDT	9	87.8	20.20
<i>p,p'</i> -DDE	12	82.9	6.35
<i>p,p'</i> -DDD	12	90.0	9.72

¹ Relatively high standard deviations possibly caused by difficulty in obtaining uniform fortification rather than by method.

BLOOD

Blood samples were collected in 10-ml Vacutainer tubes containing no anticoagulant. After clotting, 2.0 ml serum was extracted with hexane using the method of Dale, Curley, and Cueto (7). Samples were analyzed by EC/GLC with an arbitrary lower sensitivity limit of 5 parts per billion (ppb).

GAS CHROMATOGRAPHY

All analyses were performed on Micro-Tek 220 gas chromatographs equipped with H³ electron-capture detectors. Household dust residues were qualitatively verified with a chlorine-specific microcoulometric detector. Gas-chromatographic liquid phases used for this study were coated on acid-washed and silanized support. Phases were 1.5 percent OV-17/1.95 percent QF-1 (column A); 4 percent SE-30/6 percent QF-1 (column B); and 3.5 percent QF-1/6.5 percent DC-200 (column C). Operating conditions were established to yield optimum separation with reasonable retention time for the latest eluting compounds.

During the 12 months of 1968, household dust samples were collected from 28 households; blood samples were obtained from 28 heads of households and 27 spouses on the same sampling dates. Household dust samples consisted of the entire month's vacuum sweepings with at least two sweepings a week. Homes were selected on the following bases: location in Weld County, past cooperation with the program, probability and consistency of continuing participation, and willingness of the family to participate in a long-term study requiring monthly sampling. The sampling group consisted of 16 urban control households, 4 farm households, and 8 households with at least one member who was a pesticide formulator.

Control participants had no known occupational exposure to pesticides and only minimal home-use exposure. Farm participants were selected from those with highest agricultural usage of pesticides among participants in the Colorado Community Study on Pesticides (formerly under Food and Drug Administration, U.S. Department of Health, Education, and Welfare; currently under Technical Services Division, U.S. Environmental Protection Agency—Office of Pesticide Programs). The formulator group ranged from those employed in local pesticide formulating plants to professional applicators who mixed and loaded pesticides for commercial use.

Results and Discussion

Table 2, a summary of each study group and substrate, lists total number of samples, frequency of occurrence, mean of values above the minimum sensitivity limits, and range of values for all pesticides detected during the 1-year sampling period. Gas-chromatographic column C was utilized to analyze all samples through June 1968 and did not provide adequate resolution or sensitivity for determining chlordane in blood. Samples analyzed after June were analyzed on gas-chromatographic columns A and B utilizing a modification of the Florisil column elution of two fractions improving resolution of pesticides occurring in household dust samples.

Because of widespread usage of DDT over the past 25 years, residues occurring most frequently in blood were *p,p'*-DDT and its metabolite, *p,p'*-DDE; in household dust, the most common residue was *p,p'*-DDT. Also occurring frequently in household dust was *o,p'*-DDT, the technical isomer of *p,p'*-DDT. It did not occur in the blood samples because it is rapidly metabolized and excreted. Table 3 is a statistical evaluation of the 12-month average of *p,p'*-DDT and *p,p'*-DDE in blood, and *p,p'*-DDT in household dust.

Correlation coefficients based on all 28 households showed a statistically significant positive correlation. It was observed, however, through inspection of data from each household that one household consistently yielded

TABLE 2. Pesticide residues in human blood sera and household dust in 28 households, Weld County, Colo.—1968

No. SAMPLES	CONTROL GROUP		FARMER		FORMULATOR		CONTROL GROUP	FARMER	FORMULATOR	
	M 187	F 171	M 46	F 47	M 88	F 87	182	45	95	
	BLOOD RESIDUES, ppb						HOUSEDUST RESIDUES, ppm			
<i>p,p'</i> -DDT	F 94 5-14 7.7	F 96 5-68 8.1	M 36 5-19 9.5	F 11 5-6 5.4	M 84 5-68 17.9	F 56 5-21 9.4	159 1.56-35.44 6.90	42 1.60-37.80 8.87	95 2.34-226.15 30.66	
<i>p,p'</i> -DDE	F 187 5-95 28.3	F 170 5-105 24.3	M 46 14-116 48.4	F 47 7-28 17.0	M 88 16-209 54.8	F 87 9-82 30.1	4 1.50-12.28 4.37	9 1.63-7.55 3.28	46 1.50-17.10 4.83	
<i>o,p'</i> -DDT	F R X						56 1.52-10.20 2.67	16 1.62-5.31 2.91	55 1.63-21.99 6.31	
<i>p,p'</i> -DDD	F R X		1 5 5.0				2 1.73-1.81 1.77	8 2.22-19.21 6.11	9 1.59-7.03 2.95	
Methoxychlor	F R X						78 1.53-28.57 6.09	21 1.58-102.90 14.93	56 1.92-144.44 18.24	
Lindane	F R X				11 ¹ 7-23 16.8	1 5 5.0		3 1.75-2.27 2.05	43 1.54-13.72 5.85	
β -BHC	F R X	15 5-8 5.9	7 9-15 10.9	19 5-27 12.4	10 5-12 8.8	25 6-59 18.7	11 6-22 9.5			
Chlordane	F R X				6 ¹ 60-233 151		45 1.79-41.36 7.59	10 1.92-10.72 5.79	77 2.15-135.78 23.11	
Dieldrin	F R X	1 5 5.0			47 5-140 43.5	13 ² 5-14 10.1	25 1.59-10.21 2.94	15 1.59-10.63 4.42	59 1.59-40.42 8.92	
Heptachlor Epoxide	F R X				21 7-22 10.9					
Endrin	F R X								27 1.50-27.73 7.14	
Dacthal	F R X						14 1.53-32.59 7.11	22 1.90-59.71 18.50	19 1.55-41.91 7.28	

NOTE: F = Frequency of values above minimum sensitivity limit.
R = Range of values above minimum sensitivity limit.
X = Mean of values above minimum sensitivity limit.

¹ One participant only.

² Eleven values from one participant.

residue levels several magnitudes above the means of the other households. By omitting data from the one household, the correlations remained positive but lost any statistical significance, as demonstrated in Table 3. Hence the contribution of the one household to the significant correlation was disproportionate.

Mean *p,p'*-DDT in the one household's dust was 131.14 ppm; in the other seven formulator households the mean was 16.13 ppm. Mean *p,p'*-DDT and *p,p'*-DDE in blood of the male occupant of the household with highest residues were 46.8 ppb and 143.3 ppb, respectively, whereas male occupants of the other seven households had means of 12.3 ppb and 40.9 ppb, respectively. Although these data suggest a trend, they do not prove statistical correlations between *p,p'*-DDT levels in household dust and *p,p'*-DDT/*p,p'*-DDE levels in human blood.

Interpretations of frequencies and ranges of some pesticides listed in Table 2 can be made. The relatively

high frequency of chlordane occurrence in control household dust was caused by its use in many common household insecticides. Occurrence of the herbicide Dacthal in farm household dusts was caused by its use on certain produce croplands in the Weld County area. Dacthal occurred in lower levels among formulators and control groups, probably because these individuals had no history of occupational exposure to this pesticide.

Three values requiring further explanation are chlordane and lindane in the blood of a male formulator and dieldrin in the blood of his wife. These unusual findings of chlordane and lindane in blood and a related medical problem in this male participant have been published previously (8). Mean chlordane and lindane levels in the dust from this home were 76.46 ppm and 10.90 ppm, respectively; in the other seven formulators' homes mean values were 10.18 ppm and 1.58 ppm, respec-

tively. Because neither chlordane nor lindane residues are commonly found in human blood except in acute exposure situations, this observation seems to present circumstantial evidence relating household dust residues to body burden. The mean dieldrin level in this subject's household dust was 28.02 ppm compared to 2.29 ppm for the other seven formulators' households. As a result, 11 of 13 occurrences of dieldrin in the blood of formulators' wives were obtained from this participant. This case provides further circumstantial evidence relating household residue levels to blood residue levels because this woman had no history of occupational exposure to dieldrin.

TABLE 3. Correlation coefficients for levels of DDT in household dust with levels of DDT and DDE in human blood, Colorado—1968

BLOOD	HOUSEHOLD DUST ¹ <i>p,p'</i> -DDT	
	28 HOUSEHOLDS ²	27 HOUSEHOLDS
	<i>p,p'</i> -DDT	0.81
<i>p,p'</i> -DDE	0.75	0.11

NOTE: Product-moment correlation coefficients. Coefficients represent 12-month average.

¹ Coefficients first calculated for 28 households, then recalculated omitting one household with extremely high residues which overly influenced correlations; data could not be considered statistically significant.

² Values significant at the 0.01 level.

Conclusions

Data from this study have shown no quantitative relationships between pesticide levels in household dust and pesticide levels in blood. Circumstantial data from individual households indicate that at least some relationships do exist; however, no statistical significance can be demonstrated. It is evident from the current literature as well as data presented here that a simplified approach to the problem of relating pesticide body burden to a specific type of exposure, either environmental or

dietary, is difficult because of the many variables in this complex problem.

Acknowledgments

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LITERATURE CITED

- (1) Campbell, J. E., L. A. Richardson, and M. L. Schafer. 1965. Insecticide residues in the human diet. Arch. Environ. Health. 10:831-836.
- (2) Walker, S. 1967. Chairman, Biometrics Department, University of Colorado Medical Center, Denver, Colo. Personal communication.
- (3) Colen, J. M., and C. Pinkerton. 1966. Widespread translocation of pesticides by air transport and rainout. Organic Pesticides in the Environment. Advan. Chem. Ser. No. 60. 163-175.
- (4) Johnson, R. E., and R. I. Starr. 1967. Ultrasonic extraction of insecticides in soil. In Comparison of extraction methods and solvent systems over three time intervals. J. Econ. Entomol. 60:1679-1682.
- (5) Fahey, J. E., J. W. Butcher, and R. T. Murphy. 1965. Chlorinated hydrocarbon insecticide residues in soils of urban areas, Battle Creek, Michigan. J. Econ. Entomol. 58:1026-1027.
- (6) Burchfield, H. P., D. E. Johnson, and E. E. Storrs. 1965. Extraction of soil. Guide to the Analysis of Pesticide Residues, Vol. 1, section II: A 2 (1); A 2a (1); A 2b (1) U.S. DHEW-PHS.
- (7) Dale, W. E., A. Curley, and C. Cueto. 1966. Hexane extractable chlorinated insecticides in human blood. Life Sci. 5:47-54.
- (8) Starr, H. G., Jr., and N. J. Clifford. 1971. Absorption of pesticides in a chronic skin disease. Arch. Environ. Health. 22:396-400.

BRIEF

A Nomograph for the Conversion of 2,4-D Ester Concentrations in Air from $\mu\text{g}/\text{m}^3$ to ppb_v and Vice Versa¹

Raj Grover and Barry McCashin

ABSTRACT

A nomograph for the conversion of 2,4-D (2,4-Dichlorophenoxyacetic acid) ester concentrations from $\mu\text{g}/\text{m}^3$ to ppb_v and vice versa has been prepared to provide a simple and direct means for such conversions. Results obtained are shown to be comparable to those calculated.

Introduction

Data on direct measurements of pesticide residue levels in the atmosphere are being reported in increasing numbers. Air pollution aspects (1) and hazards from off-target drift of agriculturally generated pollutants (2-4), especially pesticides, have recently been reviewed. Measurements of pesticide levels in the atmosphere are generally expressed in weight/volume (w/v) units, i.e., nanogram or microgram of pesticide per cubic meter of air (ng or $\mu\text{g}/\text{m}^3$). However, the cubic meter unit is dependent on ambient conditions of temperature and pressure which should be designated. When dealing with gaseous pollutants in the atmosphere, it is often desirable to denote concentrations in relative volumes of w/v units, i.e., parts of pesticide per million or billion parts of air (ppm_v or ppb_v). Because the ratio of volumes is unaffected by fluctuations in temperature and pressure during sampling, ppb_v or ppm_v units do not change as volumes change.

Procedures for conversion of concentrations from $\mu\text{g}/\text{m}^3$ to ppb_v or ppm_v have been discussed in recent texts on air sampling methodology (5,6). However, nomographs provide a simple and direct means for such conversions and have been developed for a variety of gaseous compounds (7).

Concentrations of any gaseous compound in the air can be converted from $\mu\text{g}/\text{m}^3$ to ppb_v using the following expression:

$$y \left[\frac{\mu\text{g}}{\text{m}^3} \right] \times \frac{1}{w \times 10^6} \left[\frac{\text{g mole}}{\mu\text{g}} \right] \times v \left[\frac{\text{m}^3}{\text{g mole vol}} \right] \times 10^9 \left[\frac{\text{parts}}{\text{billion parts}} \right] = z \text{ [ppb}_v\text{]}$$

where y = concentration of the residue in $\mu\text{g}/\text{m}^3$,
 w = gram molar weight of the compound,
 v = gram molar volume of air in m^3 ,
and z = concentration of residue in ppb_v .

Example 1. Convert 40 $\mu\text{g}/\text{m}^3$ methyl ester of 2,4-D sampled at 20°C and 1 atm pressure (STP) to parts per billion (ppb_v).

$$y = 40 \left[\frac{\mu\text{g}}{\text{m}^3} \right]$$
$$w = 235.08 \text{ (g mole wt)}$$
$$v = 0.024 \left[\frac{\text{m}^3}{\text{g mole vol}} \right] \text{ at STP}$$

Substituting the values for y , w , and v in the above expression,

$$40 \times \frac{1}{235.08 \times 10^6} \times 0.024 \times 10^9 = 4.08 \text{ ppb}_v.$$

Similar conversions for other 2,4-D esters were also carried out, using different temperature and pressure conditions (Table 1). In all these conversions, determination of g mole volumes of air in m^3 at various pressure and temperature conditions is necessary.

While preparing the nomograph, extremes of pressure and temperature conditions most likely to occur in air

¹ Contribution from the Herbicide Behavior in Environment Section, Research Station, Agriculture Canada, Regina, Saskatchewan, S4P 3A2, Canada.

TABLE 1. Relative conversion values for various 2,4-D esters, from $\mu\text{g}/\text{m}^3$ to ppb_v , or vice versa, using calculations and the nomograph

2,4-D ESTER	SAMPLING CONDITIONS			CONVERSION VALUES		
	PRESSURE (MM HG)	TEMP (K)	P/T FACTOR ¹	FROM	TO	
methlyl	733	293	2.50	10 $\mu\text{g}/\text{m}^3$	1.1 ppb_v	1.1 ppb_v
iso-propyl	760	293	2.59	50 $\mu\text{g}/\text{m}^3$	4.6 ppb_v	4.5 ppb_v
n-butyl	700	323	2.17	8 ppb_v	77.1 $\mu\text{g}/\text{m}^3$	77.0 $\mu\text{g}/\text{m}^3$
iso-octyl	800	313	2.56	2 ppb_v	26.6 $\mu\text{g}/\text{m}^3$	26.3 $\mu\text{g}/\text{m}^3$

¹ Pressure/temperature factor.

sampling were selected. These were 20° to 50°C and 700 to 800 mm Hg. Pressure/temperature factors (P/T in mm Hg/K), in the range of 2 to 3, were then plotted against the ppb_v scale on the left side of the log-log paper (Fig. 1). Corresponding ester concentrations were plotted on the right side of the log-log paper in units of $\mu\text{g}/\text{m}^3$.

A number of conversions similar to those calculated were read from the nomograph using the procedure shown in Figure 1. The two sets of values, i.e., those calculated and the ones obtained from the nomograph,

showed close approximation (Table 1). Conversions beyond the range of the nomograph can also be carried out by simply shifting the decimal point to obtain the appropriate range. The resultant conversion value can then be adjusted to the correct value by placing the decimal point in the reverse direction.

In conclusion, the nomograph greatly facilitates conversion of atmospheric residue levels of 2,4-D esters from $\mu\text{g}/\text{m}^3$ to ppb_v and vice versa. It provides a simple and direct means for such conversions while still maintaining a relatively high degree of accuracy.

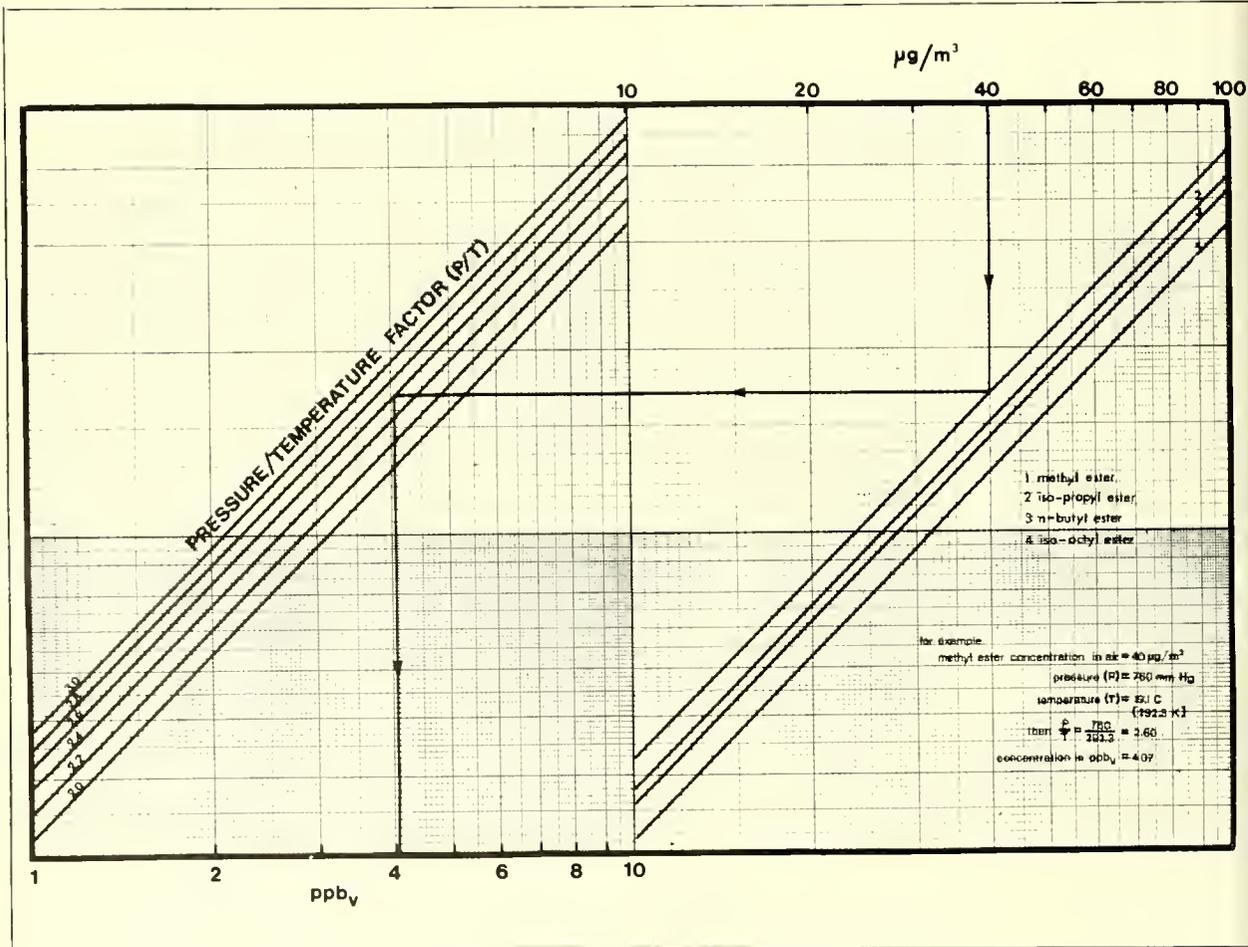


FIGURE 1. Nomograph for converting concentrations of four esters of 2,4-D from $\mu\text{g}/\text{m}^3$ to ppb_v dry air at various pressure/temperature factors (P/T in mm Hg/K)

LITERATURE CITED

- 1) *Finkelstein, H.* 1969. Air pollution aspects of pesticides. Litton Systems Inc., Environ. Syst. Div., Bethesda, Md. 173 pp.
- 2) *Grover, R., J. Maybank, K. Yoshida, and J. R. Plimmer.* 1973. Droplet and volatility drift hazards from pesticide application. Preprint No. 73-106. 29 pp. J. Air Pollut. Contr. Ass., 66th Ann. Mtg., Chicago, Ill.
- 3) *Hay, J. R., R. Grover, and K. S. McKinlay.* 1971. Biological significance of deposited pesticides. 59-64. In J. T. Bergsteinsson and W. Baier (Eds.) Meteorological Aspects of Pollution in Relation to Agricultural Pesticides. Canada Comm. Agr. Meteorol., Research Branch, Ottawa, Canada.
- (4) *Heck, W. W., O. C. Taylor, and H. E. Heggstad.* 1973. Herbaceous and ornamental plants and agriculturally generated pollutants. J. Air Pollut. Contr. Ass. 23:257-266.
- (5) *Anonymous.* 1972. Methods of air sampling and analysis. Amer. Pub. Health Ass., Washington, D.C. 480 pp.
- (6) *Ledbetter, J. O.* 1972. Air pollution: Part A—Analysis. Marcel Dekker, Inc., New York. 424 pp.
- (7) *Sheehy, J. P., W. C. Achinger, and R. A. Simon.* 1968. Handbook of air pollution, U.S. Dept. of Health, Educ., and Welfare, Environ. Health Serv., Natl. Center for Air Poll. Cont., Durham, N.C.

APPENDIX

Chemical Names of Compounds Discussed in This Issue

ALDRIN	Not less than 95% of 1,2,3,4,10,10-Hexachloro-1,4,4a,5,8,8a-hexahydro-1,4- <i>endo-exo</i> -5,8-dimethanonaphthalene
BHC (Benzene hexachloride)	1,2,3,4,5,6-Hexachlorocyclohexane (mixture of isomers). Commercial product contains several isomers of which <i>gamma</i> is most active as an insecticide.
CHLORDANE	1,2,3,5,6,7,8,8-Octachloro-2,3,3a,4,7,7a-hexahydro-4,7-methanoindene. The technical product is a mixture of several compounds, including heptachlor, chlordene, and two isomeric forms of chlordane.
2,4-D	2,4-Dichlorophenoxyacetic acid.
DCPA (Dacthal®)	Dimethyl 2,3,5,6-tetrachloroterephthalate
DDD	See TDE.
DDE	Dichlorodiphenyl dichloro-ethylene. (Degradation product of DDT.) Main component: 1,1-Dichloro-2,2-bis(<i>p</i> -chlorophenyl) ethylene <i>o,p'</i> -DDE 1,1-Dichloro-2-(<i>o</i> -chlorophenyl)-2-(<i>p</i> -chlorophenyl) ethylene <i>p,p'</i> -DDE 1,1-Dichloro-2,2-bis(<i>p</i> -chlorophenyl) ethylene
DDT	-Bis (<i>p</i> -chlorophenyl) , , -trichloroethane. Numerous isomers in addition to <i>p,p'</i> -DDT are possible, and some are present in the commercial product. <i>o,p'</i> -DDT [1,1,1-Trichloro-2-(<i>o</i> -chlorophenyl)-2-(<i>p</i> -chlorophenyl) ethane]
DICHLORBENIL	2,6-Dichlorobenzonitrile
DIELDRIN	Not less than 85% of 1,2,3,4,10,10-Hexachloro-6,7-epoxy-1,4,4a,5,6,7,8,8a-octahydro-1,4- <i>endo-exo</i> -5,8,-dimethanonaphthalene
ENDRIN	1,2,3,4,10,10-Hexachloro-6,7-epoxy-1,4,4a,5,6,7,8,8a-octahydro-1,4- <i>endo-endo</i> -5,8-dimethanonaphthalene
FENAC	2,3,6-Trichlorophenylacetic acid
HEPTACHLOR	1,4,5,6,7,8,8-Heptachloro-3a,4,7,7a-tetrahydro-4,7- <i>endo</i> -methanoindene
HEPTACHLOR EPOXIDE	1,4,5,6,7,8,8-Heptachloro 2,3-epoxy-3a,4,7,7a-tetrahydro-4,7-methanoindane
HEXACHLOROBENZENE (HCB)	Perchlorobenzene
LINDANE	Gamma isomer of benzene hexachloride (1,2,3,4,5,6-hexachlorocyclohexane) of 99+ % purity
METHOXYCHLOR	1,1,1-Trichloro-2,2-bis(<i>p</i> -methoxyphenyl) ethane
POLYCHLORINATED BIPHENYLS (PCB's)	Mixtures of chlorinated biphenyl compounds having various percentages of chlorine.
TDE (DDD)	2,2-Bis (<i>p</i> -chlorophenyl)-1,1-dichloroethane (including isomers and dehydrochlorination products)

Information for Contributors

The PESTICIDES MONITORING JOURNAL welcomes from all sources qualified data and interpretive information which contribute to the understanding and evaluation of pesticides and their residues in relation to man and his environment.

The publication is distributed principally to scientists and technicians associated with pesticide monitoring, research, and other programs concerned with the fate of pesticides following their application. Additional circulation is maintained for persons with related interests, notably those in the agricultural, chemical manufacturing, and food processing industries; medical and public health workers; and conservationists. Authors are responsible for the accuracy and validity of their data and interpretations, including tables, charts, and references. Accuracy, reliability, and limitations of the sampling and analytical methods employed must be clearly demonstrated through the use of appropriate procedures, such as recovery experiments at appropriate levels, confirmatory tests, internal standards, and inter-laboratory checks. The procedure employed should be referenced or outlined in brief form, and crucial points or modifications should be noted. Check or control samples should be employed where possible, and the sensitivity of the method should be given, particularly when very low levels of pesticides are being reported. Specific note should be made regarding correction of data for percent recoveries.

- Preparation of manuscripts should be in conformance to the CBE STYLE MANUAL, 3d ed. Council of Biological Editors, Committee on Form and Style, American Institute of Biological Sciences, Washington, D. C., and/or the STYLE MANUAL of The United States Government Printing Office.
- An abstract (not to exceed 200 words) should accompany each manuscript submitted.
- All material should be submitted in duplicate (original and one carbon) and sent by first-class mail in flat form—not folded or rolled.
- Manuscripts should be typed on 8½ x 11 inch paper with generous margins on all sides, and each page should end with a completed paragraph.
- All copy, including tables and references, should be double spaced, and all pages should be numbered. The first page of the manuscript must contain authors' full names listed under the title, with affiliations, and addresses footnoted below.
- Charts, illustrations, and tables, properly titled, should be appended at the end of the article with a notation in text to show where they should be inserted.

- Charts should be drawn so the numbers and texts will be legible when considerably reduced for publication. All drawings should be done in black ink on plain white paper.
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The Journal also welcomes "brief" papers reporting monitoring data of a preliminary nature or studies of limited scope. A section entitled *Briefs* will be included, as necessary, to provide space for papers of this type to present timely and informative data. These papers must be limited in length to two journal pages (850 words) and should conform to the format for regular papers accepted by the Journal.

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PESTICIDES IN PEOPLE

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Blood Organochlorine Pesticide Levels in Virginia Residents

Francis D. Griffith, Jr.,¹ and Robert V. Blanke²

ABSTRACT

This study attempts to establish 1972 baseline levels for 31 organochlorine pesticides and industrial chemicals in post-mortem human whole blood in Virginia. These pesticides and industrial chemicals have been detected previously in other parts of the food chain and environment.

In the present study DDT and its metabolites, DDE and TDE, were detected most frequently and at highest levels. DDT and DDE tended to appear more frequently as people grew older although TDE levels remained constant. Dieldrin and lindane showed peak levels in the middle age group.

Analyzing distribution of pesticides in blood by sex showed that females had higher levels of lindane and dieldrin and males had higher levels of DDT, DDE, and TDE. Analyzing racial distribution showed blacks with higher levels of DDT, TDE, and DDE and indicated little difference from whites for lindane and dieldrin. Higher levels were found in Richmond and Norfolk than in the Fairfax and Roanoke regions.

Introduction

This study attempts to establish 1972 baseline levels of organochlorine pesticides in human whole blood in Virginia. It follows by 6 to 12 months the completion of a basic study by the Virginia Department of Agriculture and Commerce (1) required by the Virginia General Assembly (2) on the occurrence of economic poisons in the environment. Until now, little human monitoring has been done nationally and no studies have been performed on the population of Virginia.

Pesticides which have been detected in the lower part of the food chain and the environment are those most

likely to occur in human blood. The study tested for hard organochlorine pesticides as well as some of their alternatives, such as methoxychlor and endosulfan, and some fungicides, such as captan. Polychlorinated biphenyls (PCB's), manufactured as industrial chemicals since the late 1920's, have worked their way through the environment to become manifest in eggs, poultry, fish, beef, packed cereal, and water. Another reason for monitoring PCB's is that several estuaries in Virginia have been contaminated with heavy industrial discharges.

Postmortem blood was selected as the specimen to be examined for the following reasons:

Collection techniques and consent requirements from living patients residing in geographically different regions of the State required facilities beyond authors' control.

Future monitoring can most conveniently be performed on postmortem material; the existing statewide Medical Examiner's system provides a ready mechanism for specimen collection.

Four centers throughout Virginia are assigned to collect specimens from subjects varying widely in age, sex, race, residence, and occupation and make retrievable computer records available on each case.

Similar studies in other areas have used post-mortem material (3).

The disadvantage of postmortem blood is that it differs from blood of living patients. Some decomposition has occurred, clotting factors are altered, intracellular and extracellular distribution of diffusible substances are altered, and the ratio of formed elements to serum may be modified.

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Sampling Procedures

Blood samples were taken by pathologists in the four regions of the Office of the Chief Medical Examiner: Richmond, Roanoke, Norfolk, and Fairfax. The choice of samples for analysis was based on availability. Variables such as age, race, sex, occupation, residence, and cause of death were not considered initially. Deaths had resulted from trauma, violence, or suspicious, unusual, or unnatural causes; during imprisonment; without medical attendance; suddenly, to a victim who had been in apparent good health; or following surgical or anesthetic procedures (4).

Pathologists were requested to take blood within 24 hours after death, although samples drawn as late as 72 hours after death were accepted. Samples were drawn from the heart and placed in 15-cc tubes containing 120 mg sodium fluoride and 45 mg potassium oxalate. To the tube was attached a label bearing the name and address of the deceased, date of death, and the Medical Examiner's signature. In Richmond the tubes were sealed and refrigerated until analysis. In the other regional offices, the tubes were sealed, mailed to Richmond in cardboard containers, and refrigerated upon arrival. After analysis samples were frozen at -25°C for future use.

Analytical Procedures

Aldrin and dieldrin have been extensively used throughout Virginia in recent years. Thus analytical procedures, especially the extraction step, were keyed to the recovery of dieldrin (5), which has been detected more frequently in the food chain than has DDT and is five times more toxic to rats and mice on an LD_{50} basis (6).

EXTRACTION

The whole-blood extraction procedure was a modification of the sulfuric acid method of Henderson, De Boer, and Stahr used in the 1972 Association of Official Analytical Chemists (AOAC) collaborative study for multiresidues in whole blood (7). This method was chosen because sulfuric acid released bound pesticides and sulfonated and removed some of the unsaturated interferences (8). Two ml whole blood was pipetted into a 50-ml centrifuge tube; 1.5 ml 60 percent H_2SO_4 was added and mixed on a vortex mixer for 5 seconds; a second 1.5 ml 60 percent H_2SO_4 was added and mixed for 10 seconds; and 2 ml 60 percent H_2SO_4 was added and mixed for 30 seconds. Samples were then cooled for several minutes. Pesticides were extracted with 3 ml 9:1 pesticide-grade hexane:acetone. Samples were mixed 20-30 seconds on a vortex mixer and then centrifuged at 2000 rpm for 10 minutes. The hexane-acetone layer was removed with a disposable capillary pipette and the pesticide solvent layer was put into a 13-ml Kontes graduated centrifuge tube. Hexane-acetone extraction was repeated twice more. All three solvent layer extrac-

tions were combined in the same tube. The solvent was concentrated to 0.5 ml by using a gentle stream of clean dry nitrogen on the surface of the extract.

ANALYSIS

Gas-liquid chromatographic (GLC) determinations were performed as described by Griffith and Blanke at the 87th AOAC Annual Meeting (9). Samples were run on a Dohrmann Model 2468 gas chromatograph with a microcoulometric gas titrating system (GTS-20) for halogens. Confirmations were made on a Micro-Tek GC-2000-R gas chromatograph equipped with a tritium foil electron-capture detector.

The column used in the microcoulometric system was a 6-ft-by-4-mm-ID glass column packed with 5 percent OV-210 on 80/100 mesh Gas-Chrom Q. The temperature was programmed from 210° to 234°C at $2^{\circ}\text{C}/\text{min}$. The column used in the electron-capture system was a 6-ft-by-4-mm-ID glass column packed with 4 percent SE-30/6 percent QF-1 on 80/100 mesh Supelcoport. The temperature was isothermal at 205°C . Carrier gas for both systems was nitrogen. Flow through the OV-210 column was 90 ml/min.; flow through the SE-30/QF-1 column was 120 ml/min.

Qualitative results were based on the relative retention of aldrin to the retention of the pesticide in question. Quantitation of pesticides was based on peak area using a disc integrator.

Recovery data were obtained for all compounds discussed. Most analyses were single determinations because precision experiments showed no improvement with triplicate analyses. The desired minimum detectable recovery for all pesticides was 1 ppb. Alpha BHC, lindane, heptachlor, aldrin, heptachlor epoxide, CIPC, and dieldrin were recovered at the 1 ppb level; the limit of detection for DDE, DDT, TDE, dacthal, endrin, endosulfan, and atrazine was 2 ppb. Recoveries for chlordane, dicofol, folpet, captan, chlorpropylate, PCNB, carbophenothion, phosphamidon, methoxychlor, and toxaphene varied between 10 and 40 ppb. The minimum detectable amount for PCB's (Aroclor 1221, 1232, and 1242) and PCN's (Halowax 1099) was 100 ppb because of interference from the background of the blood extract. PCB's (Aroclor 1254 and 1260) and PCN (Halowax 1014) had later eluting fractions that did not overlap the backgrounds of the blood extracts; hence the minimum detectable amounts for these chemicals was 50 ppb.

Results and Discussion

When all cases examined in this study were grouped by age (Fig. 1) a normal distribution was apparent, with the majority of samples in the 41- to 60-year age group. The mean (\bar{x}) age was 45.98 years. The age distribution in the Richmond and Fairfax regions followed this pat-

tern but distribution showed a majority in the 21- to 40-year age group in the Norfolk and Roanoke regions.

The mean age of Virginia residents in 1972 was 26.8 years; the mean age at death was 68.0 years. The Norfolk region showed a slightly younger living population of 24.2 years. Richmond and Roanoke residents averaged 28.3 and 30.2 years, respectively. The mean age of Fairfax residents and the mean age at death of residents of the other regions are unknown (10). Thus the population included in this study represents an older group than the average living Virginia resident but a younger group at death than that which occurs normally.

Sex and race distributions also deviated from the average population (Fig. 2). The racial distribution of the population examined showed a ratio of three whites to two blacks. In the Richmond and Norfolk regions, the racial distribution was 1:1, but whites represented a majority of those samples from the Fairfax and Roanoke regions. The male:female distribution was about 3:1 in all four regions of the State.

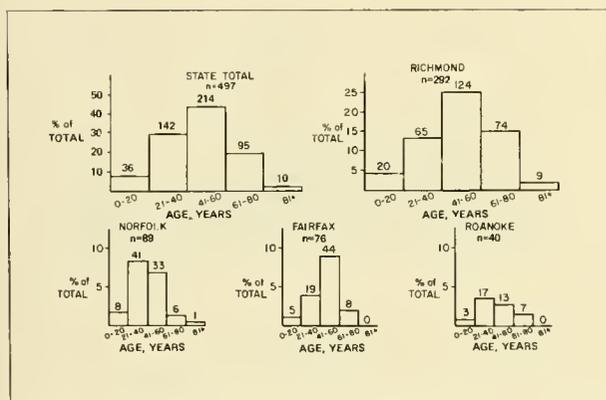


FIGURE 1. Age distribution of humans sampled for pesticide residues

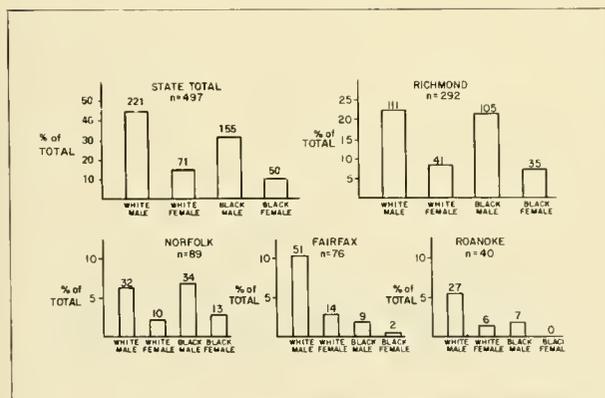


FIGURE 2. Sex and race distribution of humans sampled for pesticide residues

The male:female ratio throughout Virginia is about 1:1 and the average white:black distribution is 4:1. Thus data from the present study represent a greater proportion of males and blacks than is typical of the State's population (10). If all data from this study are averaged, the resulting baseline of pesticide levels would be misleading. However, when results in each group are taken on the basis of age, sex, race, and geographical residence, they should be comparable to those in corresponding living groups. Similar techniques are commonly used to evaluate data derived from mortality tables (11).

On a statewide basis, 15 pesticides and industrial chemicals were positively identified. Ten of these are shown in Figure 3. The remaining five did not occur in enough samples to be included. The most frequently detected pesticides were DDT and its metabolites, dieldrin, lindane, and alpha BHC. Less frequently detected were methoxychlor, heptachlor epoxide, CIPC, and PCB's. Captan was detected at levels of 20 to 30 ppb, and carbophenothion was found at levels of 8 to 60 ppb in two samples each. Chloropropylate, PCNB, and en-

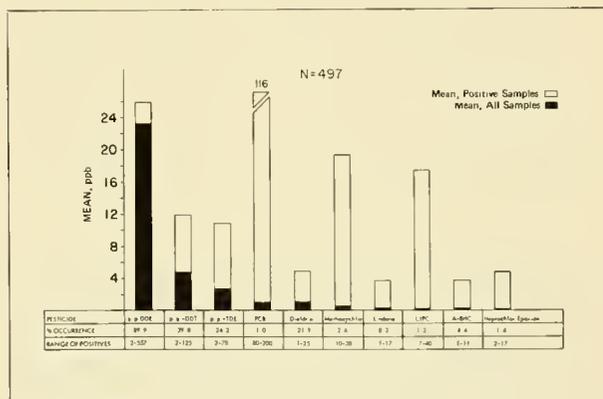


FIGURE 3. Organochlorine residues detected in human blood

drin were each detected in one sample at 27, 15, and 5 ppb, respectively.

Of equal importance are the 16 pesticides and industrial chemicals that were not detected. Chlordane was not detected; nor were the herbicides atrazine and dacthal, probably because of their rapid degradation. Toxaphene, the PCN's, and most PCB's did not appear.

Heptachlor and aldrin were not found, although their metabolites dieldrin and heptachlor epoxide were. The latter occurred in only 1.4 percent of the samples studied at an average concentration of 0.06 ppb. This is a significant decrease from the mid-sixties when that metabolite was first detected in milk (12). The current findings may indicate that milk is no longer a significant

source of PCB contamination, although such a conclusion could be verified only through extensive research into several areas, including the dietary habits of subjects whose blood was sampled.

Methoxychlor, CIPC, and PCB's were detected in a small percentage of samples with wide differences between frequency and concentration means (Fig. 3). Authors interpret this to indicate that they do not have widespread distribution and, when detected, probably indicate recent exposure.

Concentrations and frequencies of DDE and DDT in blood by age showed similar patterns (Fig. 4,5). On a statewide basis, higher concentrations and occurrences were noted with advanced age. On a regional basis, Richmond and Norfolk had generally higher DDE and DDT concentrations and occurrences than had Fairfax and Roanoke. Distribution of TDE by age differed from DDT and DDE: it was fairly uniform except in the Norfolk region (Fig. 6). Average concentrations were higher in the 0- to 20-year age group although percent occurrence was lower in this group.

Dieldrin and lindane occurred less frequently but generally showed peak levels at middle age (Fig. 7,8). In the case of lindane, no positive cases were found among the very old and only one was detected in the very young. Dieldrin distribution was skewed to an earlier age group in the Roanoke and Norfolk regions than in the other two. In Norfolk, dieldrin levels were generally lower except in the very young.

Distribution of detected pesticides by sex and race did not show any remarkable trends (Fig. 9). Females had higher levels of lindane and dieldrin; males had higher levels of DDT, DDE, and TDE. Blacks had higher levels of DDT and its metabolites but displayed little difference from whites in lindane and dieldrin concentrations. Higher pesticide levels and greater percent occurrences were found in Richmond and Norfolk than in Fairfax and Roanoke.

No correlations between residue levels and occupation could be considered because of the wide variation in occupations listed on Medical Examiner's certificates. Many people over 60 were listed as retired; others were unemployed.

Although some pesticides are known to alter microsomal enzyme activity and, consequently, drug metabolism (13), the low number of deaths by barbiturate overdose prohibited observation of any relationship between pesticide levels and drug levels.

In no case was pesticide poisoning considered the cause of death. Had it been, the pesticide would have been present in much higher levels, as observed in published findings on known overdoses and exposures (14).

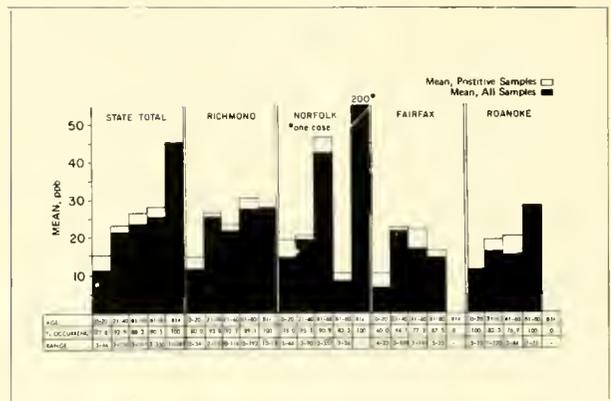


FIGURE 4. DDE residues detected in human blood by age distribution

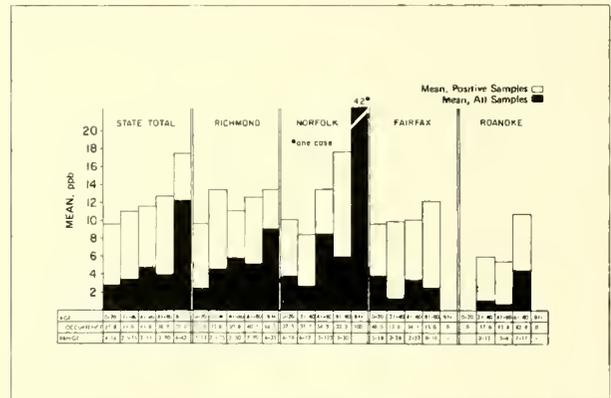


FIGURE 5. DDT residues detected in human blood by age distribution

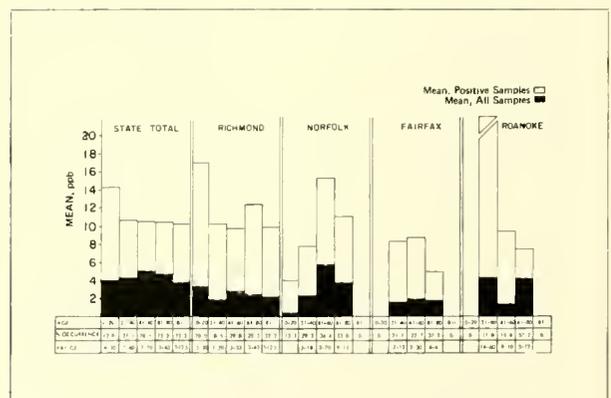


FIGURE 6. TDE residues detected in human blood by age distribution

LITERATURE CITED

- (1) *Rowe, M. B. (Commissioner)*. 1971. The 1971 Virginia pesticides study pursuant to house joint resolution 51. Virginia Department of Agriculture and Commerce, Richmond, Va.
- (2) *DuVal, Van Clief, et al. (Patrons)*. Offered February 6, 1970. House joint resolution no. 51. Directing Dept. of Agriculture and Commerce to conduct a study on the need for regulation and control of economic poisons, Virginia General Assembly, Richmond, Va.
- (3) *Davies, I. E., W. F. Edmundson, N. J. Schneider, and J. C. Cassady*. 1968. Problems of prevalence of pesticide residues in humans. *Pestic. Monit. J.* 2(2):80-85.
- (4) *Medical Examiner's Law*, Code of Virginia, Sec. 19:1-41.
- (5) *Saha, J. G., B. Bhavaraju, and Y. W. Lee*. 1969. Validity of using soil fortification with dieldrin to measure solvent extraction efficiency. *J. Agr. Food Chem.* 17(4):874-876.
- (6) *Sunshine, J. (ed.)*. 1969. *Handbook of Analytical Toxicology*. The Chemical Rubber Co., Cleveland, Ohio. Pp. 507 and 511.
- (7) *Stretz, P. E., and H. M. Stahr*. 1972. Collaborative study—determination of chlorinated pesticides in whole blood. Presented at 86th Annual Meeting of the Association of Official Analytical Chemists, Washington, D. C.
- (8) *Henderson, S. J., J. G. DeBoer, and H. M. Stahr*. 1971. Improved method for determination of chlorinated hydrocarbon pesticide residues in whole blood. *Anal. Chem.* 43(3):445-447.
- (9) *Griffith, F. D., Jr., and R. V. Blanke*. 1974. Microcoulometric determination of organochlorine pesticides in human blood. *J. Ass. Offic. Anal. Chem.* 57(3):595-603.
- (10) *Derr, B. P.* 1972. Personal communication. Virginia Department of Health, Bureau of Vital Records and Health Statistics, Richmond, Va.
- (11) *National Center for Health Statistics*. 1972. *Vital Statistics of the United States—1968*. Vol. II—Mortality. U.S. Department of Health, Education, and Welfare, Public Health Service, Health Services and Mental Health Administration, Washington, D. C.
- (12) *Midyette, J. W. (Director)*. 1965. 1964-65 Annual Report. Commonwealth of Virginia, Department of Agriculture, Division of Technical Services, Richmond, Va.
- (13) *Goth, Andres*. 1970. *Medical Pharmacology*. The C. V. Mosby Company, Saint Louis, Mo. Pp. 24-33.
- (14) *Schafer, M. L.* 1968. Pesticides in blood. *Residue Rev.* 24:19-39.
- (15) *Dale, W. E., A. Curley, and W. J. Hayes, Jr.* 1967. Determination of chlorinated insecticides in human blood. *Ind. Med. Surg.* 36(4):275-280.
- (16) *Davis, J. E., W. F. Edmundson, D. Maceo, A. Barquet, and J. Cassady*. 1969. An epidemiologic application of the study of DDE levels in whole blood. *Amer. J. Pub. Health* 59(3):435-441.
- (17) *Edmundson, W. F., J. E. Davis, G. A. Nachman, and P. L. Roeth*. 1969. *P,p'*-DDE in blood samples of occupationally exposed workers. *Pub. Health Rep.* 84(1):53-58.
- (18) *Watson, M., W. W. Benson, and J. Gabica*. 1970. Serum organochlorine pesticide levels in people in southern Idaho. *Pestic. Monit. J.* 4(2):47-50.
- (19) *Keil, J. E., W. Weston III, C. B. Loadholt, S. H. Sandifer, and J. J. Colcobough*. 1972. DDT and DDE residues in blood from children, South Carolina—1970. *Pestic. Monit. J.* 6(1):1-3.
- (20) *Rowe, M. B. (Commissioner)*. 1971. Economic poisons and ecology first annual report 1970-71. Virginia Department of Agriculture and Commerce, Richmond, Va.
- (21) *Schmid, K., and A. Rastetter*. 1970. Gas chromatographic determination of insecticide residues in dried and fermented tobacco samples from field and growth experiments. *Beitr. Tabakforsch* 5(5):201-206.
- (22) *Hayes, W. J., Jr., W. E. Dale, and C. I. Pirkle*. 1971. Evidence of safety of long-term high oral doses of DDT for man. *Arch. Environ. Health* 22:119-135.

PESTICIDES IN WATER

*Fate of Copper in Ponds*¹

A. W. McIntosh²

ABSTRACT

Treatments of 3 ppm copper sulfate (CuSO₄·5H₂O) were applied to two small aquatic systems in Michigan in 1971. To study the pathways of the added copper, samples of water, sediment, aquatic macrophytes, filamentous algae, and fish were collected and analyzed by atomic absorption. Sampling was initiated before treatment and continued up to 4 months in one of the ponds.

*Dissolved copper concentrations in water decreased rapidly immediately after treatment and then gradually to background levels. Reduction of dissolved copper may have involved initial precipitation of an insoluble compound, such as malachite, followed by sediment adsorption of soluble copper complexes and copper released from aquatic plants. Levels of copper in sediment increased rapidly at first and gradually later in the study. Aquatic plants and filamentous algae accumulated very high levels of copper. Uptake rates were apparently affected by water temperature and growth stages of the plants. Data indicate that aquatic macrophytes developing in one pond 10 weeks after treatment took up copper from the sediment. Although green sunfish (*Lepomis cyanellus*) accumulated copper soon after treatment, levels returned to background later in the study.*

Introduction

Levels of copper generally below 20 ppb are routinely observed in natural waters. When higher values are found in surface waters, it is likely that the metal has been added by copper and brass tubing, industrial effluents, or copper compounds used for control of undesirable aquatic organisms or plants (1).

Limited research has been conducted concerning the fate of copper in aquatic systems, including copper pathways in canals and irrigation ditches (2-4), bogs (5), ponds (6,7), and lakes (8). In assessing the ecological effects of a heavy metal, components concentrating it must be identified and characterized. Little effort has been devoted to determining the role of these aquatic system components in copper dispersal.

In the present study in which copper sulfate (CuSO₄·5H₂O) was added to two small ponds in Michigan in 1971, intensive sampling of water, sediment, algae, plants, and fish was conducted for periods of 7 weeks to 4 months to assess the role of each component in copper distribution.

Methods and Materials

STUDY SITE

A circular settling pond about 13.7 m in diameter and 2 m deep served as the study site. Located at the old East Lansing Sewage Treatment Plant, the pond is among a number of sites used by the Michigan State University Department of Fisheries and Wildlife for limnological research. In June 1970 the pond was drained and the bottom was covered with 10 to 15 cm black soil. The system was refilled and left undisturbed while populations of macrophytes and filamentous algae developed.

Early in May 1971 the system was divided with a polyethylene sheet, effectively forming two separate ponds. By June, 100 green sunfish (*Lepomis cyanellus*) had been collected from other sources. They were weighed, marked by fin-clipping, and released into each system. Copper sulfate solutions were prepared in distilled water from commercial grade copper sulfate and applied by hand to the surface of each pond. Application dates and dosages appear in Table 1.

¹ Department of Fisheries and Wildlife, Michigan State University, East Lansing, Mich. Research supported by Predoctoral Research Fellowship No. 5-F1-WP-26,436-02, Water Quality Office, U.S. Environmental Protection Agency, Washington, D.C.

² Department of Bionucleonics, Purdue University, West Lafayette, Ind. 47906. Reprints available from this address.

TABLE 1. Copper sulfate dosage rates and schedules

SITE	APPLICATION DATE	DOSAGE, PPM
Pond A	July 12, 1971	3
Pond B	September 26, 1971	3

NOTE: Ponds A and B are halves of one settling pond.

Water chemistry parameters including pH, alkalinity, hardness, and dissolved oxygen were determined throughout the study (Fig. 1,2). Techniques outlined in *Standard Methods for the Examination of Water and Wastewater* (9) were used for chemical tests. Duplicate water samples were collected for analysis from the top and bottom quarters of each pond with a Kemmerer water sampler.

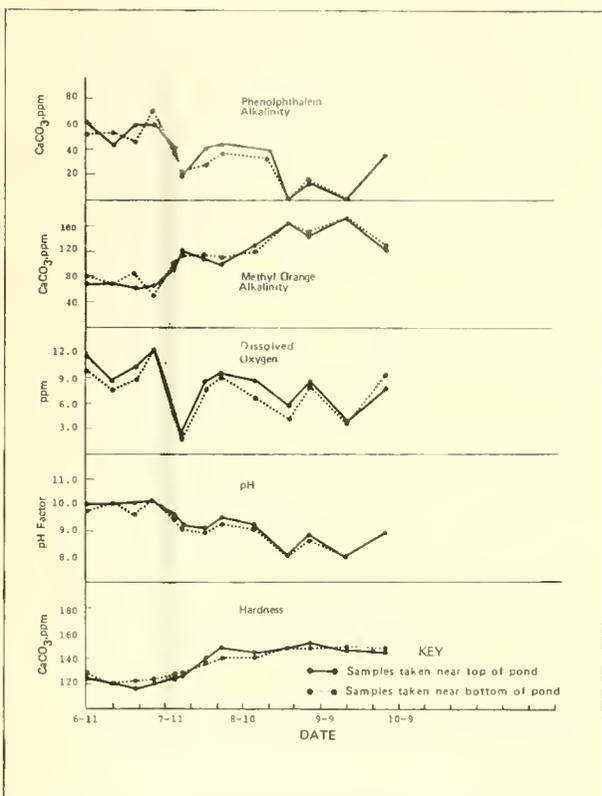


FIGURE 1. Changes in water chemistry parameters, Pond A

NOTE: Each point represents average of two samples. Shaded area denotes treatment with 3 ppm copper sulfate.

Sampling and Analysis

Water for copper analyses was collected at three stations established near the outside, middle, and inside of each semicircular pond. A water column was removed with a polyethylene tube and a subsample was collected. Preparation followed procedures outlined in *Methods*

for *Chemical Analysis of Water and Wastes* (10). Copper passing through a 0.45- μ membrane filter represented dissolved copper; the fraction remaining on the filter was considered suspended copper.

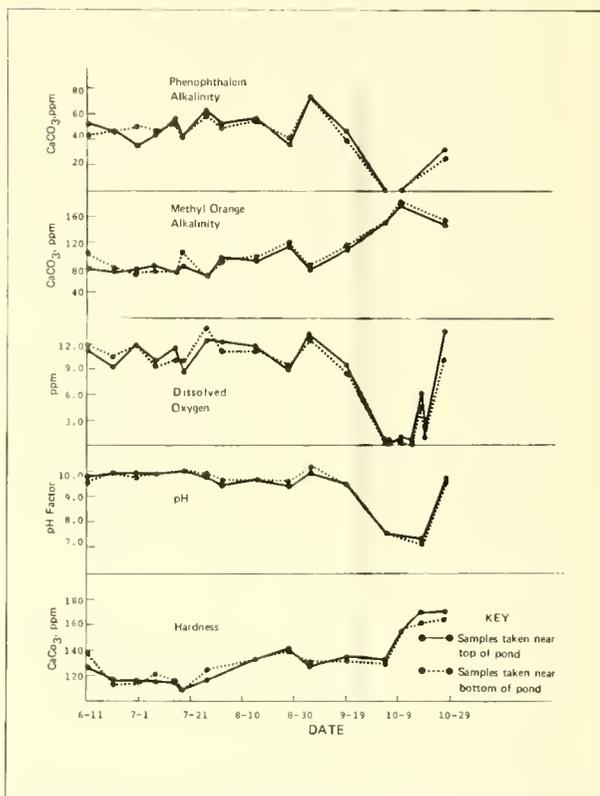


FIGURE 2. Changes in water chemistry parameters, Pond B

NOTE: Each point represents average of two samples. Shaded area denotes treatment with 3 ppm copper sulfate.

At each sampling period, two sediment samples were collected with a core sampler and frozen in dry ice. The top 1-2-in. layer was removed and dried at 100° C for 96 hours. Samples were ground and 5 ml 8N HCl/g sediment was added. This slurry was held at a temperature near boiling for 20 hours, cooled, filtered, and diluted to volume with deionized distilled water.

Plant samples were collected, rinsed in distilled water, blotted, and dried at 100° C for 96 hours. Tissues were digested by adding 10 ml 8N HNO₃ and boiling to dryness. Five ml 6N HCl was then added and the mixture was reheated to dissolve the residue. The solution was filtered and diluted to the desired volume.

Fish were trapped, sacrificed, rinsed in distilled water, weighed, and digested in 5 ml concentrated HNO₃/g fish for 24 hours. The solution was filtered and diluted to volume.

Samples of all components were taken before treatment to determine background levels of copper (Table 2). Samples were collected after treatment for 4 months in Pond A and for 7 weeks in Pond B.

TABLE 2. Background copper levels in two Michigan ponds, 1971

COMPONENT	AVERAGE CONCENTRATION, COPPER, PPM	RANGE, PPM	No. SAMPLES
WATER			
Dissolved copper ¹	0.0145	0.00-0.05	38
Suspended copper ²	0.0357	0.00-0.09	38
Total	0.0502	0.00-0.11	38
SEDIMENTS ³	27.68	1.08-73.60	51
PLANT TISSUE ³			
<i>Chara</i> sp.	15.92	6.09-36.70	20
<i>Oedogonium</i> sp.	34.40	12.54-51.68	19
<i>Elodea Nuttallii</i>	26.31	2.33-50.51	28
<i>Potamogeton crispus</i>	26.31	4.69-55.80	20
FISH ⁴			
Green sunfish	0.56	0.00-1.64	22

¹ Filtered through 45- μ membrane filter.

² Fraction left on membrane filter.

³ Dry-weight basis.

⁴ Whole-body wet-weight basis.

The presence of copper was determined with a Jarrell-Ash atomic absorption spectrophotometer Model 800. Sample concentrations were determined by comparing their readings to those of copper sulfate standards prepared several times during the tests. To insure accuracy, three standards were compared to those of another investigator; the discrepancy was less than 10 percent.

During analyses, uncontaminated samples were spiked with copper to determine percent recovery. Recoveries for plant tissues ranged from 89.9 to 114.4 percent with a mean of 101.2 percent; recoveries from sediments ranged from 94.7 to 120.0 percent with a mean of 109.9 percent.

Reproducibility was determined by reading the same samples on different occasions. When tested with a paired-t test, pairs of readings were not significantly different at the 5 percent level.

Copper added to the ponds accumulated on upper sediment surfaces. Because little downward movement of copper into sediment was expected during the test period, sediment copper values were expressed as weight accumulated on sediment surfaces. Average pretreatment copper concentrations were calculated in $\mu\text{g/g}$ for pond sediment, and total μg copper present in the upper layer was determined for each core sample taken after treatment. The average $\mu\text{g/g}$ pretreatment copper concentration was subtracted from the total μg copper present in the upper layer after treatment to yield μg copper deposited on the upper surface of each core.

Results and Discussion

WATER

Dissolved copper concentrations in Pond A diminished gradually after rapid decline of initial peaks (Fig. 3). High concentrations at stations A1 and A2 shortly after treatment were probably caused by slow dispersal of copper sulfate. Malachite ($\text{Cu}_2(\text{OH})_2\text{CO}_3$) precipitation, a slow process reaching equilibrium only several days after application (11), may have played a large role in the decline.

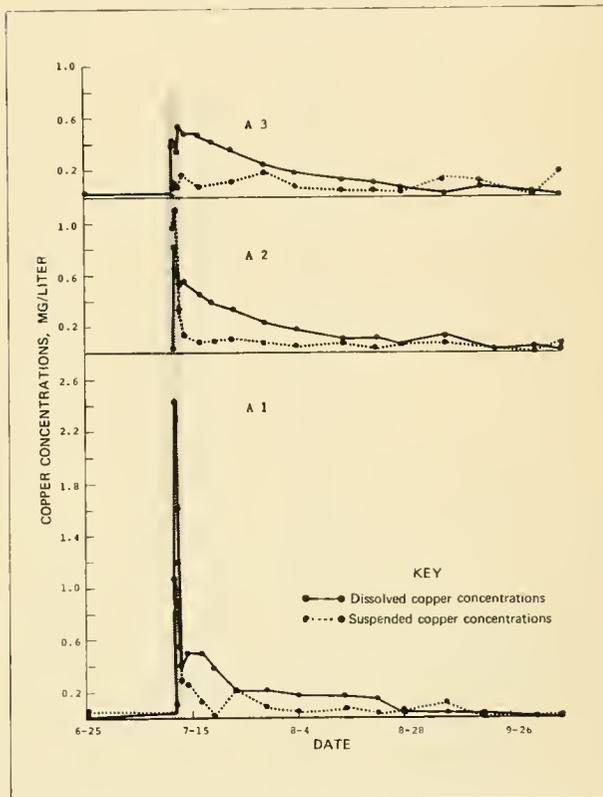


FIGURE 3. Changes in dissolved and suspended copper concentrations, Pond A, three sites

NOTE: Shaded area denotes treatment with 3 ppm copper sulfate.

Levels of organic acids in the range of 4 to 40 ppm carbon in water may increase the amount of metal stabilized in solution by several orders of magnitude (12). Ten sediment samples from Pond A contained an average of 11 percent organic matter; organic complexes in the overlying water may have slowed the decline of dissolved copper.

Suspended copper levels in Pond A showed no trends. Although an initial peak occurred, concentrations of suspended copper soon declined to background levels (Table 2).

Dissolved copper concentrations in Pond B followed a pattern similar to that of Pond A following treatment (Fig. 4). Copper levels peaked initially, and subsequently decreased. However, sudden increases in dissolved copper occurred at all stations about 3 weeks after treatment. This rise, coinciding with the decomposition of extensive masses of *Chara*, was probably caused by release of copper from its tissues. After these secondary peaks, a rapid decrease in dissolved copper levels occurred. Detrital particles from the decomposing *Chara* may have aided in removing copper from solution.

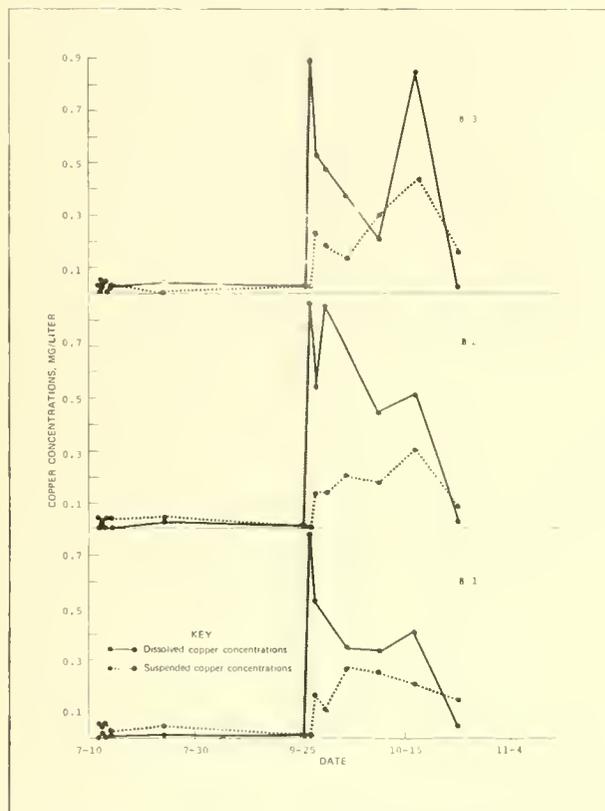


FIGURE 4. Changes in dissolved and suspended copper concentrations, Pond B, three sites

NOTE: Shaded area denotes treatment with 3 ppm copper sulfate.

Suspended copper concentrations in Pond B increased slightly after treatment and then rose to levels between 0.3 and 0.5 mg/liter after 21 days. Copper-bearing particles from disintegrating *Chara* may have caused the elevated levels.

In general, a rapid loss of dissolved copper from solution has occurred in most experiments performed in alkaline water (5,13). In the present study, significant levels of dissolved copper remained after several weeks, possibly because of copper-containing organic complexes in the pond water.

SEDIMENTS

After treatment in Pond A, copper accumulated in sediment rapidly at first and then gradually (Fig. 5). Precipitation of insoluble compounds probably accounted for the initial increase. Later accumulations may have been caused by gradual adsorption of dissolved copper and of copper released from plants and algae. Although sediments collected copper more quickly in Pond B than in Pond A, overall accumulation patterns of the two ponds were similar. Published research indicates that copper is rapidly adsorbed by pond sediments and that the amount of copper fixed is determined by the amount of organic matter and nature of clay minerals present (7). Because sediment in the current study contained a high level of organic matter (11 percent) copper was probably fixed once it reached the bottom.

Evidence indicates that sediment acts as the ultimate repository of copper added to an aquatic system. Precipitation of copper compounds followed by gradual adsorption of copper complexes from water probably occurred in the present study.

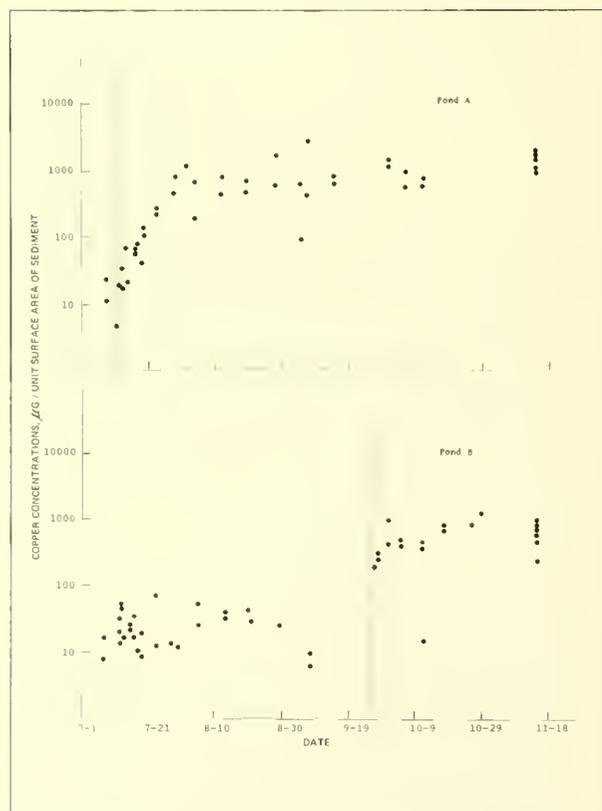


FIGURE 5. Copper accumulation in sediment surface sampled by core, Ponds A and B

NOTE: Shaded area denotes treatment with 3 ppm copper sulfate.

PLANT TISSUES

Plant tissue rapidly accumulated high levels of copper in Pond A (Fig. 6). The ratio of copper concentration in dried tissue to the initial concentration in water after dosage was greater than 3000:1 for the three species present (Table 3).

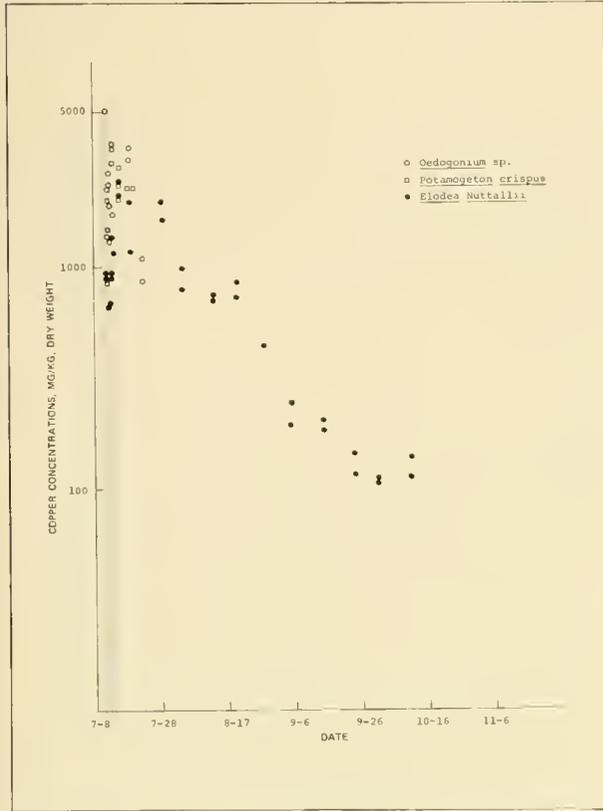


FIGURE 6. Copper accumulated by plant tissue, Pond A
NOTE: Shaded area denotes treatment with 3 ppm copper sulfate.

TABLE 3. Concentration factors of copper in dried plant tissue relative to theoretical initial concentration in pond water after treatment

PLANT	COPPER CONCENTRATION RATIO (PLANTS:WATER, PPM)	
	POND A	POND B
<i>Chara</i> sp.	—	1360
<i>Potamogeton crispus</i>	4616	1716
<i>Elodea Nuttallii</i>	3018	3329
<i>Oedogonium</i> sp.	4358	2846

Declining copper concentrations noted in *Elodea* (Fig. 6) may have been caused by loss of copper-bearing tissue by disintegration and an interruption of growth processes and subsequent copper accumulation.

Copper concentrations in macrophytes which developed in Pond A after treatment were slightly above back-

ground levels (Fig. 7). Copper concentrations near background levels in water indicate that uptake from sediment may have occurred. These results corroborate those of Bartley, who found that pond weeds in an irrigation canal accumulated residual copper from the hydrosol (2).

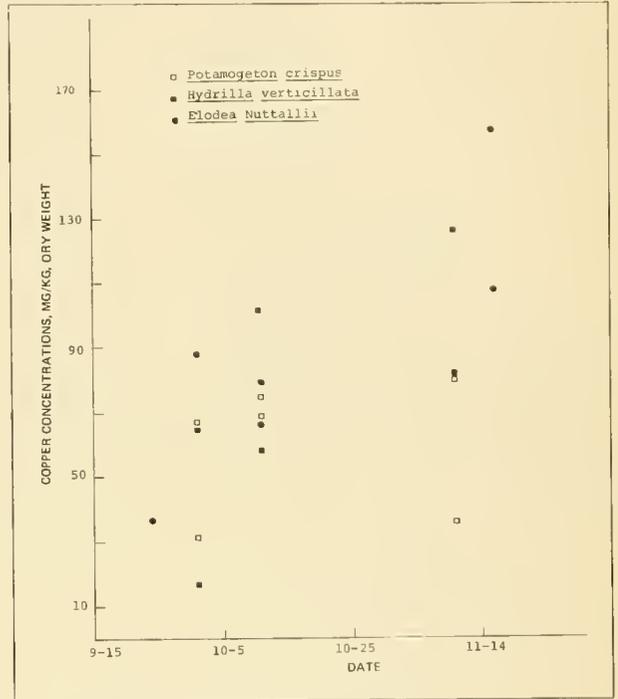


FIGURE 7. Copper accumulated by plants growing after sulfate treatment, Pond A

Copper was also taken up rapidly by plants in Pond B (Fig. 8). Residue levels were generally lower (Table 3) and increased more gradually than they did in Pond A. Water temperatures in Pond B, which were 5° C lower than those in Pond A, may have been responsible.

Copper levels in *Elodea* in Pond B were higher than those in either *Potamogeton* or *Oedogonium*; in Pond A, however, *Elodea* had copper concentrations lower than those in the other two species. Uptake may have been related to growth activities; species which grew most rapidly during treatment accumulated highest levels of copper.

The current study shows that aquatic plants are capable of concentrating very high levels of copper. Differences in accumulation between species seemed related to growth conditions of plants. Species growing most rapidly during treatment had highest levels.

FISH

Slight increases in fish whole-body copper concentrations occurred after treatment in both ponds (Fig. 9). Fish in Pond A had levels of about 3 ppm copper 1 week after treatment and again 47 days after treatment.

Levels decreased to the background value of about 0.5 ppm 79 days after treatment. Pond B fish showed copper increases up to about 2 ppm 10 days after treatment; 51 days after treatment residues had decreased to background levels.

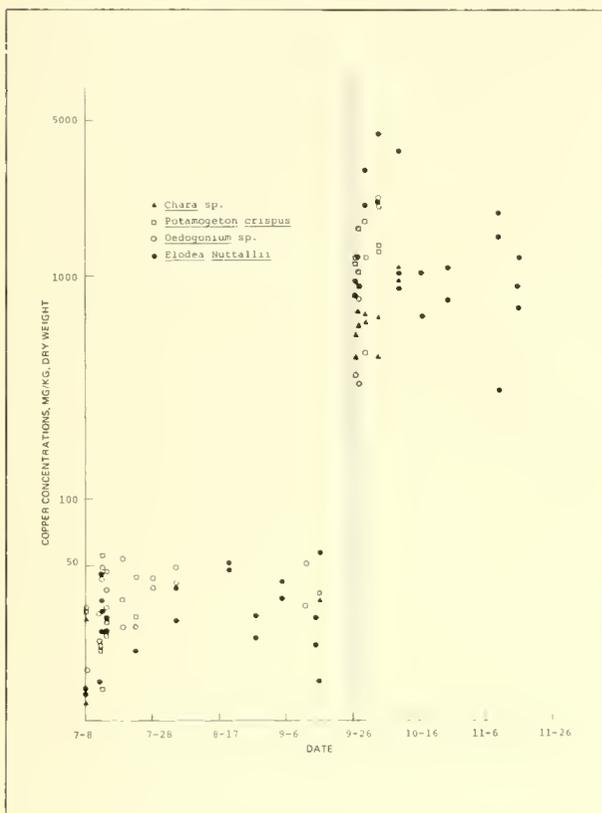


FIGURE 8. Copper accumulated by plant tissues, Pond B

NOTE: Shaded area denotes treatment with 3 ppm copper sulfate.

COMPONENTS OF COPPER DISTRIBUTION

The fraction of applied copper in each major component of Ponds A and B was estimated on each sampling date. Plant values were calculated by estimating the weight of plant masses and total copper accumulated in the masses. Water concentrations included copper in dissolved and suspended states. Weight of copper on the total sediment surface at each sampling time was estimated by multiplying the average copper value of an individual core sample by a factor calculated by dividing total sediment surface area by core surface area.

Figure 10 graphs only water and sediment copper for Pond A because plant tissues always contained less than 1 percent of the total copper applied. A clear relation existed between water and sediment copper fractions in Pond A: a decrease of copper in water with a concomitant increase in sediment copper occurred. The

estimated amount of copper in sediment at the end of the experiment was greater than 90 percent of the total applied.

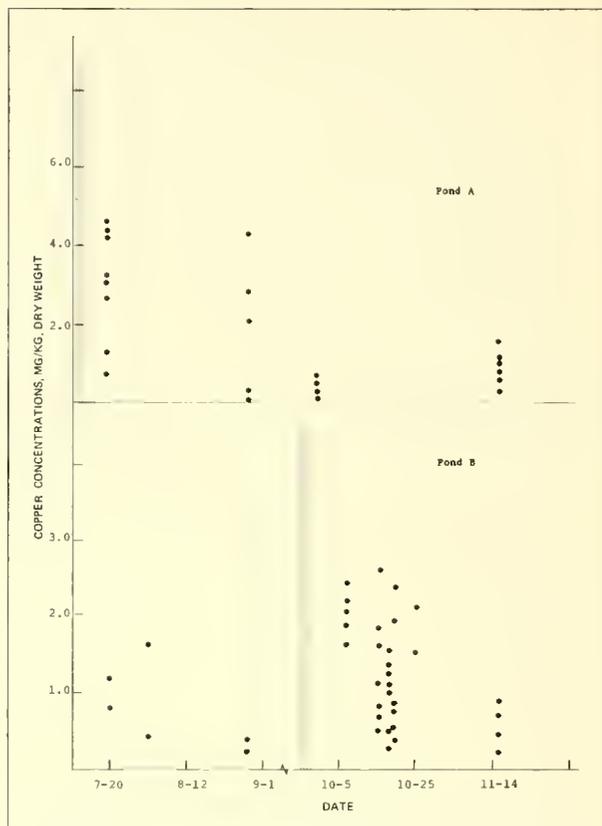


FIGURE 9. Copper accumulated by green sunfish, Ponds A and B

NOTE: Shaded area denotes treatment with 3 ppm copper sulfate.

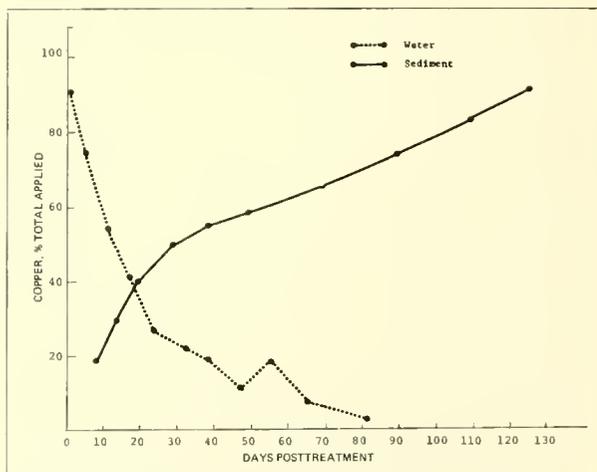


FIGURE 10. Total applied copper present in water and sediment, Pond A

Plant tissue, mostly *Chara*, played a significant role in Pond B copper dynamics (Fig. 11). Percentage of copper in plant tissues 14 days after treatment was estimated to be about 10 percent of the total applied. Copper was released shortly thereafter during decomposition. Sediment accumulation followed a pattern similar to that of Pond A. Copper values in the water were influenced by release of copper from dying *Chara* tissue.

Conclusion

As expected, copper moved rapidly from water to sediment in the ponds observed in this study. However, phenomena such as binding of metals by organic compounds in the water and rapid uptake of metals by aquatic plants and algae cannot be overlooked in assessing dispersal of a metal in aquatic systems.

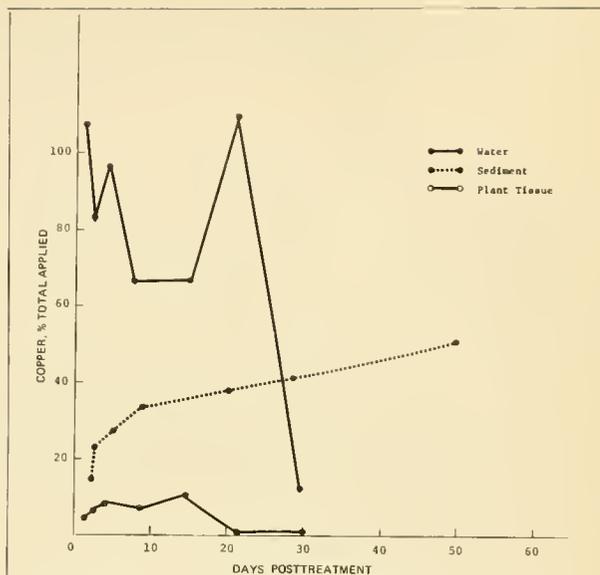


FIGURE 11. Percent of total applied copper present in water, sediment, and plant tissue, Pond B

LITERATURE CITED

- (1) Kopp, J. F., and R. C. Kroner. 1967. A five-year summary of trace metals in rivers and lakes of the United States. U.S. Dep. Interior; Compilation of Data, October 1, 1962—September 30, 1967. 28 pp.
- (2) Bartley, T. R. 1969. Copper residue on irrigation canal. Rept. Bur. Reclamation, U.S. Dep. Interior. 16 pp.
- (3) Nelson, J. L., V. F. Bruns, C. C. Coutant, and B. L. Carlile. 1969. Behavior and reactions of copper sulfate in an irrigation canal. *Pestic. Monit. J.* 3(3):186-189.
- (4) Chancellor, R. J., A. V. Coombs, and H. S. Foster. 1958. Control of aquatic weeds by copper sulphate. *Proc. 4th Brit. Weed Cont. Conf.* Pp. 80-84.
- (5) Deubert, K. H., and I. E. Demoranville. 1970. Copper sulfate in flooded cranberry bogs. *Pestic. Monit. J.* 4(1):11-13.
- (6) Toth, S. J., and D. N. Riemer. 1968. Precise chemical control of algae in ponds. *J. Amer. Water Works Ass.* 60(3):367-371.
- (7) Riemer, D. N., and S. J. Toth. 1970. Adsorption of copper by clay minerals, humic acid and bottom muds. *J. Amer. Water Works Ass.* 62(3):195-197.
- (8) Riley, G. A. 1939. *Limnological studies in Connecticut.* *Ecol. Monogr.* 9(1):54-94.
- (9) American Public Health Association. 1965. *Standard Methods for the Examination of Water and Wastewater.* 12th ed. New York. 873 pp.
- (10) U.S. Environmental Protection Agency. 1971. *Methods for Chemical Analysis of Water and Wastes.* Water Quality Office, Cincinnati, Ohio. 312 pp.
- (11) Stiff, M. J. 1971. The chemical states of copper in polluted fresh water and a scheme of analysis to differentiate them. *Water Res.* 5:585-599.
- (12) Ong, H. L., V. E. Swanson, and R. E. Bisque. 1970. Natural organic acids as agents of chemical weathering. U.S. Geol. Survey Prof. Paper 700-C:C-130-C-137.
- (13) Mulligan, H. F. 1969. Management of aquatic vascular plants and algae. In *Eutrophication: Causes, Consequences, Correctives.* National Academy of Sciences, Washington, D.C. 661 pp.

RESIDUES IN FOOD AND FEED

Preliminary Survey of Ethylenethiourea Residues in the Canadian Food Supply, 1972

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ABSTRACT

A preliminary monitoring program was initiated in 1972 to determine ethylenethiourea (ETU) content of the Canadian food supply. Of 167 samples analyzed, 90 were domestic and 77 were imported. Samples were analyzed by electron-capture/gas-liquid chromatography. Thirty-three percent of the samples contained detectable ETU residues; most of these were 0.020 ppm or less. Highest levels, 0.047 and 0.083 ppm, were found in canned spinach and orange peel, respectively.

Introduction

Ethylenebisdithiocarbamates are widely used as fungicides and may, under conditions of aeration (1) or cooking (2), degrade to ethylenethiourea (ETU). The compound has been identified as a component of commercial ethylenebisdithiocarbamate formulations (3,4). Toxicological studies have shown ETU to be goitrogenic (5), carcinogenic (6), and teratogenic (7). In view of these findings, the present survey was conducted in 1972 to establish ETU levels in the Canadian food supply.

Sampling Procedures

A total of 167 samples were analyzed. Of these, 85 were obtained by the Inspection Services of the Quebec Region, Health Protection Branch, and 82 were obtained by the Inspection Services of the Ontario Region. Both domestic and imported products were analyzed: 90 of the former and 77 of the latter. Of the 77 imports, 56 were from the U.S.A., 9 from Mexico, 5 from Holland, 2 from Switzerland, 2 from Chile, 1 from Morocco, 1 from Israel, and 1 from Poland.

For small fruits and vegetables (e.g., grapes, Brussels sprouts, beans), minimum sample size was 3 lb. For medium-size fruits and vegetables (e.g., apples, oranges, potatoes), minimum samples were 3 lb or 10 units. For large commodities (e.g., cabbage, lettuce), a minimum number of 3 was used for each sample. For canned goods, 5 cans of each type were combined to make 1 sample. A 1-lb minimum of cereal or wheat product was obtained for each sample. All samples were cut, blended, and stored in mason jars in a freezer before analysis.

Analytical Procedures

The method of analysis was a modification of one described previously (8). Stored samples were thawed and a 5.0-g portion was homogenized with 50 ml absolute ethanol in a Sorvall Omni-Mixer. Solids were removed from the homogenate by filtration through Whatman No. 1 paper using a slight negative pressure and a filtrate diluted to 100 ml with distilled water. Twenty-ml aliquots of the diluted extract were placed in 50-ml round-bottomed flasks, and 0.1 ml benzyl chloride was added. The benzyl chloride had been purified previously by passage through a column of alumina as described by Onley et al. (9) for n-bromobutane. After refluxing the contents of the flasks for 30 minutes samples were cooled and transferred to 125-ml separatory funnels with 30 ml distilled water. Hydrochloric acid (1 N; 1.0 ml) was added and samples were extracted with two (1 × 10 ml and 1 × 5 ml) solutions of chloroform which were later discarded. Potassium hydroxide (1 N; 5.0 ml) was added to the aqueous phase and the s-benzyl ETU was immediately extracted with 10 ml chloroform. Extracts were dried by passage through a small bed of sodium sulfate and placed in 12-ml vials containing 10 µl paraffin oil. Chloroform was removed by evaporation under a stream of nitro-

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gen. By varying nitrogen flow, the rate of evaporation was controlled enough that 1.5 hours or more were required to remove 10 ml. More rapid evaporation sometimes leads to losses of derivative.

Samples were trifluoroacetylated by adding a solution of 10 percent trifluoroacetic anhydride in 0.50 ml benzene and permitting them to react for 15 minutes at room temperature. The solvent was evaporated almost to dryness under a gentle stream of nitrogen and the trifluoroacetylation was repeated with an additional 0.50 ml reagent for 15 minutes. After removal of the solvent, samples were dissolved in 1.0 ml benzene and a 5.0- μ l aliquot was analyzed by gas-liquid chromatography (GLC).

GLC was performed on a Varian Aerograph 1400 fitted with a tritium foil electron-capture detector and a 6-ft-by- $\frac{1}{8}$ -in.-ID glass column. The column was packed with 4 percent SE-30, 6 percent QF-1 on Chromosorb W HP and operated at 200° C with a nitrogen flow of 100 ml/min. The injection port and detector were maintained at 220° C. Under these conditions trifluoroacetylated *s*-benzyl ETU had a retention time of 12 minutes.

ETU, added at levels of 0.05 and 0.10 ppm to 17 commodities, was recovered at a mean of 96.0 percent \pm a standard deviation of 8.9 percent. The minimum detect-

able limit, defined as twice background, was 0.01 ppm. Because of low levels of ETU encountered in the samples, GLC/mass spectral confirmation (8) was not attempted.

Results and Discussion

Results of the analyses are presented in Table 1. Of the 167 composite samples analyzed for ETU residues, 112 samples (67 percent) did not contain detectable levels and 55 samples (33 percent) contained residues ranging from 0.01 to 0.15 ppm. Most of the samples (92 percent) contained 0.02 ppm or less ETU. Notable exceptions were some samples of canned spinach with an average of 0.047 ppm and orange peels with an average of 0.083 ppm. Of the 90 domestic samples, 29 composites (32 percent) contained detectable levels of ETU compared to 26 composites (34 percent) of the 77 imported foods containing detectable ETU levels.

Acknowledgments

Authors wish to thank K. A. McCully, Field Operations Directorate, Health Protection Branch, for organizing this project; G. Léveillé, Health Protection Branch, Montreal, Canada, for advice in preparing this report; and C. Fortin and R. Gauthier, Health Protection Branch, Montreal, Canada, for technical assistance.

TABLE 1. *Ethylenthiourea* residues in foods sampled from Quebec and Ontario, Canada—1972

FOOD	TYPE	No. SAMPLES ANALYZED	No. POSITIVE SAMPLES	MEAN OF POSITIVE SAMPLES, PPM	RANGE OF POSITIVE SAMPLES, PPM
Potatoes	Fresh	13	4	0.025	0.010-0.050
Tomatoes	Fresh	10	3	0.020	0.010-0.030
Tomatoes	Canned	5	4	0.018	0.010-0.020
Apples	Fresh	10	4	0.028	0.020-0.050
Lettuce	Fresh	10	3	0.013	0.010-0.020
Carrots	Fresh	9	5	0.010	0.010-0.010
Carrots	Canned	1	0	ND	ND
Green beans	Fresh	4	0	ND	ND
Green beans	Canned	5	2	0.020	0.020-0.020
White kidney beans	Canned	1	0	ND	ND
Cabbage	Fresh	8	1	0.010	ND
Cabbage	Canned	1	0	ND	ND
Sauerkraut	Canned	3	0	ND	ND
Broccoli	Fresh	10	4	0.020	0.010-0.040
Brussels sprouts	Fresh	8	2	0.020	0.020-0.020
Celery	Fresh	7	4	0.015	0.010-0.020
Cherries	Canned	10	0	ND	ND
Spinach	Fresh	7	2	0.025	0.020-0.030
Spinach	Canned	5	3	0.047	0.040-0.050
Cucumber	Fresh	7	1	0.050	ND
Dill pickles	Jarred	3	0	ND	ND
Grapes	Fresh	10	5	0.020	0.010-0.050
Oranges (peel)	Fresh	5	3	0.083	0.030-0.150
Oranges (pulp)	Fresh	5	3	0.020	0.020-0.020
Wheat	Fresh	5	2	0.015	0.010-0.020
Flour	Bagged	3	1	0.040	ND
Puffed wheat	Boxed	1	0	ND	ND
Shredded wheat	Boxed	1	1	0.010	ND
Wheat germ	Boxed	1	0	ND	ND
Wheat germ flakes	Boxed	1	0	ND	ND
Wheat hearts	Boxed	1	1	0.010	ND
Bran flakes	Boxed	1	0	ND	ND
Cereals	Boxed	1	0	ND	ND

NOTE: ND = none detected.
Canned implies use of tin can; jarred implies use of glass jar.

LITERATURE CITED

- (1) Ludwig, R. A., G. D. Thorn, and D. M. Miller. 1954. Studies on the mechanism of fungicidal action of disodium ethylenebisdithiocarbamate (Nabam). *Can. J. Bot.* 32:48-54.
- (2) Newsome, W. H., and G. W. Laver. 1973. Effect of boiling on the formation of ethylenethiourea in zineb-treated foods. *Bull. Environ. Contam. Toxicol.* 10(3): 151-154.
- (3) Johnson, E. I., and J. F. C. Tyler. 1962. Occurrence of ethylenethiourea in thiocarbamate fungicides and its detection in fruit juice. *Chem. Ind. (London)* 305-306.
- (4) Bontoyan, W. R., J. B. Looker, T. E. Kaiser, P. Giang, and B. M. Olive. 1972. Survey of ethylenethiourea in commercial ethylenebisdithiocarbamate formulations. *J. Ass. Offic. Agr. Chem.* 55:923-925.
- (5) Graham, S. L., and W. H. Hansen. 1972. Effects of short term administration of ethylenethiourea upon thyroid function of the rat. *Bull. Environ. Contam. Toxicol.* 7:19-25.
- (6) Meland, B. M., J. H. Weisburger, E. K. Weisburger, J. M. Rice, and R. Cypher. 1972. Thyroid cancer in rats from ethylene thiourea intake. *J. Nat. Cancer Inst.* 99:583-584.
- (7) Khera, K. S. 1973. N,N'-ethylenethiourea: teratogenicity study in rats and rabbits. *Teratology* 7:243-252.
- (8) Newsome, W. H. 1972. Determination of ethylenethiourea residues in apples. *J. Agr. Food Chem.* 20: 967-969.
- (9) Onley, J. H., and G. Yip. 1971. Determination of ethylene thiourea residues in food, using thin layer and gas chromatography. *J. Ass. Offic. Anal. Chem.* 54(1):165.

RESIDUES IN FISH, WILDLIFE, AND ESTUARIES

Pesticide and Mercury Residues in Commercially Grown Catfish¹

A. B. Crockett,² G. B. Wiersma,² H. Tai,³ and W. Mitchell³

ABSTRACT

In 1970, 54 commercial catfish farms in Arkansas and Mississippi were sampled for pesticide and mercury residues. Pesticide residues above FDA action levels were detected in 15 percent of the fish samples. Data on residues in sediment, fish feed, and source water suggest that fish were not being contaminated from these sources. Average fish residue per county was, however, strongly correlated with the percent of total acres planted in cotton and soybeans. Results strongly suggest that cotton production was the primary source of contamination. Actual routes of movement have not been clearly defined but aerial transport seems most probable.

Introduction

In February 1970 the Plant Protection Division, Agricultural Research Service, U.S. Department of Agriculture, initiated a study to determine the magnitude and source of pesticide residues in commercially grown catfish. The study was undertaken to investigate reports of illegal residues of DDT, endrin, and dieldrin in commercially raised catfish of the Mississippi delta, which is the major catfish-growing area of the United States. Analyses for mercury were included for scientific interest.

Although little information is available on pesticide residues in cultured catfish, it is generally known that fish can concentrate chlorinated hydrocarbon pesticides.

Bevenue et al. (1) reported that chlorinated pesticides can be concentrated to 33,000 and 36,000 times the level found in the water by carnivorous and detrital fish, respectively. Morris and Johnson (2) studied the dieldrin level of fish in Iowa streams and found that catfish contained higher pesticide levels than other rough fish and much higher concentrations than game fish. A study of wild catfish in Nebraska revealed the frequent presence of DDTR (DDT + DDE + TDE) and dieldrin (3).

Channel catfish have been included regularly as a preferred species for sampling in the National Pesticides Monitoring Program for fish because they are near the top of the food chain (4). The two monitoring sites located in the commercial fish-raising area of Arkansas consistently reported endrin residues during the spring and fall of 1967 and 1968 (5). DDT residue levels in fish from these two areas are among the highest detected in the Mississippi River System (6).

Sampling Procedures

Sampling was conducted in Arkansas and Mississippi because those States encompass the most intensive catfish farming area in the United States. Fifty catfish farms were selected on a probability basis: i.e., each farm had an equal chance of being selected. Approximately 1 farm in 12 was examined. At each farm, fish, source water, pond water, and sediment were sampled from one pond; a feed sample was also collected. Sample collection commenced in March 1970 and was completed by the end of April.

Catfish samples were composed of two or three fish, each about 2 years old and weighing 0.5-0.7 kg. As

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specified in the U.S. Department of Health, Education, and Welfare Food and Drug Administration regulatory methodology, only edible fish flesh was examined for pesticide residues.

One gallon of source water and a composite gallon sample of pond water collected from 5 to 10 different pond locations were taken from each farm.

One composite sediment sample was collected from each pond with a weighted dredge. At least five drag subsamples were taken within 10 feet of shore; another five drags were taken farther from shore.

A sample of catfish feed was collected: when possible, from different feedbags or lots.

Analytical Methods

SEDIMENT

After decanting and discarding excess water, the remaining portion was mixed for 5 minutes in a paint shaker and a 300-g sediment sample was taken. The sample was extracted with 600 ml 3:1 hexane:isopropanol by concentric rotation for 4 hours. Alcohol was removed by three water washes and the hexane extract was dried through anhydrous sodium sulfate. It was then ready for gas-liquid chromatographic (GLC) analysis. A separate portion of sediment was dried at 120°C for 24 hours to obtain a moisture content value. Analytical data on sediment samples were calculated on a dry-weight basis.

WATER

The gallon water sample was shaken before removal of a 500-g subsample. The sample contained some suspended matter and was not filtered before extraction.

The 500-ml sample was extracted three times with 60 ml methylene chloride by shaking in a 1,000-ml separatory funnel. The three extracts of about 180 ml were combined and concentrated to about 5 ml, 100 ml hexane was added, and the sample was concentrated again to 5 ml. All concentrations were performed under a three-ball Snyder column except the final adjustment to 2.5 ml which was performed in a centrifuge tube with a gentle stream of air. At this point the sample extract was ready for analysis.

TISSUE, ALGAE, AND FEED SAMPLES

Feed samples were received in 1-gallon and ½-gallon cans and thoroughly mixed to give a representative sample. Catfish were beheaded, skinned, and eviscerated and the meat and bone were thoroughly macerated in a Hobart food grinder.

A 20-g sample was mixed with 100 ml isopropanol for 2-3 minutes in a Waring blender. Three hundred ml hexane was added and the sample was rotated concentrically for 2 hours. An aliquot representing 15 g was taken, the isopropanol was removed by two water

washes, and the hexane was extract-dried through sodium sulfate.

Algae and feed were processed in the same manner as tissue except that 100-g samples of feed were used.

Partitioning of Samples—An aliquot of 15 g was partitioned as follows: the 50-ml hexane sample extract was shaken with 100 ml acetonitrile in a 500-ml separatory funnel, the bottom acetonitrile layer was saved, and the hexane layer was discarded. This step was carried out three times and the acetonitrile layers were combined. The combined acetonitrile extracts were backwashed with 25 ml acetonitrile-saturated hexane and the hexane layer was discarded. The acetonitrile sample extract was concentrated to approximately 10 ml under a three-ball Snyder column and 100 ml hexane was added. The latter two operations were repeated twice and the sample was essentially in hexane. The hexane extract was adjusted to appropriate volume and held at low temperature for subsequent florisol column cleanup and fractionation.

Cleanup and Fractionation—A chromatographic column consisting of a 125-ml flask reservoir attached to an 11-by-500-ml glass tube with a teflon stopcock and a removable glass tip was prepared by placing a small pad of hexane-washed glass wool in the bottom of the column and adding anhydrous granular sodium sulfate to the 1-inch level. Eighteen g 60-120 mesh florisol was poured into the column and evenly packed by tapping the column with a light mallet.

The column was prewashed with 100 ml nanograde hexane and the sample extract representing 5 g of the original sample was quantitatively added to the column when the level of the hexane prewash had reached the top of the upper layer of Na₂SO₄. When the sample extract level reached the top of the column, 100 ml 5 percent methylene chloride in hexane was added and a 250-ml flask marked Fraction 1 was placed under the column. When the liquid level again drained to the top of the column, 100 ml nanograde methylene chloride was added to the reservoir and the original flask was replaced by a second, marked Fraction 2. One ml 0.01 percent Nujol in hexane was added to each elution.

Each elution was concentrated to approximately 5 ml under a Snyder column. One hundred ml hexane was added to each elution and the fractions were again concentrated to approximately 5 ml. Each elution was quantitatively transferred to a 15-ml centrifuge tube and placed in a 40°C water bath. A gentle stream of air was directed into the tubes and the sample volume was reduced to 2.5 ml. Fractions were injected separately onto a gas-liquid chromatograph.

Gas-Liquid Chromatographic Analysis—At least two columns were used for each sample; a third column was also used when necessary. Operating parameters varied for the three columns:

Column 1. 4.8 percent OV-17/6.2 percent QF-1 on Gas-Chrom Q

Temperatures: Injector 250° C
Oven 200° C
Detector 210° C

Column 2. 3 percent DC-200 on Gas-Chrom Q

Temperatures: Injector 245° C
Oven 175° C
Detector 205° C

Column 3. 9 percent QF-1 on Gas-Chrom Q

Temperatures: Injector 230° to 245° C
Oven 70° C
Detector 200° to 205° C

Carrier gas was 5 percent methane in argon or pre-purified nitrogen at 80-100 ml/min.

Recoveries were performed for each type of sample. Recoveries were consistent with values from the same type of samples in previous work completed in this laboratory.

Chlorinated pesticides used for recovery studies were heptachlor, heptachlor epoxide, gamma chlordane, *o,p'*-DDE, *p,p'*-DDE, dieldrin, endrin, *o,p'*-DDT, *p,p'*-DDT, *p,p'*-TDE, and aldrin; organophosphorus compounds used were phorate, diazinon, methyl parathion, ethyl parathion, DEF, trithion, and ethion. Recovery was 90 to 100 percent on water and sediment, and 80 percent on tissue, algae, and feed.

Toxaphene was quantitated by comparing the four major peaks with corresponding peaks on a calibrated standard chromatogram whenever possible. In some cases only two peaks could be compared with corresponding peaks from the standard. Chlordane was quantitated by use of the gamma chlordane peak or, if necessary, by comparison with a technical chlordane standard. Quantitations were confirmed by dual-column or triple-column cross-checking and use of *p*-values (7).

Limits of Detection—Minimum detection limits (MDL) in fish, algae, feed, and sediment were 0.01 ppm for all pesticides except mixtures such as chlordane, toxaphene, polychlorinated biphenyls (PCB's), and a few compounds such as EPN or Guthion, which elute later on GLC columns. In these cases, the MDL was 0.03 to 0.10 ppm, depending on the compound and the noise level. Corresponding limits for water were 0.01 or 0.03 to 0.10 ppb.

Mercury Analysis—A sample of mercury weighing approximately 2 g was placed in a 250-ml Erlenmeyer

flask and 25 ml concentrated sulfuric acid was added. The sample was heated until the organic matter had dissolved. Organic matter was further oxidized by adding 1.0 ml 30 percent hydrogen peroxide until the sample was colorless. Fifty ml distilled water was added to the sample. After cooling, 5 percent potassium permanganate was added, one drop at a time, until a permanent pink color was attained.

Twenty ml sodium chloride—hydroxylamine sulfate was added and the flask was positioned in the aeration system. Ten ml stannous sulfate was added and the mercury was swept into the cell as elemental mercury. The absorbance reading of the mercury was compared with a standard curve plotted from known amounts of mercury which had been analyzed by the same methods applied to the samples. The MDL was 0.01 ppm. This method of analysis was patterned after that of Hatch and Ott (8).

Results

All fish examined showed pesticide residues. Results of the fish analyses (Table 1) indicate that DDTR and mercury were found in all samples; dieldrin, endrin, and toxaphene were present in 89, 76, and 96 percent of the samples, respectively. Chlordane was found once and aldrin existed at low levels in three samples. No other chlorinated hydrocarbon pesticides were detected.

Although most fish samples contained residue levels below the FDA action level or tolerance, a number of samples exceeded the limit. FDA action levels were exceeded by 2 percent of the DDTR samples, 6 percent of the aldrin/dieldrin samples, 4 percent of the endrin samples, and 7 percent of the toxaphene samples. In total, 15 percent of the fish samples exceeded present limits for one or more residues. Toxaphene appears to be the most serious contaminant because it exceeded the action level most frequently and its average concentration was closest to its limit. Average concentration of the four samples exceeding the 5 ppm limit was 13.0 ppm.

Possible sources of pesticide residues in fish would appear limited to source water, sediment, feed, and crops. While it is conceivable that stocked fingerlings were a source of pesticides, no evidence in the study indicates this to have been the case. All the farmers claimed that

TABLE 1. Pesticide and mercury residues in commercial catfish

	NO. SAMPLES	PERCENT WITH RESIDUES	AVERAGE CONCENTRATION, PPM	FDA ACTION LIMIT, PPM	PERCENT SAMPLES EXCEEDING LIMIT	RANGE DETECTED RESIDUES, PPM
DDTR	54	100	1.07	5	2	0.09-8.71
Aldrin/Dieldrin	54	89	0.07	0.3	6	0.01-0.87
Endrin	54	76	0.06	0.3	4	0.01-0.41
Toxaphene	54	96	2.1	5	7	0.2-20.7
Mercury	50	100	0.07	0.5	0	0.02-0.35

NOTE: Samples represent edible portions of catfish.

they had not applied any of the contaminating pesticides to the fish ponds.

WATER

Thirty-five samples of pond and souree water were examined for chlorinated hydrocarbons. In no instance was any pesticide detected at the 0.01 ppb level. No fish from wells were analyzed for chlorinated hydrocarbons because these compounds are insoluble in water and are not leached to any appreciable extent.

To determine whether lower-level contamination existed, residues in catfish were statistically compared according to the water source in which the fish had been caught. A comparison of log-transformed means of DDT, dieldrin, endrin, and toxaphene residues was made between catfish raised in well water and those raised in surface water. Well-water catfish had significantly higher pesticides (95 percent level) in all cases. These data do not, however, indicate that the pesticide came from wells but, rather, that the pesticide source was associated with wells. Further explanation appears under the crop section of this paper.

During a resampling of some of the fish ponds, several algae samples were collected and analyzed. All five samples showed DDT and toxaphene residues. DDTR and toxaphene levels ranged from 0.10 to 0.97 and from 0.20 to 1.41 ppm, respectively. The absence of chlorinated hydrocarbons from pond water can probably be explained by their low solubility in water. Algae residues, however, indicate that pesticides must have been in the water at some time.

Surface runoff could be a source of pesticide residues but the absence of residues from sediment, which is also transported in runoff, does not support this theory. In addition, commercial fish ponds are generally constructed to avoid surface runoff if clean water is available.

SEDIMENT

Fifty-three sediment samples were examined for chlorinated hydrocarbons. The only chemical found was DDTR, which was present in 18 samples. A correlation

analysis of all samples was run to estimate the level of association between DDTR in fish and DDTR in sediment. Results showed a correlation coefficient (r) of 0.287, which indicates a significant deviation from zero at the 95 percent level. If DDTR were derived from the original soil prior to pond formation, the DDT level probably would decrease as the pond aged. No significant difference from zero could be established. Another consideration is that DDTR and toxaphene in fish are closely correlated (99 percent level, $r = 0.60$, $n = 54$), which suggests they are derived from the same source. The absence of toxaphene from sediment samples suggests that sediment is not the source of fish residues for this insecticide.

The absence of pesticide residues from sediment samples could also indicate poor sampling techniques. In the resampling of ponds, DDTR was the only pesticide found. Toxaphene, however, was found in algae which eventually becomes detritus and enters the sediment. Absence of residues could mean that fine surface sediment was not adequately sampled.

FEED

All fish feed from the 43 farms sampled had detectable residues (Table 2). In addition to pesticides shown in Table 2, small amounts of heptachlor, heptachlor epoxide, and Aroclor 1254 were detected in a few samples. A correlation analysis did not indicate a significant association between DDTR, dieldrin, endrin, and toxaphene levels in feed and fish (Table 2). In addition, DDTR and toxaphene residues, which correlate closely in fish, are not correlated in feed ($r = 0.200$). Pesticide residues in feed certainly contribute to the residues found in fish, but the amount appears negligible compared with other sources.

CROPS

To determine whether pesticides used on crops had contributed to contamination of catfish, authors compared the percent of total county acres to which insecticides had been applied (9) with the average fish residue for that county. Resulting correlation coefficients indicate a significant deviation from zero (99 percent level) in

TABLE 2. Principal pesticide residues in fish feed

	NO. SAMPLES	PERCENT WITH RESIDUES	AVERAGE CONCENTRATION, PPM	RANGE DETECTED RESIDUES, PPM	CORRELATION COEFFICIENT, FISH: FEED
DDTR	43	91	0.120	0.02-0.84	0.005
Dieldrin	43	74	0.007	0.01	0.166
Endrin	43	14	0.002	0.01-0.02	-0.149
Chlordane	43	21	0.016	0.01-0.28	ND
Toxaphene	43	42	0.06	0.1-0.3	0.099
Malathion	43	74	0.051	0.01-0.32	ND

NOTE: $n = 43$, $r = 0.301$ at 95% confidence level; $r = 0.391$ at 99% confidence level.
ND = data insufficient to calculate.

TABLE 3. Correlations between land use practices and insecticide residues in catfish

	ACRES RECEIVING INSECTICIDE, %	ACRES IN HARVESTED CROPS, %	ACRES IN COTTON, %	ACRES IN SOYBEANS, %
MISSISSIPPI ¹				
DDTR				
Corr. Coef.	0.794	0.701	0.830	0.636
95% Conf. Interval	0.551-0.913	0.386-0.870	0.621-0.929	0.281-0.838
DIELDRIN				
Corr. Coef.	0.662	0.587	0.706	0.590
95% Conf. Interval	0.323-0.851	0.208-0.813	0.395-0.872	0.213-0.814
ENDRIN				
Corr. Coef.	0.732	0.690	0.818	0.587
95% Conf. Interval	0.439-0.884	0.369-0.864	0.596-0.923	0.208-0.813
TOXAPHENE				
Corr. Coef.	0.687	0.675	0.767	0.563
95% Conf. Interval	0.363-0.863	0.343-0.857	0.502-0.901	0.174-0.800
ARKANSAS ²				
DDTR: Corr. Coef.	0.295	-0.285	-0.211	-0.238
DIELDRIN: Corr. Coef.	-0.007	0.176	0.143	0.170
ENDRIN: Corr. Coef.	0.547	-0.195	-0.046	-0.171
TOXAPHENE: Corr. Coef.	0.197	-0.019	-0.021	0.024

Mississippi but not in Arkansas (Table 3). Similar results were obtained when the percent of total county acres in harvested crops (9) was compared with average fish residues.

The major crops and primary recipients of insecticides in Arkansas and Mississippi are soybeans and cotton (9). In the period preceding this study, DDT, endrin, dieldrin, and toxaphene were registered for use on cotton. Of these insecticides, only DDT and toxaphene had been used for more than seed treatment of soybeans. Frequently a combination of DDT and toxaphene had been used several times a year on cotton but usually soybeans had been treated just once every few years to control insect outbreaks (10).

Correlations comparing the percent of total county acres in cotton or soybeans in Mississippi and average insecticide residues in fish showed significant deviation from zero at the 99 percent level for both crops (Table 3). Correlation coefficients for cotton and soybeans were not significantly different, but cotton always resulted in a more significant deviation from zero for each insecticide. Correlations in Arkansas were again not significant.

The absence of correlation in Arkansas may be due to two factors. Most Arkansas sites sampled were located in the highly agricultural eastern counties, but in Mississippi, sites were scattered throughout the State. Only in Mississippi, therefore, could agricultural areas be compared with nonagricultural areas. A second reason for the insignificant correlations in Arkansas may be that the northeastern counties have fewer insect problems and generally apply a smaller amount of pesticides than do the southeastern counties.

Because Mississippi data were considered more informative, they were chosen for further examination. Missis-

sippi data were segregated into high-cotton areas (>10 percent of the total county acres in cotton) and low-cotton areas (<10 percent of the total county acres in cotton). Mean pesticide levels in catfish were calculated after logarithmic transformation; both cotton areas were compared using a 95 percent confidence interval about the mean. Since residue data were not normally distributed, log transformation was used to help normalize them.

Results indicate that fish in high-cotton areas have significantly higher concentrations of DDTR, endrin, and toxaphene than they have in low-cotton areas (Table 4). This relationship could account for the high correlation between DDT and toxaphene in fish, for DDT and toxaphene had often been applied together on cotton.

TABLE 4. Mean pesticide residues and 95 percent confidence intervals for fish from high-cotton versus low-cotton areas, Mississippi

	RESIDUES, PPM			
	GEOMETRIC MEAN, HIGH-COTTON AREA	GEOMETRIC MEAN, LOW-COTTON AREA	95% CONF. INTERVAL, HIGH-COTTON AREA	95% CONF. INTERVAL, LOW-COTTON AREA
DDTR	1.48	0.34	2.40 -0.91	0.53 -0.22
Dieldrin	0.042	0.014	0.090-0.017	0.024-0.007
Endrin	0.063	0.010	0.122-0.030	0.019-0.005
Toxaphene	2.73	0.42	4.42 -1.68	0.85 -0.21

High pesticide levels found in fish grown in well water can also be explained by the association between wells and high-cotton areas: 16 of the 19 farms in Mississippi which use wells as the sole water source are located in high-cotton counties. Residues in sediment were also related to high-cotton counties. Of 12 sediment samples with pesticide residues, 11 were located in such counties.

Pesticide residues in catfish are closely correlated with crops and pesticide use. Considering that larger amounts of pesticides are applied to cotton than to any other crop in this area of the South, this study strongly suggests that cotton is the primary source of contamination in fish ponds. Data indicate that neither source water nor surface runoff appear to be the mechanism of pesticide transport. These data and the general absence of pesticide residues in sediments indicate that aerial transport of pesticides may be the major route of catfish contamination.

LITERATURE CITED

- (1) *Bevenue, A., J. W. Hylin, Y. Kawano, and T. W. Kelley. 1972.* Organochlorine pesticide residues in water, sediment, algae and fish, Hawaii—1970-71. *Pestic. Monit. J.* 6(1):56-64.
- (2) *Morris, R. L., and L. G. Johnson. 1971.* Dieldrin levels in fish from Iowa streams. *Pestic. Monit. J.* 5(1): 12-16.
- (3) *Stucky, N. P. 1970.* Pesticide residues in channel catfish from Nebraska. *Pestic. Monit. J.* 4(2):62-66.
- (4) *Johnson, R. E., T. C. Carver, and E. H. Dustman. 1967.* Residues in fish, wildlife, and estuaries. *Pestic. Monit. J.* 1(1):7-13.
- (5) *Henderson, C., W. L. Johnson, and A. Inglis. 1969.* Organochlorine insecticide residues in fish. *Pestic. Monit. J.* 3(3):145-171.
- (6) *Henderson, C., A. Inglis, and W. L. Johnson. 1971.* Organochlorine insecticide residues in fish—fall 1969. *Pestic. Monit. J.* 5(1):1-11.
- (7) *Bowman, M. C., and M. Beroza. 1965.* Extraction *p*-values of pesticides and related compounds in six binary solvent systems. *J. Ass. Offic. Anal. Chem.* 48(5):943-952.
- (8) *Hatch, W. R., and W. L. Ott. 1968.* Determination of submicrogram quantities of mercury by atomic absorption spectrophotometry. *Anal. Chem.* 40(14): 2085-2087.
- (9) *Bureau of the Census. United States Census of Agriculture. 1969.* Vol. 1, Section 2, Tables numbered 8 for Arkansas and Mississippi.
- (10) *Ford, Rutledge F. 1973.* Area Agronomist, U.S. Department of Agriculture, Extension Service, Ark. Personal communication.

Residues of Methoxychlor and Other Chlorinated Hydrocarbons in Water, Sand, and Selected Fauna Following Injections of Methoxychlor Black Fly Larvicide into the Saskatchewan River, 1972¹

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ABSTRACT

In May 1972, 0.309 ppm methoxychlor black fly larvicide was applied in a single test on the North Saskatchewan River. Eight to nine days later residues of 0.05-0.10 ppm methoxychlor occurred in sand 21-22 km downstream from the point of injection. Methoxychlor was not detected in water, insect larvae, shellfish, or muscle tissues of three fish species on the same sampling date. Perhaps because of relatively high oil content in goldeye fish, methoxychlor residues in muscle tissues were 1.0-1.5 ppm in 8 percent of those sampled, 0.21-0.99 in 21 percent, and 0.02-0.20 in 37 percent. In 34 percent of the goldeye fish no residues were detected. Goldeye and other fish collected before or 17 weeks after this injection did not contain detectable levels of methoxychlor. River water in two samples of the injected slug of water collected 6.5 km downstream from the point of injection contained 0.14 and 0.16 ppm methoxychlor. The suspended solids filtered from these samples contained 40 and 47 percent of this methoxychlor (437 and 892 ppm, respectively). Thus methoxychlor may act selectively against filter-feeding species, especially black fly larvae.

Introduction

DDT black fly larvicide was injected once or twice into one or both branches of the Saskatchewan River during most years from 1948 through 1967. By 1968 residues in muscle tissues of fish from the river included up to 0.05 ppm DDT, 0.05 ppm DDD, and 0.06 ppm DDE (1).

Methoxychlor black fly larvicide was injected experimentally on 11 occasions into the north and south branches of the river from 1968 through 1972 (2).

At the conclusion of these tests, and specifically in conjunction with a single test on the North Saskatchewan River in May 1972, samples of water, riverbed sands, clams, insect larvae, and fish were analyzed for methoxychlor residues. It is the single test in May 1972 from which most of the specific data in this paper have been compiled.

Tests with single 15-minute injections of methoxychlor as a black fly larvicide commenced in the South Saskatchewan River in 1968 and in the North Saskatchewan River in 1969. The total number of 15-minute injections of methoxychlor at each of four sites is shown in Figure 1. A commercial 24 percent emulsifiable concentrate was used in seven of the eight experimental injections into the South Saskatchewan River and in all six 15-minute injections into the North Saskatchewan River; a commercial 50 percent wettable powder was used in one 1968 application in the South Saskatchewan River. A total of 285 kg technical methoxychlor was used in the eight injections into the South Saskatchewan; 450 kg was applied in the six injections into the North Saskatchewan. These were the only potential sources of methoxychlor residues in either branch of the Saskatchewan River up to and including May 23, 1972.

That day marked the beginning of the study reported here, a study designed specifically to determine whether methoxychlor residues existed before or after a single 15-minute injection of 0.309 ppm methoxychlor into the North Saskatchewan River at Cecil Ferry (Fig. 1) on May 23. The injection period at Cecil Ferry lasted from 2:37 to 2:52 p.m. The injected mass of water passed the Cecil Rapids site about 4:40 to 5:15 p.m., as indicated by the solvent odor and by drogues that

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had been released at the Cecil Ferry site at the leading and trailing edges of the treated mass of water. The treated water is assumed to have passed the Lacolle Falls site during the night of May 23-24. Figure 1 shows all three sites where samples were collected for analyses of residues. Also on May 23, 0.186 ppm methoxychlor was injected for 15 minutes into the South Saskatchewan River from Birch Hills Ferry. Total injected amounts of technical methoxychlor were 65.0 and 32.7 kg, respectively.

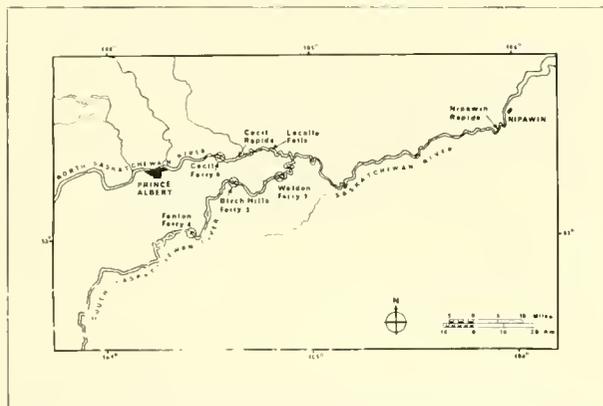


FIGURE 1. North and South Saskatchewan Rivers, central Saskatchewan, showing injection sites and numbers of methoxychlor black fly larvicide injections, 1968-72

Prior to May 23, 1972, methoxychlor had last been injected into the river May 21 and June 4, 1971, when two 15-minute injections of 0.143 and 0.301 ppm were made from the Birch Hills Ferry and two 15-minute

injections of 0.299 and 0.301 ppm were made from Cecil Ferry.

Sampling

Samples for residue analyses were collected only from the North Saskatchewan River, either from the Cecil Ferry crossing, site of the methoxychlor injection; from Cecil Rapids, 6.5 km downstream from Cecil Ferry; or from Lacolle Falls, 21-22 km downstream from Cecil Ferry (Fig. 1). Average width of the river was about 250 m. Its volume discharges were 236 m³/second on May 23, about 340 m³/second on June 1, and about 140 m³/second on September 19. The riverbed consisted of gravel and rocks interspersed with occasional beds of sand. There were numerous rapids including Lacolle Falls in this section of the river, all navigable by canoe.

Water samples were collected only at midriver sites, either the Cecil Ferry crossing or Cecil Rapids (Table 1); samples were taken before, during, and after passage of the injected water. These samples were collected by hand in Teflon-coated jars which were opened and filled beneath the water surface.

Sand was collected beneath about 60 cm flowing water several meters from both river margins near Lacolle Falls. A hand shovel with 5-cm sides was guided along the riverbed to collect only the uppermost layer of sand to a depth of 0.5 cm. Mussels ranging from about 0.2 to 0.6 cm in diameter were washed out of sand collected from under 30-60 cm water along the north side of the North Saskatchewan River at

TABLE 1. Methoxychlor residues in samples of water and sand collected from North Saskatchewan River, May-June—1972

DATE COLLECTED	LOCATION	MATERIAL COLLECTED	METHOXYCHLOR CONTENT, PPM
RIVER WATER			
May 20: 2 samples	Cecil Ferry	Whole water	ND
		Suspended solids	ND
		Filtrate	ND
May 23: prior to arrival of treated water	Cecil Rapids	Whole water	ND
		Suspended solids	ND
		Filtrate	ND
May 23: 15 min after arrival of leading edge of treated water	Cecil Rapids	Whole water	0.160
		Suspended solids	892.0
		Filtrate	0.085
May 23: 30 min after arrival of leading edge of treated water	Cecil Rapids	Whole water	0.140
		Suspended solids	437.0
		Filtrate	0.084
May 30	Cecil Rapids	Whole water	ND
		Suspended solids	ND
		Filtrate	ND
June 1	Cecil Rapids	Whole water	ND
		Suspended solids	ND
		Filtrate	ND
SAND			
May 16	Lacolle Falls, N. side	NA	ND
May 16	Lacolle Falls, S. side	NA	ND
June 1	Lacolle Falls, N. side	NA	0.10
June 1	Lacolle Falls, S. side	NA	0.05

NOTE: ND = not detected (<0.01 ppm methoxychlor).
NA = not applicable.

Lacolle Falls. Odonata larvae about 1.5 cm long were also extracted from the sand along with the mussels. Trichoptera larvae about 1.0 cm long were collected from submerged rocks at midriver sites near Lacolle Falls. About 100 small mussels, 100 Odonata larvae, and 30 Trichoptera larvae were collected on each sampling date. Black fly larvae were not available for this study. A nylon net with mesh openings of less than 0.1 mm was used to collect insects drifting in water at Cecil Rapids before and during passage of methoxychlor-injected water. A seine was used to collect fish at Lacolle Falls on May 16 but overnight gill net sets were used on May 17 and 31, June 1, and September 19.

All samples of sand, mussels, insect larvae, and fish were wrapped immediately in aluminum foil and frozen in solid CO₂. They were stored at -18° C until analysis.

Analytical Procedures

All solvents were pesticide analysis grade and were redistilled in glass. Water samples were analyzed within 24 hours of collection. Two-liter aliquots of thoroughly mixed water samples were filtered under suction to remove suspended solids. The filtrate was extracted with 200 ml hexane three times. The combined hexane extract was dried over anhydrous sodium sulfate, concentrated to a suitable volume, and analyzed by electron-capture/gas-liquid chromatography (EC/GLC).

Suspended solids were collected on filter paper, air dried, and weighed. Samples weighing about 0.2 g each were extracted by shaking for 1 hour with 25 ml 4:1 hexane:acetone mixture and filtered. Residues were reextracted twice with the same amounts of solvent mixture. The combined extract was dried over anhydrous sodium sulfate and concentrated to about 10 ml. The concentrated extract was chromatographed on a 20-g florisil column containing 3 percent water and eluted with 200 ml 6 percent diethyl ether in petroleum ether, followed by 200 ml 16 percent diethyl ether in petroleum ether. Combined eluents were concentrated to a suitable volume and analyzed by GLC.

All fish specimens were filleted and only edible muscle tissues without any skin were analyzed for pesticide residues. Fish specimens of the same species and similar sizes were first analyzed as composite samples. For this purpose 4- or 5-g muscels from 4 or 5 fish were pooled into 20-g samples; pesticide residue levels were determined by the method described previously by Fredeen et al. (1). If any pooled samples showed residues of methoxychlor, all fish specimens representing the composite were then analyzed separately by the same method.

Mussels, drift net collections, and insect larvae samples were also analyzed by Fredeen's method although they

were extracted with 5 ml acetonitrile for each gram of sample.

Riverbottom material which consisted mostly of sand was partly air-dried and thoroughly mixed. Twenty-g aliquot samples were extracted with 1:1 hexane:acetone by the method described earlier by Saha (3). Extracts were cleaned and analyzed as described by Fredeen et al. (1).

GAS CHROMATOGRAPHY

An Aerograph Hi-Fy gas chromatograph, Model 600D, was used for quantitative analysis. Operating conditions were:

Column:	Aluminum, 5 ft by 1/8 in. ID, packed with 4 percent SE-30 and 6 percent QF-1 on 80-100 mesh chromosorb W.
Detectors:	Electron-capture, with tritium ionizing source.
Temperatures:	Column 185° C. Injector 200° C. Detector 200° C.
Carrier gas:	Oxygen-free nitrogen.
Flow rate:	40 ml/min
Electrometer:	Range 1 Sensitivity 4

Under these conditions retention time for aldrin was 3.0 minutes. Retention times for other organochlorine insecticides relative to aldrin were: heptachlor, 0.94; heptachlor epoxide, 1.81; *p,p'*-DDE, 2.47; dieldrin, 2.81; *p,p'*-DDD, 3.25; *p,p'*-DDT, 3.78; and *p,p'*-methoxychlor, 7.25.

All samples were analyzed for the above-mentioned organochlorine insecticides. Percent recoveries obtained when these chemicals were added at 0.10 and 0.25 ppm to 20-g samples of fish, extracted, and analyzed as above were: heptachlor, 78-92 percent; aldrin, 68-82 percent; heptachlor epoxide, 87-101 percent; *p,p'*-DDE, 68-85 percent; dieldrin, 84-102 percent; *p,p'*-DDD, 71-87 percent; *p,p'*-DDT, 86-98 percent; and *p,p'*-methoxychlor, 86-108 percent. The lower limit of detection was 0.01 ppm. Data reported below are not corrected for percent recovery. Any sample showing more than 0.1 ppm of any of the above organochlorine insecticides was also analyzed by thin-layer chromatography (TLC) according to the method of Kovacs (4).

GAS CHROMATOGRAPHY/MASS SPECTROMETRY

Presence of methoxychlor in excess of 0.2 ppm in gold-eyes was confirmed by gas-liquid chromatography/mass spectrometry (GLC/MS). A Finnigan Model 3000 quadrupole mass spectrometer, connected to a Varian Aerograph Model 1400 gas chromatograph by means of an all-glass single-stage jet separator, was used. A 5-ft-by-1/8-in.-ID glass column packed with 3 percent OV-1 on 60- to 80-mesh Gas Chrom Q was used for GLC separation. Column temperature was 210° C and helium flow rate was 15 ml/min. Mass spectra were recorded at 70 eV electron energy and sweep time of 10 seconds. Mass spectrum could be obtained when

2.5 µg reference methoxychlor was injected into the gas chromatograph.

About 100 g fish containing more than 0.2 ppm methoxychlor as shown by gas chromatographic analysis was extracted and cleaned by the method described above. Cleanup extract was concentrated to about 100 µl, and 5- to 25-µl samples were injected into the GLC/MS system. Recorded spectra were compared with those of reference methoxychlor. Presence of methoxychlor in water was also confirmed by GLC/MS.

Results and Discussion

RESIDUES IN RIVER WATER

Methoxychlor was detected only in river water collected directly from treated water that passed the sampling point in Cecil Rapids (Table 1). No residues were detected in water collected either before or 1 week after the passage of the injected water.

The leading edge of the treated water, indicated by drogues and the odor of the concentrate, required 2 hours to travel from the injection point to Cecil Rapids. Water collected at Cecil Rapids 15 minutes after arrival of the leading edge contained 0.16 ppm methoxychlor; water collected another 15 minutes later contained 0.14 ppm. The injected water thus required at least 30 minutes to pass this site, indicating a doubling of its volume during its travel 6.5 km downstream from the point of injection. At the same time methoxychlor concentration was reduced by 50 percent from 0.309 to 0.14-0.16 ppm. This indicates that the treated mass of water became progressively more diluted, simultaneously expanding in volume as it moved downstream to the point where sand and faunal samples were collected.

The two water samples collected from Cecil Rapids 15 and 30 minutes after arrival of the leading edge contained about 85 and 125 ppm suspended solids, respectively. More than half the suspended solids consisted of very fine sand with particle diameters of 0.05-0.1 mm. The remainder consisted of silt and clay particles and a small proportion of organic material. Suspended solids in these two water samples contained 892 and 437 ppm methoxychlor, respectively; filtrates contained 0.085 and 0.084 ppm, respectively. Thus the suspended solids contained about 47 and 40 percent, respectively, of the total methoxychlor extracted from the two water samples.

Merna et al. (5) noted that when methoxychlor was added to lake water containing plankton, most of the compound eventually became associated with the particulate fraction. Fredeen et al. (6) showed that suspended solids filtered from the South Saskatchewan River 68 miles downstream from the application point of DDT black fly larvicide contained 0.24 to 2.26 ppm

DDT. The DDT absorbed onto these suspended particles was believed able to act as a selective poison against filter-feeding insect larvae, including *Simulium arcticum*, the target species. Because methoxychlor is also readily adsorbed onto suspended particles, it could also be more toxic to filter-feeding insect larvae in the Saskatchewan River than to nonfilter feeders. Methoxychlor applied to the river did prove much more destructive to *Simulium* larvae than to Trichoptera larvae. However, nonfilter feeders such as Plecoptera larvae were also severely affected (2).

RESIDUES IN SAND

Nine days after methoxychlor injection, sand and silt collected from the riverbed 21-22 km downstream from the point of injection also contained methoxychlor (Table 1). Sand from the north side of the river contained 0.1 ppm methoxychlor; sand from the south side contained 0.05 ppm. The difference in concentrations may have been caused by differences in sampling depths or by the varied proportions of sand and silt deposited on each side. Unfortunately no information is available on these characteristics. No residues were detected in samples collected before the May 23 injection. The limited number of samples did not enable authors to calculate the rate of methoxychlor loss from the injected water. The fact that no methoxychlor was detected in any pretreatment samples proves that residues did not persist from treatments in 1971 or earlier.

RESIDUES IN MUSSELS

No methoxychlor residues were detected in mussels collected from riverbed sand 21-22 km downstream from the point of injection (Table 2). In 1968 Bedford et al. (7) showed that two species of freshwater mussels in the Red Cedar River in Michigan contained DDT and its metabolites, plus aldrin and methoxychlor. Concentrations of methoxychlor in these mussels range from nondetectable to 0.22 ppm. At the time of their study in the mid 1960s, methoxychlor, DDT, and malathion were used annually in the vicinity of the Red Cedar River to control elm bark beetles and mosquitoes. Thus it is presumed that mussels in the Red Cedar River were continuously exposed to these chemicals for long periods of time. Mussels collected from the river had been exposed to about 0.15 ppm methoxychlor in the water for only an hour or so; they were exposed to about 0.1 ppm in sand for about 8 days. Kapoor et al. (8) showed that in an aquarium ecosystem, snails exposed to methoxychlor for about 13 days accumulated relatively large amounts of the compound, whereas the methoxychlor content of fish remained in dynamic equilibrium with levels in their environment.

RESIDUES IN INSECT LARVAE

No methoxychlor residues were detected in the larvae of Odonata or Trichoptera collected alive from the riverbed either 6-7 days before or 8-9 days after treatment

of the river with methoxychlor on May 23, 1972 (Table 2). However, larvae of these and other families of aquatic insects, including Plecoptera, Ephemeroptera, and Diptera, that were disabled by methoxychlor and collected with a net during the actual passage of injected water, contained an average of 17.5 ppm methoxychlor. Presumably fish that ate insects disabled or killed by such a treatment would be exposed to relatively high concentrations.

RESIDUES IN PRETREATMENT FISH

No methoxychlor was found in any pretreatment fish except goldeye (Table 3), although other chlorinated hydrocarbons were detected. DDT and related compounds were detected in 60 percent of the goldeye and 64 percent of the suckers; heptachlor and heptachlor epoxide were detected in 60 percent of the goldeye. Levels of these chemicals indicated by GLC were less than 0.1 ppm, too low to be confirmed by TLC. No residues of chlorinated hydrocarbons were detected in pickerel, sauger, or northern pike.

RESIDUES IN POSTTREATMENT FISH

Methoxychlor was detected in the muscle tissues of 66 percent of the goldeye collected 8-9 days after the 15-minute injection of 0.309 ppm methoxychlor about 21-22 km upstream from the fish-collecting site. In 37 percent of the goldeye, methoxychlor concentrations in muscle tissues ranged from 0.02 to 0.20 ppm; in 21 percent, concentrations ranged from 0.21 to 0.99 ppm; in 8 percent of this species, they ranged from 1.0 to 1.5 ppm; and in 34 percent, there were no detectable residues. Presence of methoxychlor could be confirmed in 47 percent of the goldeye by TLC, and in 21 percent by mass spectrometry. Mass spectra in these samples were the same as those of the reference methoxychlor. No methoxychlor was detected in any other species of fish collected 8-9 days after treatment.

As in pretreatment samples, other chlorinated hydrocarbons were also detected in these fish. Residues were less than 0.1 ppm except in the goldeye where levels of up to 0.16 ppm aldrin and dieldrin and up to 0.51 ppm DDT and related compounds were detected.

TABLE 2. *Methoxychlor residues in clams and insect larvae collected from North Saskatchewan River, May-June—1972*

DATE COLLECTED	LOCATION	SPECIMEN	METHOXYCHLOR CONTENT, PPM
May 16	Lacolle Falls, N. side	About 100 small mussels	ND
May 17	Lacolle Falls, N. side	About 100 small mussels	ND
May 31	Lacolle Falls, N. side	About 100 small mussels	ND
May 16	Lacolle Falls, N. side	About 100 Odonata larvae	ND
May 17	Lacolle Falls, N. side	About 100 Odonata larvae	ND
May 31	Lacolle Falls, N. side	About 100 Odonata larvae	ND
June 1	Lacolle Falls, N. side	About 30 Trichoptera larvae	ND
June 1	Lacolle Falls, S. side	About 30 Trichoptera larvae	ND
May 23: before treatment	Cecil Rapids, midriver	About 50 insect larvae	ND
May 23: during treatment	Cecil Rapids, midriver	About 1,000 disabled insect larvae	17.5

NOTE: ND = not detected (<0.01 ppm methoxychlor).

TABLE 3. *Residues of chlorinated hydrocarbon insecticides in muscle tissues of fish collected from North Saskatchewan River before and after methoxychlor injection, May 1972*

COMMON NAME	NO. FISH ANALYZED	HEPTACHLOR AND HEPTACHLOR EPOXIDE		ALDRIN AND DIELDRIN		DDT, DDE, AND DDD		METHOXYCHLOR	
		PERCENT OF POSITIVE SAMPLES	RANGE, PPM	PERCENT OF POSITIVE SAMPLES	RANGE, PPM	PERCENT OF POSITIVE SAMPLES	RANGE, PPM	PERCENT OF POSITIVE SAMPLES	RANGE, PPM
May 16 and 17, 1972									
Goldeye	25	60	0.02-0.05	40	0.01-0.08	60	0.01-0.04	0	ND
Sucker	14	0	ND	0	ND	64	0.01-0.04	0	ND
Pickrel and Sauger	12	0	ND	0	ND	0	ND	0	ND
Northern Pike	8	0	ND	0	ND	0	ND	0	ND
May 31 and June 1, 1972									
Goldeye	38	39	0.01-0.05	29	0.01-0.16	39	0.03-0.51	66	0.02-1.5
Sucker	3	0	ND	66	0.02-0.03	33	0.03	0	ND
Pickrel and Sauger	7	100	0.02	14	0.01	0	ND	0	ND
Northern Pike	19	26	0.02	0	ND	47	0.01	0	ND
September 19, 1972									
Goldeye	6	0	ND	0	ND	0	ND	0	ND
Sucker	9	0	ND	0	ND	0	ND	0	ND
Pickrel and Sauger	6	0	ND	0	ND	0	ND	0	ND
Northern Pike	2	0	ND	0	ND	0	ND	0	ND

NOTE: ND = not detected (<0.01 ppm).

RESIDUES IN FISH: 17 WEEKS POSTTREATMENT

Methoxychlor could not be detected in the muscle tissues of any species of fish including goldeye collected from this same site September 19, 1972.

RESIDUES IN FISH: GENERAL CONSIDERATIONS

Considering their similar trophic levels, it was surprising that goldeye and other fish species had such disparate residues of methoxychlor 8-9 days after injection. The authors had expected relatively low concentrations of residues in goldeye, which graze mainly on insect colonies attached to rock surfaces, and relatively high concentrations in fish-feeding species such as pickerel, sauger, and northern pike, and in suckers, which are bottom-feeders and could have engorged on masses of immobilized larvae.

The relatively higher concentrations of methoxychlor and other chlorinated hydrocarbons in goldeye muscle tissues may be explained by the relatively high oil content of their muscle tissues. Schmidt (9) reported that muscle tissue of one sample of six goldeye contained 6.57 percent fat; three samples of pickerel including 18 fish contained 2.84-3.34 percent fat; three samples of suckers including 18 fish contained 3.01-3.68 percent fat; and two samples of pike including 11 fish contained 1.40-1.86 percent fat.

Let us assume that methoxychlor extracted from muscle tissues of goldeye fish in this study originated only from the fat fraction, and that these muscle tissues contained 6.57 percent fat. Then, in 37 percent of the goldeyes, methoxychlor concentrations in fat fractions could have ranged from 0.3 to 3.0 ppm; in 21 percent, from 3.2 to 15.0 ppm; in 8 percent, from 15.2 to 22.7 ppm; and in 34 percent, concentrations would be less than 0.3 ppm. These levels do not demand government action, both because of the residues' ephemeral nature, presumably due to brief exposure in the river and rapid elimination from the fish, and because fish fat, unlike the fat of livestock, is not used separately as a food item for humans. In the case of livestock fat, concentrations of methoxychlor above 3 ppm rate government intervention.

Conclusions

Results indicate that a single 15-minute injection of 0.309 ppm methoxychlor into the Saskatchewan River contaminated water and biota for a short time at least as far as 22 km downstream. However, no detectable residues of methoxychlor remained from similar treatments of previous years.

Like other organochlorine insecticides, notably DDT, methoxychlor was readily adsorbed onto suspended particles in water resulting in very high residue concentrations.

No residues were detected in insect larvae or mussels that inhabited the riverbed. Of all fish species examined here, only goldeye showed tendencies to accumulate methoxychlor. Concentrations which did accumulate in the edible flesh of about 80 percent of the goldeye were smaller than the concentration injected into the water 8-9 days earlier. The absence of methoxychlor residues in other species of fish may have been related to the relatively low oil content of their muscle tissues, as well as their ability to rapidly eliminate it from their systems as indicated by Kapoor et al. for *Gambusia affinis* fish (8). No methoxychlor residues were detected in goldeye or other fish 17 weeks after the experimental treatment.

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LITERATURE CITED

- (1) Fredeen, F. J. H., J. G. Saha, and L. M. Royer. 1971. Residues of DDT, DDE and DDD in fish in the Saskatchewan River after using DDT as a blackfly larvicide for twenty years. *J. Fish. Res. Bd. Can.* 28(1): 105-109.
- (2) Fredeen, F. J. H. 1974. Tests with single injections of methoxychlor black fly (*Diptera: Simuliidae*) larvicides in large rivers. *Can. Entomol.* 106(3):285-305.
- (3) Saha, J. G. 1971. Comparison of several methods for extracting chlordanes residues from soil. *J. Ass. Offic. Anal. Chem.* 54(1):170-174.
- (4) Kovacs, M. F., Jr. 1963. Thin-layer chromatography for chlorinated pesticide residue analysis. *J. Ass. Offic. Anal. Chem.* 46(5):884-893.
- (5) Merna, J. W., M. E. Bender, and J. R. Novy. 1972. The effects of methoxychlor on fishes. I. Acute toxicity and breakdown studies. *Trans. Amer. Fish. Soc.* 101(2): 298-301.
- (6) Fredeen, F. J. H., A. P. Arnason, and B. Berck. 1953. Adsorption of DDT on suspended solids in river water and its role in blackfly control. *Nature (London)* 171: 700.
- (7) Bedford, J. W., E. W. Roelofs, and M. J. Zabik. 1968. The freshwater mussel as a biological monitor of pesticide concentrations in a lotic environment. *Limnol. Oceanogr.* 13(1):118-126.
- (8) Kapoor, I. P., R. L. Metcalf, R. F. Nystrom, and G. K. Sangha. 1970. Comparative metabolism of methoxychlor, methiochlor and DDT in mouse, insects, and in a model ecosystem. *J. Agr. Food Chem.* 18(6):1145-1152.
- (9) Schmidt, P. J. 1948, 1949. Analyses of freshwater fishes from Canadian interior provinces. *Industr. Memo. F.R.B. Canada No. 9 and 12. Pacific Fish. Exp. St. Vancouver. Mimeo. 15 pp.*

Organochlorine Residues in Starlings, 1972

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ABSTRACT

During the fall of 1972 starlings were collected from 130 sites in conjunction with the National Pesticide Monitoring Program. They were analyzed for DDT and its metabolites, dieldrin, heptachlor epoxide, benzene hexachloride, polychlorinated biphenyls and, for the first time in the series, oxychlorane and HCB. Mean DDT and dieldrin residue levels have declined significantly since 1967 and a regression analysis suggests that levels of DDT and its metabolites should fall below a mean of 0.1 ppm for the 1974 starling collection.

Introduction

As part of the National Pesticide Monitoring Program, a nationwide sample of starlings is collected and analyzed biennially to help measure environmental levels of persistent organochlorine compounds. Data for residues of these contaminants were first derived from analyses of three collections taken in 1967 and 1968 and reported by Martin in 1969 (1). The rationale for selecting starlings as a subject species appeared in that pilot study: they are a terrestrial avian species found year-round throughout most of the contiguous United States; they are generally regarded as expendable; and their omnivorous feeding habits can be expected to reflect pesticide intake from insects, fruits, grain, and miscellaneous other foods. Collections from fall 1970 were reported by Martin and Nickerson in 1972 (2). The present paper presents data from the fall 1972 collection and compares portions of the data to those

obtained in previous collections. Using these data, authors can examine some trends with greater confidence than in past studies and make tentative estimates for residue levels of DDT and dieldrin in future collections. Focus of the estimates will be national rather than regional, leaving the problem of substantial geographical variation for the future.

Sampling

As described in previous publications, the sampled area is composed of 40 blocks of 5° latitude and longitude, ranging from 24° to 49° latitude and 64° to 124° longitude (1,2). One to four starling sampling sites were randomly selected from each block. The same sites have been used for all collections. Figure 1 shows the location of all sampling sites and Table 1 lists locations successfully sampled during the November-December 1972 collection. Each sample location is identified by a row number, a column letter, and a site number: e.g., the site near Tacoma, Wash., is designated 1-A-1. In 1972, collections were made at 130 (94 percent) of 139 sampling locations.

In previous years, Texas, a State of high pesticide use, posed a major problem. Thus collection efforts were intensified in 1972 and collections were successful in five of the nine preselected sites. Hopefully sampling in Texas will be improved further by extending the collection period into January when the starlings are in larger flocks.

Most starling samples consisted of a pool of 10 birds which had been trapped or shot. Each pool was wrapped in aluminum foil, placed in polyethylene bags, and frozen for shipment to the laboratory.

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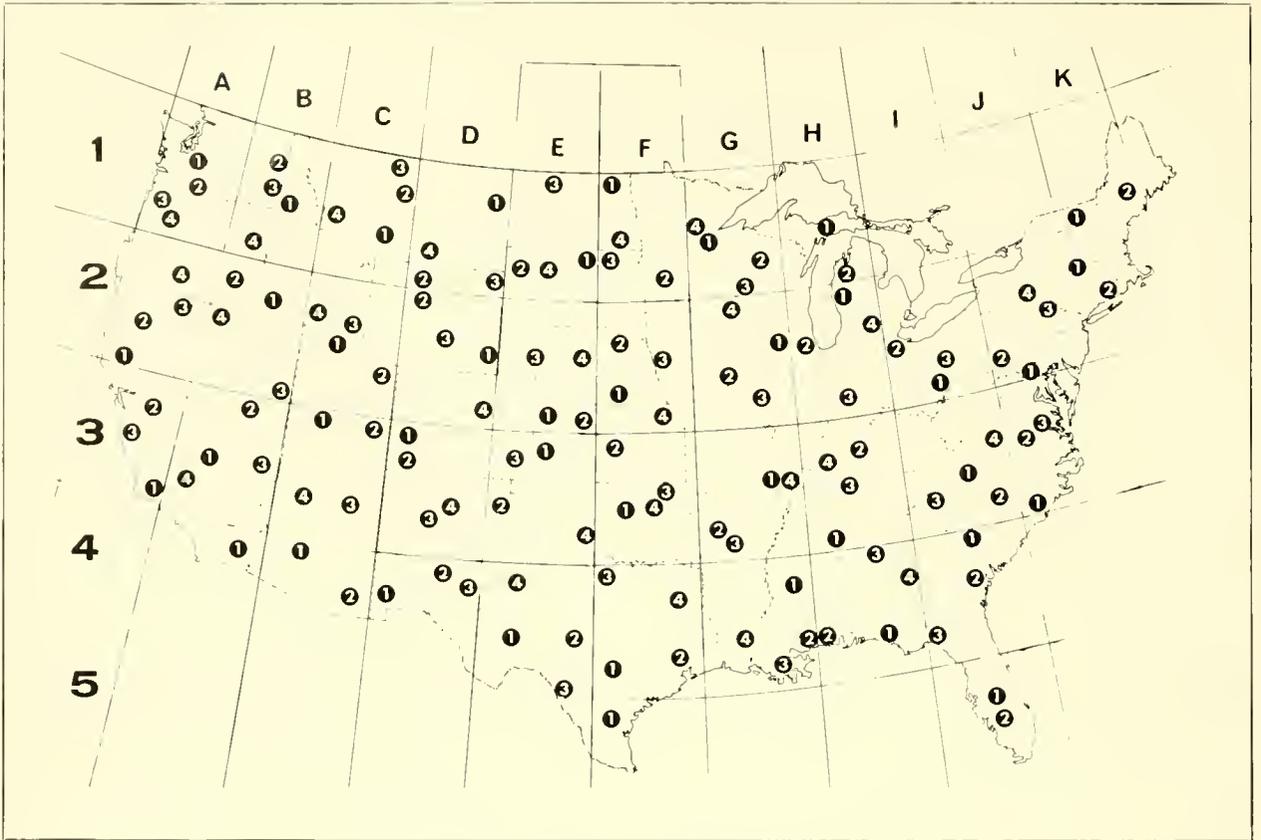


FIGURE 1. Starling monitoring sites, 1972

Analytical Methods

Residue analyses were performed as described previously (1,2) by WARF Institute, Inc., under contract with the U.S. Department of Interior—Bureau of Sport Fisheries and Wildlife (predecessor of the Fish and Wildlife Service). Technicians prepared the birds by removing their beaks and feet, then skinning their bodies. Each pool was ground in a Hobart food chopper until homogenized. The only major change in methodology involved use of 11 percent OV-17 + QF-1 (mixed phase) on 80/100 Gas-Chrom Q in the second column. Flow rate involved a retention time of 4-5 minutes for heptachlor epoxide. This new procedure separated oxychlorane from heptachlor epoxide, and HCB from BHC.

For the determination of DDE, DDD, DDT, dieldrin, and polychlorinated biphenyls (PCB's), instrument conditions were:

Temperatures: Column 200° C.
 Injector 230° C.
 Detector 240° C.

Column: 4-ft-by-4-mm glass packed with 5 percent DC-200 on 80/100 Gas-Chrom Q.

Carrier Gas: Nitrogen.

Flow: Involved retention time of 6-8 minutes for *p,p'*-DDT.

For the determination of HCB, alpha BHC, gamma BHC (lindane), beta BHC, heptachlor epoxide, and oxychlorane, instrument conditions were:

Temperatures: Column 180° C.
 Injector 220° C.
 Detector 235° C.

Column: 4-ft-by-4-mm 11 percent OV-17 + QF-1 (mixed phase) on 80/100 Gas-Chrom Q (available from Applied Science Cat. No. 12970).

Carrier Gas: Nitrogen.

Flow: Involved retention time of 4-5 minutes for heptachlor epoxide.

Recovery rates for DDE, DDD, DDT, PCB's, dieldrin, and BHC ranged from 78 to 97 percent. Residue data were not corrected for recovery. Recovery and confirmatory tests were performed internally by the commercial laboratory on a quality control basis. Limits of detection ranged from 0.005 to 0.1 ppm.

TABLE 1. *Starling sampling sites listed by State and county, 1972*

STATE	COUNTY	SITE NUMBER	STATE	COUNTY	SITE NUMBER
Alabama	Marion	3-H-1	Nebraska	Keith	2-E-3
	Talladega	4-H-3		Brown	2-E-4
Arizona	Navajo	3-C-3		Lancaster	2-F-1
	Yavapai	3-C-4		Clay	2-F-2
	Maricopa	4-C-1	Nevada	White Pine	2-B-3
	Graham	4-C-2		Humboldt	2-B-4
Arkansas	Yell/Pope	3-G-2		Nye	3-B-2
	Louoke/Pulaski	3-G-3		Clark	3-B-3
California	Colusa	2-A-1	New Mexico	Bernalillo	3-D-3
	Shasta	2-A-2		Torrance	3-D-4
	Modoc	2-A-3		Luna	4-D-1
	Ventura	3-A-1		Otero	4-D-2
	Stanislaus	3-A-2		Chaves	4-D-3
	Monterey	3-A-3		Quay	3-E-2
	Inyo	3-B-1	New York	Jefferson	2-J-4
	Kern	3-B-4		Rensselaer	2-K-1
	Imperial	4-B-1	North Carolina	Wilkes	3-I-1
Colorado	Weld	2-D-4		Union	3-I-2
	Montrose	3-D-1		Macon	3-I-3
	Crowley	3-D-2		Pender	3-J-1
Connecticut	New London	2-D-2	North Dakota	McLean	1-E-3
Florida	Bay	4-H-1		Grand Forks	1-F-1
	Madison	4-I-3		Ransom	1-F-4
	Polk	5-I-1	Ohio	Pickaway	2-I-1
	Hardee	5-I-2		Wood	2-I-2
Georgia	Pike	4-H-4		Noble	2-I-3
	Wayne	4-I-2	Oklahoma	Greer	3-E-4
Idaho	Nez Perce	1-B-1		Canadian	3-F-1
	Owyhee	2-B-1		Nowata	3-F-3
	Franklin	2-C-3		Okmuigee	3-F-4
	Minidoka	2-C-4	Oregon	Yamhill	1-A-3
Illinois	Stephenson	2-G-1		Lane	1-A-4
	Adams	2-G-3		Klamath	2-A-4
	Kane	2-H-2		Baker	1-B-4
Indiana	Hendricks	2-H-3		Harney	2-B-2
Iowa	Fremont	2-F-3	Pennsylvania	Somerset	2-J-2
	Jasper	2-G-2		Luzerne	2-J-3
	Marshall	2-G-4	South Carolina	Aiken	4-I-1
Kansas	Rawlins	2-E-1	South Dakota	Potter	1-E-1
	Phillips	2-E-2		Butte	1-E-2
	Kearny	3-E-1		Hughes	1-E-4
	Nemaha	2-F-4		Brown	1-F-3
	Marion	3-F-2	Tennessee	Davidson	3-H-3
Kentucky	Ohio	3-H-2	Texas	Kinney	4-E-3
	Hopkins	3-H-4		Cochran	4-E-4
Louisiana	Jefferson	4-G-3		Comal	4-F-1
	Rapides	4-G-4		Clay	4-F-3
Maine	Penobscot	1-K-2		San Patricio	5-F-1
Maryland	Prince Georges	2-J-1	Utah	Weber	2-C-1
Michigan	Chippewa	1-H-1		Duchesne	2-C-2
	Grand Traverse	1-H-2		Sevier/Millard	3-C-1
	Kent	2-H-1		Grand	3-C-2
	Ingham	2-H-4	Vermont	Addison	1-K-1
Minnesota	Aitkin	1-G-4	Virginia	Amherst	3-I-4
Mississippi	Leake	4-G-1		Prince George	3-J-2
	Harrison	4-G-2		Caroline	3-J-3
	Jackson	4-H-2	Washington	Pierce	1-A-1
Missouri	Butler	3-G-1		Yakima	1-A-2
	Bollinger	3-G-4		Spokane	1-B-2
Montana	Meagher	1-C-1		Whitman	1-B-3
	Blaine	1-C-2	Wisconsin	Clark	1-G-2
	Missoula	1-C-4		Trempealeau	1-G-3
	Richland	1-D-1	Wyoming	Big Horn	1-D-2
	Yellowstone	1-D-4		Crook	1-D-3
				Goshen	2-D-1
				Washakie	2-D-2

Statistical Procedures

National averages for DDT with its metabolites and dieldrin from all five collections were calculated by two methods (Table 2). The geometric mean provides an appropriate measure of central tendency and should approximate the median value in these skewed distributions (see reference 2, Table 4). The arithmetic means average 2.2 times higher than the geometric means for DDT and metabolites, and 2.7 times higher for dieldrin. The arithmetic mean is a better measure of environmental load and is the appropriate value to use in determining, for example, how much pesticide a Cooper's hawk would be likely to ingest if it ate 100 starlings. The estimate cannot be precise because of the low probability of encountering starlings with unusually high concentrations of pesticides (Tables 3,4). In calculating the means, values given as <0.015-<0.010 ppm in the

pilot study of this series (1) were assigned values of 0.005 ppm. For 1972, trace was called 0.002 ppm.

The confidence intervals around the geometric means reflect the nationwide variability in residue levels and are not the most sensitive indicators of differences between the annual means. Residue values of DDT and its metabolites from each station were compared with those of dieldrin for the periods summer-winter 1967-68 versus fall 1968, fall 1968 versus fall 1970, and fall 1970 versus fall 1972. Statistically significant correlation coefficients ranged from 0.59 to 0.70 for DDT and from 0.26 to 0.56 for dieldrin, indicating that a sign test (3) for paired values is an appropriate measure of temporal differences, even though the residual variance is high.

Having established that certain differences between years were statistically significant, regression analysis

TABLE 2. Geometric and arithmetic means of DDT and dieldrin residues in starlings, 1972

COLLECTING PERIOD	No. STATIONS SAMPLED	LIPIDS, % WET WEIGHT	DDT & METABOLITES, PPB WET WEIGHT	DIELDRIN, PPB WET WEIGHT
Summer 1967	116	3.20 (3.01-3.41)	679 (536-861) AM 1755	27 (21-34) AM 82
Winter 1967-68	122	7.42 (6.99-7.87)	830 (670-1028) AM 2019	99 (74-134) AM 240
Fall 1968	122	5.84 (5.47-6.23)	569 (473-685) AM 1135	40 (32-49) AM 84
Fall 1970	125	5.40 (5.00-5.82)	445 (366-539) AM 916	36 (29-46) AM 117
Fall 1972	130	6.24 (5.89-6.61)	442 (420-464) AM 847	35 (28-45) AM 98

NOTE: Values in parentheses represent 95 percent confidence intervals for geometric mean.
AM = Arithmetic mean.

TABLE 3. Sites with residue levels of DDT and its metabolites greater than 3.0 ppm in baseline, 1970, or 1972 collections

SITE NUMBER	DDT RESIDUES, PPM		
	BASELINE DATA, 1967-68	1970	1972
3-A-1	1.903	3.660	1.930
3-B-4	4.376	2.837	2.330
2-C-2	9.551	NS	0.640
3-C-2	3.163	NS	0.610
4-C-1	23.902	14.874	0.140
4-D-1	1.930	4.780	1.100
4-D-3	19.680	1.479	3.550
2-E-1	0.199	0.202	4.130
3-E-4	4.948	5.318	0.330
3-G-3	5.950	5.313	8.040
4-G-1	8.128	3.413	4.950
4-G-2	1.580	4.801	0.710
4-G-4	4.220	1.210	11.800
4-H-3	2.347	3.060	3.290
4-H-4	3.510	2.546	0.880
4-I-1	5.483	3.026	5.080
4-I-3	5.668	3.872	1.680

NOTE: NS = No sample collected.

TABLE 4. Sites with residue levels of dieldrin greater than 0.3 ppm in baseline, 1970, and/or 1972 collections

SITE NUMBER	DIELDRIN RESIDUES, PPM		
	BASELINE DATA, 1967-68	1970	1972
1-A-3	0.528	0.160	0.160
1-A-4	0.492	0.140	0.130
1-B-1	0.115	0.050	1.560
1-B-2	0.237	0.280	0.710
1-B-3	0.587	0.600	0.037
1-B-4	0.418	0.018	0.009
3-E-1	0.102	0.420	0.041
2-G-1	0.280	0.590	0.090
2-G-3	0.657	3.590	0.390
2-G-4	0.032	1.520	0.310
3-G-1	0.403	0.230	0.260
3-G-3	0.317	0.067	0.110
3-G-4	0.207	0.520	0.350
4-G-2	0.970	0.067	0.011
2-H-2	0.208	0.330	0.170
2-H-3	0.056	0.260	0.340
4-H-1	0.135	0.087	0.310
2-I-2	0.193	0.230	0.730
3-I-1	1.385	0.018	0.076
4-I-2	0.027	0.750	0.022
4-I-3	0.055	0.044	1.200
3-J-1	0.333	0.160	0.530

was used to determine the relationship between residue levels and estimates of pesticide usage. The residue values for fall 1967 were estimated by converting the summer and winter values to a lipid basis and interpolating on a logarithmic scale. Mean lipid values from the three fall collections (Table 2) were then used to estimate the wet-weight residue concentrations for the missing collection.

Residue levels of organochlorine compounds from the 130 stations sampled in 1972 are presented in Table 5.

Results and Discussion

DDT AND METABOLITES

Differences between the residue levels in collections from summer 1967 and winter 1967-68 were not statistically significant (Table 2). Levels in the fall 1968 samples, however, were consistently lower than those found in the corresponding averages for the summer/winter samples, suggesting that a significant change in residue levels had occurred within what had been con-

sidered the baseline periods (1). Pesticide use preceding the four fall periods was assumed to be proportional to U.S. Department of Agriculture values for domestic disappearance (4). Residue levels and pesticide use are highly correlated (Fig. 2) and an extrapolation from the data points predicts a mean residue level well below 0.1 ppm for 1974.

Considerable caution should be exercised in projecting estimates far beyond this data base. The high correlation from only four data points could be fortuitous; authors believe use patterns to be more relevant than mere tonnage in determining exposure. Results from 1974 should provide a more reliable fix on the slope.

Sites having DDT and metabolite residues greater than 3.0 ppm in baseline, 1970, and/or 1972 are listed in Table 3. Sites containing the highest DDT and metabolic levels in 1972 (greater than 3.0 ppm) were found in southeastern New Mexico (4-D-3), northwestern Kansas (2-E-1), central Arkansas (3-G-3), central Louisiana (4-D-3), north-central Alabama (4-H-3), and South Carolina (4-I-1).

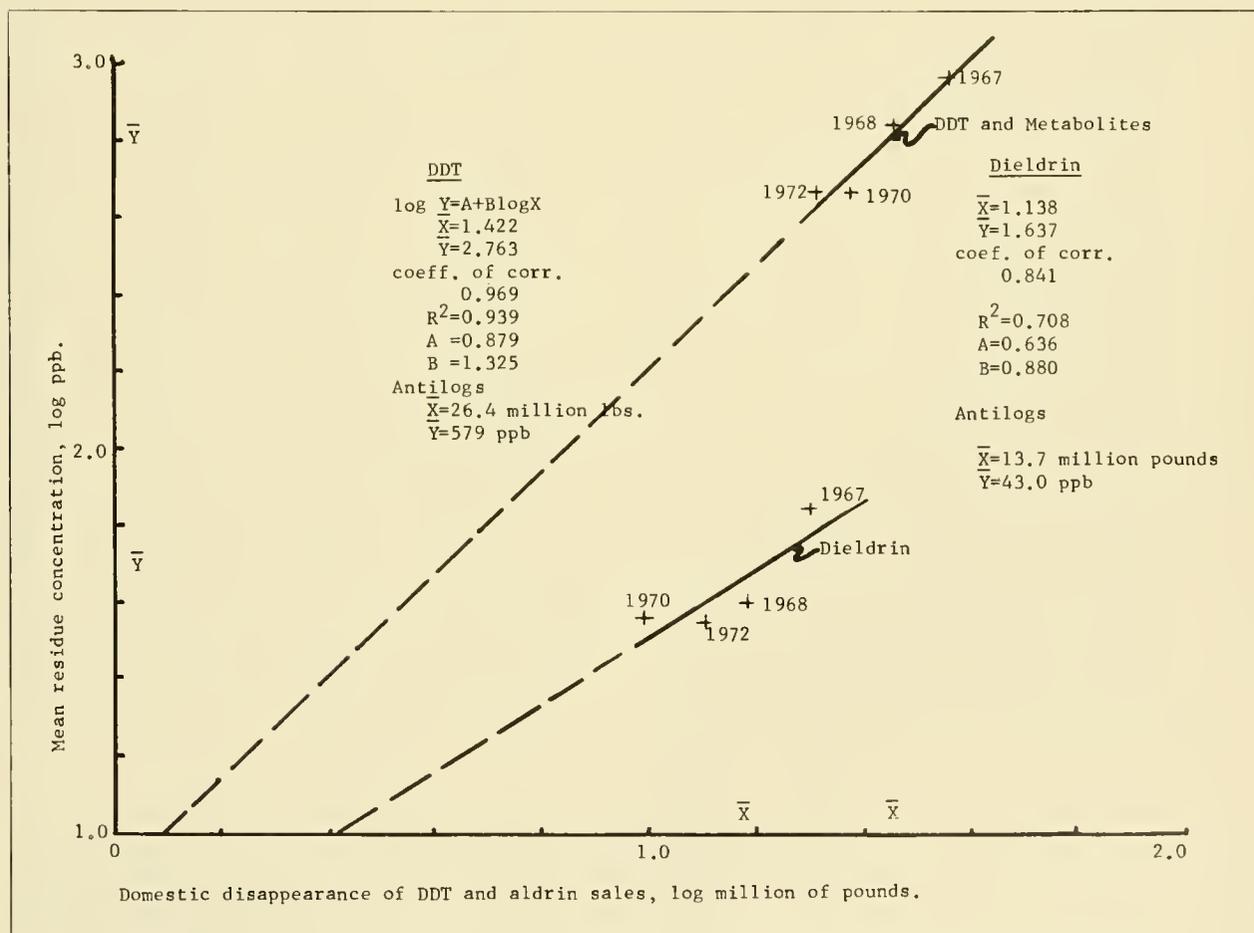


FIGURE 2. Regressions of pesticide residues in starlings on indices of pesticide use, 1967-68, 1970, 1972

TABLE 5. Organochlorine residue levels in starlings, 1972

SITE No. ¹	WET WEIGHT, G	LIPID WEIGHT, G	DDE	DDD	DDT	DDT/META-BOLITES	PCB's ²	DIELDRIN	HEPTA-CHLOR EPOXIDE	OXYCHLOR-DANE	BHC	HCB
1-A-1	20.03	1.28	0.310	0.017	0.031	0.360	0.360	0.086	0.008	0.007	0.006	0.007
1-A-2	19.97	1.50	1.390	0.006	0.011	1.410	0.063	0.140	0.026	TR	0.036	3.330
1-A-3	20.24	0.83	0.950	0.015	0.017	0.980	0.140	0.160	TR	TR	ND	0.036
1-A-4	20.00	1.19	0.780	0.017	0.019	0.820	0.160	0.130	0.006	TR	TR	0.011
2-A-1	20.16	0.53	0.470	0.008	0.010	0.490	0.074	0.021	TR	TR	0.011	0.011
2-A-2	20.08	0.85	0.630	TR	0.010	0.640	0.100	0.055	0.009	TR	TR	0.014
2-A-3	20.02	1.69	0.077	TR	0.005	0.082	0.056	0.016	TR	TR	0.007	0.011
2-A-4	20.09	1.13	0.490	0.520	0.017	1.030	0.110	0.050	0.013	TR	0.007	0.066
3-A-1	20.10	0.85	1.900	0.014	0.019	1.930	0.170	0.016	0.005	0.008	TR	0.012
3-A-2	20.10	1.06	0.940	0.022	0.053	1.010	1.400	0.037	TR	0.005	TR	TR
3-A-3	20.00	1.32	0.300	0.011	0.019	0.330	0.190	0.019	0.006	0.006	0.007	TR
1-B-1	20.02	1.89	0.660	0.028	0.021	0.710	0.120	1.560	0.009	TR	0.006	2.340
1-B-2	20.03	2.91	0.300	0.014	0.021	0.330	0.170	0.710	0.010	0.007	TR	0.590
1-B-3	20.06	0.95	0.190	TR	0.011	0.200	0.037	0.037	0.210	0.010	0.035	0.550
1-B-4	20.33	1.36	0.150	0.008	0.012	0.170	0.100	0.009	TR	TR	0.010	0.036
2-B-1	20.09	0.98	0.270	0.011	0.029	0.310	0.230	0.060	0.007	TR	0.006	0.057
2-B-2	20.15	1.27	0.170	0.008	0.017	0.200	0.120	0.019	TR	TR	0.009	0.006
2-B-3	20.04	1.96	0.650	0.006	0.014	0.670	0.250	0.046	0.025	ND	0.009	0.007
2-B-4	20.20	1.58	0.240	TR	0.006	0.250	0.099	0.019	0.011	0.006	0.006	0.009
3-B-1	20.02	0.62	2.340	0.009	0.034	2.380	0.370	0.070	0.017	0.017	0.005	0.018
3-B-2	20.29	0.91	0.180	TR	0.006	0.190	0.099	0.039	TR	0.009	0.006	0.005
3-B-3	20.05	1.56	0.620	0.047	0.160	0.830	1.870	0.270	0.053	0.031	0.009	0.037
3-B-4	20.01	1.39	2.310	TR	0.022	2.330	0.140	0.037	TR	0.006	TR	0.024
4-B-1	20.01	0.75	1.440	TR	0.017	1.460	0.190	0.026	TR	TR	TR	0.009
1-C-1	20.54	1.26	0.091	0.009	0.032	0.130	0.370	0.025	0.046	0.030	0.010	0.006
1-C-2	20.05	1.28	0.078	0.016	0.019	0.110	0.210	0.021	0.050	0.009	0.016	0.007
1-C-4	20.48	1.05	0.081	0.013	0.024	0.120	0.290	TR	0.009	ND	0.005	0.009
2-C-1	20.18	1.39	0.350	TR	0.015	0.370	0.150	0.017	0.008	0.006	0.006	TR
2-C-2 ³	20.24	1.13	0.630	TR	0.007	0.640	0.068	TR	0.008	TR	TR	TR
2-C-3	20.11	1.02	0.530	0.006	0.012	0.550	0.120	0.017	0.027	0.009	0.005	TR
2-C-4	20.14	1.66	0.970	0.006	0.012	0.990	0.087	0.028	0.021	0.007	0.006	0.006
3-C-1	20.00	1.66	0.630	TR	0.009	0.640	0.150	0.034	0.011	0.008	0.006	TR
3-C-2 ⁴	20.16	1.60	0.590	0.006	0.011	0.610	0.200	0.160	0.012	0.007	0.006	0.006
3-C-3	20.02	0.99	0.590	0.005	0.020	0.610	0.250	0.012	TR	TR	TR	TR
3-C-4	19.98	1.01	0.490	TR	0.014	0.500	0.110	0.300	0.007	0.006	0.006	TR
4-C-1	19.99	1.82	0.130	TR	0.009	0.140	0.081	0.021	0.008	TR	0.011	0.025
4-C-2	19.99	0.91	1.490	0.011	0.022	1.520	0.160	0.020	0.006	TR	0.006	TR
1-D-1	20.34	1.39	0.025	TR	TR	0.025	0.037	0.018	0.005	TR	0.006	TR
1-D-2 ⁵	20.09	1.02	0.077	TR	0.006	0.083	0.100	0.005	0.006	TR	TR	TR
1-D-3 ⁶	20.02	1.66	0.058	0.011	0.052	0.120	0.750	0.009	0.007	TR	0.006	0.005
1-D-4	20.38	1.85	0.076	TR	0.009	0.085	0.061	0.025	0.007	TR	0.005	0.007
2-D-1	19.95	1.49	0.071	0.008	0.017	0.096	0.250	0.006	0.010	ND	TR	0.005
2-D-2 ⁴	20.16	0.72	0.050	TR	0.006	0.056	0.099	0.006	0.009	ND	0.007	TR
2-D-4	20.06	1.75	0.220	TR	0.016	0.240	0.190	0.049	0.011	0.011	0.007	TR
3-D-1	20.05	0.92	0.260	TR	0.012	0.270	0.120	0.066	0.013	0.013	TR	TR
3-D-2	20.02	1.34	0.079	TR	0.009	0.088	0.094	0.007	TR	TR	0.009	TR
3-D-3	20.04	0.91	0.470	0.017	0.042	0.530	0.450	0.007	TR	TR	TR	TR
3-D-4	20.06	1.25	0.790	0.005	0.014	0.800	0.160	0.021	TR	TR	0.010	TR
4-D-1	19.99	0.85	1.090	TR	0.013	1.100	0.160	0.010	TR	TR	TR	0.005
4-D-2	19.90	0.61	0.630	TR	0.009	0.640	0.130	0.005	TR	TR	TR	TR
4-D-3	19.99	1.26	3.520	0.013	0.019	3.550	0.190	0.028	0.019	0.008	TR	0.007
1-E-1	20.01	2.00	0.120	0.009	0.022	0.150	0.120	TR	0.005	ND	TR	TR
1-E-2	20.11	1.60	0.068	0.008	0.017	0.093	0.190	0.007	0.005	ND	0.006	TR
1-E-3	20.12	0.95	0.078	0.005	0.007	0.085	0.099	0.009	0.005	TR	TR	TR
1-E-4	20.13	2.10	0.023	0.008	0.027	0.058	0.220	0.007	0.006	ND	0.009	TR
2-E-1	19.98	0.87	4.070	0.023	0.040	4.130	0.360	0.041	0.019	0.005	0.008	TR
2-E-2	20.01	1.42	0.190	0.014	0.036	0.240	0.270	0.005	0.017	0.005	0.016	0.007
2-E-3	20.16	1.26	0.110	TR	0.006	0.120	0.081	0.005	TR	0.011	0.006	TR
2-E-4	20.13	1.16	0.056	0.005	0.012	0.073	0.160	0.024	TR	TR	0.007	TR
3-E-1	20.03	1.62	0.120	TR	0.005	0.120	0.062	0.041	0.009	TR	0.007	0.009
3-E-2	20.02	0.95	0.150	0.014	0.059	0.220	0.520	0.017	0.019	TR	0.006	0.027
3-E-4	20.03	0.93	0.320	TR	0.007	0.330	0.094	0.100	0.038	0.009	0.007	0.006
4-E-3	20.14	1.23	2.060	0.006	0.013	2.080	0.200	0.048	0.011	0.007	TR	0.007
4-E-4	20.23	1.03	1.020	TR	0.006	1.030	0.074	0.043	0.019	0.009	TR	0.009
1-F-1	20.09	0.51	0.270	TR	0.007	0.280	0.100	0.005	0.006	TR	TR	TR
1-F-3	20.08	1.60	0.032	0.005	0.012	0.049	0.160	0.008	0.006	TR	TR	TR
1-F-4	20.28	2.14	0.044	TR	0.005	0.049	0.068	TR	TR	TR	0.007	TR
2-F-1	20.21	1.86	0.330	0.027	0.046	0.400	0.520	0.060	0.027	0.013	0.009	TR
2-F-2	20.21	1.77	0.230	TR	0.007	0.240	0.099	0.074	0.020	0.012	0.012	0.005
2-F-3	20.09	1.33	0.170	TR	0.012	0.180	0.110	0.260	0.034	0.007	TR	TR
2-F-4	20.04	1.41	0.150	TR	0.012	0.160	0.094	0.024	0.009	TR	0.011	0.006

TABLE 5 (cont'd). Organochlorine residue levels in starlings, 1972

SITE NO. ¹	WET WEIGHT, G	LIPID WEIGHT, G	DDE	DDD	DDT	DDT/META-BOLITES	PCB'S ²	DIELDRIN	HEPTA-CHLOR EPOXIDE	OXYCHLOR-DANE	BHC	HCB
3-F-1	20.52	1.21	0.130	TR	0.014	0.140	0.150	0.072	0.017	0.007	TR	0.023
3-F-2	19.97	1.19	0.420	TR	0.012	0.430	0.130	0.012	TR	TR	TR	TR
3-F-3	20.03	1.54	0.370	0.032	0.080	0.480	0.840	0.017	0.008	0.006	0.012	TR
3-F-4	20.12	2.14	0.440	TR	0.019	0.460	0.190	0.033	0.007	TR	TR	TR
4-F-1 ³	20.10	1.09	1.060	TR	0.011	1.070	0.200	0.027	0.012	0.012	TR	0.025
4-F-3	20.13	1.10	0.620	TR	0.016	0.640	0.200	0.016	0.017	0.011	TR	TR
5-F-1	20.18	1.75	1.040	0.029	0.036	1.110	0.280	0.061	0.011	0.005	TR	0.008
1-G-2	20.15	1.26	0.230	0.008	0.022	0.260	0.220	0.027	0.009	TR	0.006	0.022
1-G-3	20.11	2.11	0.390	0.023	0.053	0.470	0.550	0.016	0.017	0.014	0.009	0.006
1-G-4	20.28	1.67	0.150	0.017	0.035	0.200	0.320	0.020	0.020	0.007	0.020	0.007
2-G-1	20.10	2.15	0.680	0.022	0.042	0.740	0.420	0.090	0.082	0.032	0.007	TR
2-G-2	20.01	2.21	0.110	0.006	0.013	0.130	0.100	0.280	0.077	0.016	0.006	TR
2-G-3	20.25	1.63	0.140	0.009	0.033	0.180	0.340	0.390	0.110	0.033	0.007	0.019
2-G-4	20.08	2.57	0.230	0.022	0.063	0.320	0.410	0.310	0.039	0.034	0.008	TR
3-G-1	20.04	1.49	0.550	0.025	0.029	0.600	0.210	0.260	0.034	0.014	0.006	0.011
3-G-2	20.05	1.04	0.220	0.012	0.077	0.310	0.720	0.035	0.057	0.028	0.008	0.014
3-G-3	20.04	1.14	7.950	0.044	0.049	8.040	0.220	0.110	ND	ND	TR	0.044
3-G-4	19.97	1.37	0.940	0.019	0.039	1.000	0.290	0.350	0.031	0.018	0.014	0.080
4-G-1	20.02	0.81	4.920	0.013	0.020	4.950	0.160	0.039	0.021	0.009	TR	0.024
4-G-2	20.09	0.92	0.680	TR	0.028	0.710	0.290	0.011	0.012	0.009	TR	0.009
4-G-3	20.11	0.84	0.710	TR	0.091	0.800	1.020	0.016	ND	ND	TR	0.044
4-G-4	20.29	1.71	11.700	0.089	0.046	11.800	0.220	0.150	0.065	0.018	0.011	TR
1-H-1	20.04	1.85	0.180	0.021	0.069	0.270	0.700	0.023	0.011	TR	0.007	0.007
1-H-2	19.96	1.26	0.680	0.054	0.059	0.790	0.370	0.023	0.008	0.008	0.005	TR
2-H-1	20.02	1.69	0.780	0.032	0.096	0.910	0.990	0.025	0.054	0.054	0.006	0.006
2-H-2	20.03	1.40	0.440	0.018	0.046	0.500	0.410	0.170	0.049	0.011	0.009	TR
2-H-3	20.04	1.15	0.560	0.011	0.026	0.600	0.250	0.340	0.031	0.007	TR	0.550
2-H-4	20.04	2.31	0.500	0.018	0.057	0.580	0.530	0.024	0.026	0.024	0.024	0.029
3-H-1	20.97	1.14	1.790	0.016	0.030	1.840	0.170	0.065	0.037	0.029	0.007	TR
3-H-2	20.00	1.79	0.130	0.020	0.049	0.200	0.520	ND	0.016	0.009	ND	0.140
3-H-3	20.06	1.16	0.440	0.006	0.031	0.480	0.370	0.030	0.011	0.012	TR	TR
3-H-4	20.07	1.28	0.660	TR	0.011	0.670	0.110	0.084	0.026	0.009	0.008	0.095
4-H-1	20.07	0.91	1.060	TR	0.022	1.080	0.290	0.310	0.091	0.100	TR	0.044
4-H-2	19.98	1.03	0.780	0.013	0.028	0.820	0.300	0.025	0.053	0.025	ND	0.059
4-H-3	22.04	1.06	0.890	0.840	1.560	3.290	19.900	0.029	0.071	ND	TR	TR
4-H-4	20.11	0.86	0.870	TR	0.013	0.880	0.250	0.280	0.028	TR	TR	TR
2-I-1	19.98	1.75	0.180	0.041	0.036	0.260	0.320	0.170	0.041	0.021	ND	0.210
2-I-2	20.05	1.79	0.500	0.046	0.065	0.610	0.650	0.730	0.150	0.034	0.012	0.280
2-I-3	20.02	1.44	0.260	0.009	0.031	0.300	0.250	0.028	0.024	0.010	0.018	0.046
3-I-1	20.02	0.77	0.370	0.016	0.042	0.430	0.470	0.076	0.023	0.025	TR	TR
3-I-2	20.03	0.94	1.090	0.009	0.040	1.140	0.440	0.160	0.011	0.009	TR	TR
3-I-3	20.01	0.90	0.150	0.006	0.016	0.170	0.160	0.028	0.008	0.006	TR	TR
3-I-4	20.90	0.77	0.570	TR	0.011	0.580	0.160	0.031	0.020	0.008	TR	0.007
4-I-1	20.03	0.88	5.040	0.015	0.024	5.080	0.190	0.050	0.041	0.012	TR	TR
4-I-2	20.00	1.07	0.600	0.011	0.053	0.660	0.860	0.022	ND	ND	TR	0.010
4-I-3	20.15	0.97	1.640	TR	0.037	1.680	0.410	1.200	0.014	0.038	TR	TR
5-I-1	20.02	0.78	0.460	TR	0.020	0.480	0.190	0.033	ND	ND	TR	TR
5-I-2	20.17	0.83	0.420	0.013	0.029	0.460	0.320	0.017	TR	0.011	ND	ND
2-J-1	20.08	0.45	0.380	0.008	0.021	0.410	0.230	0.120	0.022	0.015	TR	0.042
2-J-2	20.12	1.36	0.310	0.007	0.019	0.340	0.170	0.047	0.030	0.021	0.030	0.035
2-J-3	20.09	1.43	0.380	0.007	0.023	0.410	0.210	0.068	0.028	0.012	0.007	TR
2-J-4	20.09	2.02	0.150	0.007	0.016	0.170	0.200	0.011	TR	TR	TR	TR
3-J-1	21.21	1.12	1.110	0.014	0.039	1.160	0.390	0.530	0.038	0.035	ND	ND
3-J-2	20.05	1.05	1.610	0.008	0.056	1.670	0.520	0.130	ND	ND	TR	TR
3-J-3	20.01	1.25	0.530	0.031	0.046	0.610	0.540	0.097	0.021	0.027	ND	0.014
1-K-1	20.07	0.96	0.370	0.006	0.018	0.390	0.200	0.016	0.005	0.005	TR	TR
1-K-2	20.03	1.58	0.390	0.011	0.026	0.430	0.250	0.027	0.014	0.012	TR	TR
2-K-1	20.28	1.11	0.890	0.007	0.052	0.950	0.960	0.006	0.007	TR	0.005	0.008
2-K-2	20.22	1.17	0.250	0.012	0.026	0.290	0.290	0.021	0.019	0.019	TR	0.007

NOTE: Weights expressed in grams; residues expressed in ppm ($\mu\text{g/g}$) wet weight.

TR = trace.

ND = not detected.

¹ PCB levels estimated by examining peak between DDD and DDT with Aroclor 1254 as standard.² Samples from each site composed of 10 birds except as indicated.³ Sample composed of 9 birds.⁴ Sample composed of 7 birds.⁵ Sample composed of 5 birds.⁶ Sample composed of 8 birds.

DIELDRIN

The difference between summer 1967 and winter 1967-68 dieldrin residue levels was much greater than that for DDT, and this seasonal difference was highly significant (Table 2). Residue levels the following fall were significantly lower than the summer/winter means. The vast majority of dieldrin residues found in the environment are derived from use of aldrin; aldrin/dieldrin sales (5) are roughly correlated with residue levels in starlings (Fig. 2). Results suggest that dieldrin levels may decline slightly in 1974 but should drop sharply in 1975 with the suspension of most uses of aldrin/dieldrin. Again, a more reliable fix on the slope will be generated from future collections.

Highest dieldrin residues (Table 4) were found in Washington (1-B-2), Idaho (1-B-1), Illinois (2-G-3), Iowa (2-G-4), Missouri (3-G-4), Indiana (2-H-3), Florida (4-H-1 and 4-I-3), Ohio (2-I-2), and North Carolina (3-J-1).

BHC

The compound BHC, including alpha, beta, and gamma isomers, was found in nearly all samples taken. Levels were extremely low; the highest was 0.036 ppm. BHC levels from the 1972 collection are not compared with those from past collections because HCB is being reported separately for the first time.

HCB

Although HCB has been used primarily outside the United States as a grain fungicide, it is possible that the compound has contaminated the environment in this Nation through industrial uses. In general, HCB levels were quite low, 0.1 ppm or less; almost half the samples had residues of 0.005 ppm or less. There were two sites which had high residue levels: 1-A-2 in Washington (3.330 ppm) and 1-B-1 in Idaho (2.340 ppm). Two other sites in Washington (1-B-2 and 1-B-3) had HCB levels exceeding 0.5 ppm.

HEPTACHLOR EPOXIDE

Nearly all samples collected in 1972 contained residues of heptachlor epoxide. Levels were relatively low, ranging from 0.005 to 0.210 ppm; only three sites had levels exceeding 0.1 ppm. Oxychlordane, which has been reported with heptachlor epoxide in the past, is being reported separately this year. Direct comparisons between previous heptachlor epoxide levels and the 1972 results are not made at this time.

OXYCHLORDANE

A breakdown byproduct of chlordane, oxychlordane, was found in nearly all samples at very low levels. The highest residue detected was 0.1 ppm.

PCB'S

Except for three sites, PCB's were found in all samples at levels below 1 ppm. Exceptions were sites 3-B-3 in Nevada, 1.87 ppm; 4-G-3 in Louisiana, 1.020 ppm; and 4-H-3 in Alabama, 19.9 ppm. The 1970 Alabama level was estimated to be 24.3 ppm; further monitoring is planned at this site to attempt to identify the source of contamination.

Acknowledgments

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LITERATURE CITED

- (1) Martin, William E. 1967. Organochlorine insecticide residues in starlings. *Pestic. Monit. J.* 3(2):102-114.
- (2) Martin, William E., and Paul R. Nickerson. 1972. Organochlorine residues in starlings—1970. *Pestic. Monit. J.* 6(1):33-40.
- (3) Remington, Richard D., and M. Anthony Schork. 1970. *Statistics with Applications to the Biological and Health Sciences*. Prentice-Hall, Inc., Englewood Cliffs, N.J. 418 pp.
- (4) Fowler, D. Lee, and John N. Mahan. 1973. *The Pesticide Review 1973*. Agricultural Stabilization and Conservation Service, USDA, Washington, D.C. 60 pp.
- (5) Sloan, J. 1973. Shell Ex. 111. Consolidated Aldrin/Dieldrin Hearings, FIFRA Docket Numbers 145 et al., Washington, D.C.

Organochlorine Residues in Alaskan Peregrines¹

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ABSTRACT

Organochlorine residue levels in eggs of Alaskan peregrines have remained essentially constant over the period 1969-73 despite decreased usage of these compounds in the United States and Canada. Studies on reproductive success in Great Britain and data on eggshell-thinning suggest that DDE residues above 20 ppm wet weight in peregrine eggs are associated with inability to maintain population levels. Residues in mainland Alaska are well above this critical figure and the reproductive rate is low. On the Colville River in northwestern Alaska, the last young falcons will fledge in 1975 and the remaining adult population will disappear by 1980 unless the present rate of reproductive failure is drastically and quickly reversed. In the Aleutians, however, levels range from 5 to 7 ppm and the reproductive rate is adequate to maintain the population.

Introduction

The decline of the peregrine (*Falco peregrinus*) has been one of the most dramatic events ascribed to the use of persistent pesticides (1). Although the species is too rare for specimens to be collected solely for analysis, a number of infertile or addled eggs and dead young have been obtained from Alaskan locales in recent years. This limitation on collection means that the data are not selected as randomly as researchers would

like, a common problem with data on many top predators. Following restrictions on uses of organochlorines instituted in North America in recent years, residue levels of DDT and its metabolites in lower trophic levels have decreased (2-5). Because it has been predicted that organochlorine residues in higher trophic levels will continue to rise for several years after the input decreases (6), authors considered it important to examine levels in a top predator over this period.

Alaskan peregrines can be divided into two main groups: interior and maritime. The mainland population is highly migratory and winters in Central and South America (1); the maritime population is essentially resident (7). Although both populations are essentially bird eaters, each group preys upon different species. White et al. (8) found that 65 percent, by weight, of the food of Aleutian peregrines consisted of alcidae, which winter offshore in the Aleutians. Residue levels of DDE ranged from 0.001 to 0.094 ppm wet weight for eight individuals of four alcid species (7). Truly migratory species comprised less than 3 percent of the prey.

Cade et al. (9) found that migratory waterfowl comprised half the food of the peregrines along the Yukon River; shorebirds and gulls represented about one quarter. Only one major prey species, the Canada jay (*Perisoreus canadensis*), is nonmigratory. In 1966 this species accounted for 11 percent by weight of the prey observed at aeries. A similar pattern was exhibited on the Colville River in 1967-69: of more than 45 species of prey found at aeries, only Ptarmigan (*Lagopus lagopus* and *L. mutus*) are permanently resident in Alaska. The Ptarmigan comprise only 14 of 433 prey species (10).

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Thus the mainland population not only migrates into areas of heavy pesticide use, but most of its prey species are also migratory. On the other hand, because Aleutian peregrines have little direct contact with pesticides, their levels reflect the background contamination of the North Pacific.

Methods

In most cases eggs were blown by routine oological methods and the contents were immediately preserved in 10 percent formalin. If possible, eggs were rapidly shipped intact. Expression of residue levels on a wet-weight basis requires that all eggs be at the same stage of development and weighed shortly after collection. These conditions cannot be met for much of the field work in Alaska. Therefore, authors prefer to use the oven-dried weight. The amount of extractable fat was measured so that results could also be expressed on a lipid-weight basis. To compare results to those in much of the published work, divide ppm dried weight by 5 to give the wet-weight value.

Samples were dried for 48 hours at 45°C and then ground with coarse anhydrous Na₂SO₄. Samples were extracted in Soxhlet thimbles for 8 hours with a 1:3 mixture of ethyl ether:petroleum ether. A florisis column was used to remove fats and other interfering substances. A varian aerograph gas chromatograph equipped with ⁶³Ni electron-capture detectors and two 0.6-cm-by-1.8-m columns was used for pesticide quantification. Liquid phases and solid supports were 2 percent QF-1 on 40/50 Anakrom ABS and 5 percent SE-30 on 60/80 Chromosorb W. Operating conditions were:

Temperatures: Inlet 225° C.
 Detector 275° C.
 Column 200° C.
 Carrier Gas: Dry Nitrogen.

Polychlorinated biphenyls (PCB's) were quantitated on

two peaks after saponification. Recovery rates were 85 to 95 percent and values were not corrected.

Results and Discussion

Levels of DDE found in peregrine eggs during 1968-73 are listed in Table 1. There is no indication of any change in residue levels for either the interior or maritime populations. Small sample sizes and the nonrandom nature of the collections preclude statistical analysis. A few individual eggs were collected from the same site in different years, so comparisons can be made on a site basis. Two eggs from cliff 68 on the Colville River had DDE levels of 146 and 199 ppm oven-dried weight and shell index figures of 1.57 and 1.27 in 1968; an egg from this site in 1971 had a DDE level of 174 ppm and a shell index of 1.54. Shell index represents weight (mg) divided by the product of the length and breadth (mm) of the empty eggshell (11). In 1968 at Shivugak, on the Colville, the residue level was 276 ppm with an index of 1.57. In 1971 two eggs from this cliff had values of 215 and 352 ppm with index values of 1.46 and 1.37. Thus, neither from a consideration of individual sites nor from overall averages is there any evidence of a decrease in residue levels.

Ten young peregrines were found dead in aeries along the Colville River in 1969; eight were found in 1971 (12). Nine of the 1969 young but none of the 1971 young could be analyzed. Residue levels in the muscle, liver, and brain are given in Table 2. These values are compared with those found in four young collected in 1966 (9), although they are not strictly similar. The 1966 specimens were alive when collected from various places, whereas the 1969 sample consisted of young found dead in the nest, apparently having starved after abandonment. Starvation may account for the higher residue levels in the brain in 1969. Nevertheless, even the highest brain levels, 42 ppm dry weight, are low compared to levels normally considered lethal (13).

TABLE 1. DDE levels in Alaskan peregrine eggs, 1968-73

AREA	YEAR	DDE ¹			SHELL INDEX			THINNING, %	SIGNIFICANCE OF THINNING
		NUMBER	MEAN	ST. DEV.	NUMBER	MEAN	ST. DEV.		
INTERIOR ALASKA									
Colville River	1968	11	193.9	159.8	11	1.42	0.13	24.9	<0.001
	1969	5	163.8	87.4	5	1.53	0.15	23.5	<0.01
	1971	7	210.8	92.0	7	1.49	0.09	21.2	<0.005
Yukon River	1968	11	105.6	53.0	11	1.49	0.10	16.8	<0.001
Tanana River	1969	3	344.3	81.0	3	1.42	0.14	20.2	ND
	1973	3	302.7	84.1	3	1.44	0.18	19.1	ND
ALEUTIANS									
Amchitka	1969	6	25.0	3.6	6	1.74	0.10	7.4	<0.01
	1970	6	39.8	26.4	6	1.73	0.21	8.0	<0.05
	1971	3	24.1	15.1	3	1.73	0.19	8.0	ND
	1973	7	26.3	9.2	7	1.72	0.16	8.3	<0.05

NOTE: Pre-1946 values used to calculate percentage thinning for the various areas are: Colville 1.89, Aleutians 1.88, and Yukon 1.78; the value for the Yukon is probably too low (12). Data for the Colville 1968 and 1969, Yukon 1969, and Amchitka 1969 and 1970 have been reported previously (12) but not on a year-by-year basis.
 ND = no data; sample too small.

¹ Residues are ppm oven-dry weight.

TABLE 2. DDE levels in young peregrines found dead in aeries along Colville River, Alaska

TISSUE	1969 ¹		1966 ^{2,3}	
	MEAN	ST. DEV.	RANGE	RANGE
Muscle	5.1 ± 2.0		1.2-19.0	6.3
Liver	11.7 ± 4.0		1.2-33.0	1.6
Brain	17.6 ± 4.7		1.1-42.0	1.6

NOTE: Residues are ppm oven-dry weight.

¹ Samples of all tissue represent nine individuals.

² Samples of all tissue represent four individuals.

³ See Literature Cited, reference 9.

The possibility that organochlorines were involved in the failure of parental care remains to be explored; abnormal behavior of adult falcons at their aeries certainly appears to have increased in recent years.

Three clutches of peregrine eggs laid in captivity during the Cornell breeding project have also been analyzed for residues. Eggs from a bird taken as a nestling from the Colville River in 1968 had DDE levels of 7.8 ppm dry weight and a shell index of 1.82 in 1972. Eggs from a Yukon River bird taken as a nestling in 1966 and raised on a diet of fresh fowl and coturnix quail had DDE residue levels of 9.0 ppm in 1972 and 7.7 ppm in 1973. Shell index figures were 1.79 and 1.80, respectively. The bird's controlled diet of fowl and quail thus resulted in low residue levels and a shell index approaching levels common before application.

PCB levels follow quite a different pattern from those of DDE (Table 3). In the Alaskan interior, the ratio of total DDT to PCB's is almost 1:1, whereas in the Aleutians the ratio is down to about 1:5. No other organochlorines were detected above trace amounts.

TABLE 3. PCB levels in peregrine eggs, Alaska

AREA	YEAR	PCB			ΣDDT: PCB
		NUMBER	MEAN	ST. DEV.	
INTERIOR ALASKA					
Colville River	1971	7	173.4	54.9	1.22
Tanana River	1973	3	350.1	256.9	0.66
ALEUTIANS					
Amchitka	1971	3	114.4	77.4	0.20
Amchitka	1973	7	144.6	68.3	0.18

NOTE: Residues are ppm oven-dry weight.

EFFECT OF ORGANOCHLORINE RESIDUES

The relation between DDE residues in eggs and the thickness of eggshells of Alaskan peregrines was plotted in 1971 (12). Data from the present study which are plotted in Figure 1 confirm the original plot. It is significant that residues from the lightly contaminated eggs of captive birds closely fit the regression line. A decrease in thickness of 20 percent or more is associated

with population declines (14); in the peregrine this critical thickness corresponds to about 20 ppm wet weight DDE in the eggs. Equivalents for dry weight and lipid are 100 and 500 ppm, respectively. Residues in eggs do not affect shell thickness, however; they are used merely as convenient indicators of circulating levels in mother birds at the time of egg maturation.

Direct embryonic effects of DDE are probably unimportant, because high levels are necessary to affect reproduction in species in which eggshell thinning does not occur and when the eggs are incubated artificially (15,16). PCB's appear to be considerably more embryotoxic than DDE (17).

It is not clear whether eggshell breakage is purely the result of structural failure, or whether it is caused by the mother bird's abnormal behavior on the nest. Ratcliffe (18) feels that the behavioral component may be quite important. In the bird's diet, DDE levels of 40 ppm (19) and PCB's of 10 ppm (17) have been shown to cause behavioral changes leading to decreased reproductive success in ringed turtle doves (*Streptopelia risoria*).

Ideally, one would like to determine what level of organochlorine residues in peregrine eggs interferes with the productivity necessary for a stable population. The best available data are from Great Britain. Ratcliffe showed that in 1962 reproduction was low in England, Wales, and southern Scotland, and that only in the Highlands of Scotland were peregrines reproducing normally (18). In southern England only 3 percent of the sites had young who hatched. The rate in Wales was 4 percent; in northern England, 7 percent, and in southern Scotland, 5 percent. In the Highlands of Scotland 38 percent of the sites had young who hatched. By 1971 substantial improvement had occurred in northern England and southern Scotland, but reproduction was still poor in Wales and southern England. In 1971 the rate of sites hatching young was 7 percent in southern England, 4 percent in Wales, 24 percent in northern England, and 24 percent in southern Scotland. In the Highlands, this index of productivity remained essentially constant. Total organochlorine pesticide residue levels in eggs from northern England declined from 24.8 ppm wet weight in 1962-66 to 7.9 ppm in 1967-71.

Corresponding values for southern Scotland were 14.5 and 11.0 ppm. Values for the Highlands were below 10 ppm throughout; no values are available for southern England or Wales for either period. About 90 percent of the residues are DDE. Nevertheless, other compounds, especially dieldrin, remain a problem.

Lockie et al. noted that, concurrent with an increase of breeding success of the golden eagle (*Aquila chrysaetos*), mean levels of dieldrin decreased from 0.86 to 0.34 ppm (20). This correlation does not apply to the

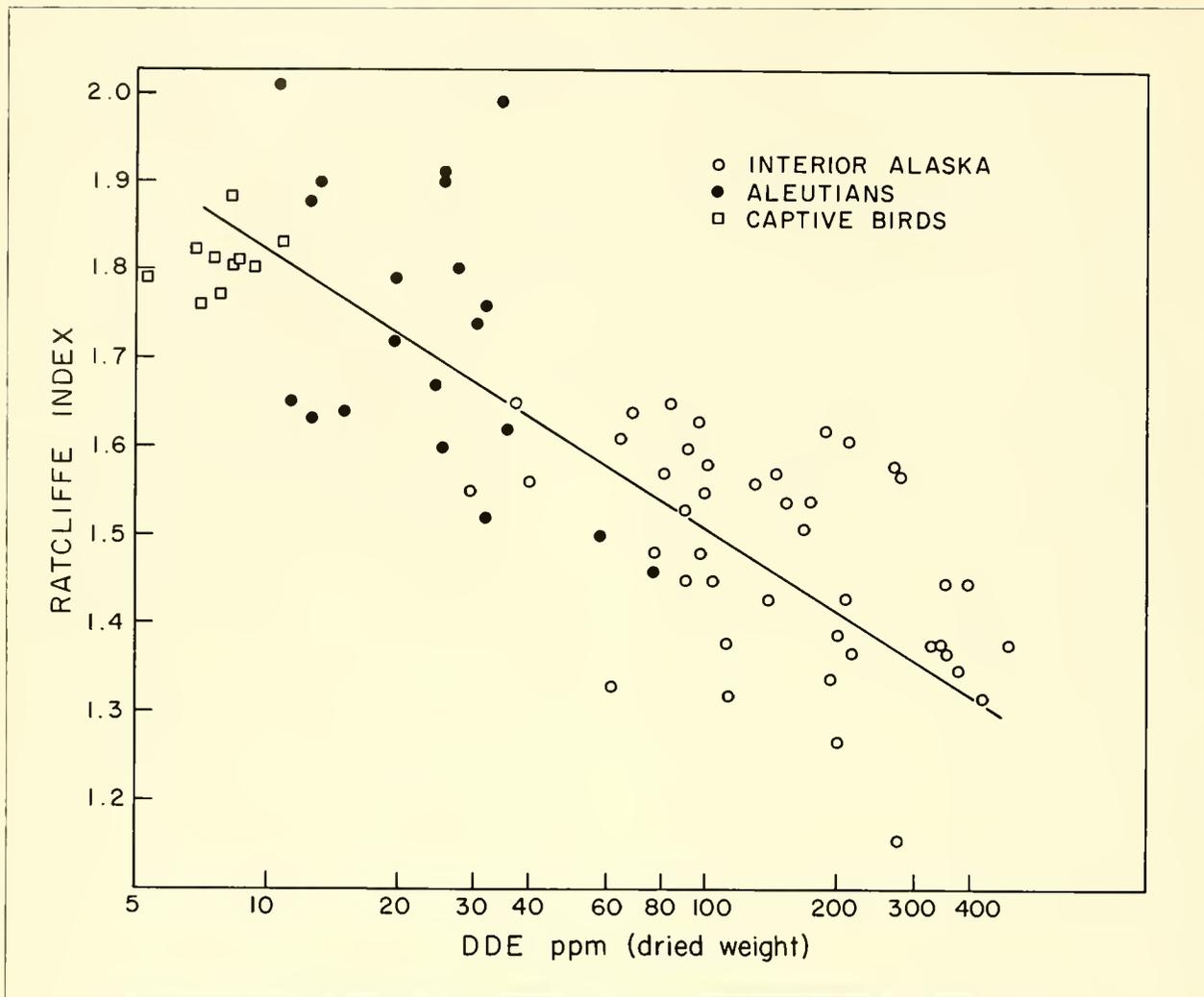


FIGURE 1. Relation between shell thickness index and DDE residues in eggs of Alaskan Peregrines.

peregrine. Ratcliffe's data show that the highest mean level of dieldrin, 1.2 ppm, occurred in the Highlands in 1962-66 when the peregrine was reproducing well (19). Residue levels in northern England decreased from 1962-66 to 1967-71, but they increased in southern Scotland.

Although the residue levels represent 5-year periods, and the information on reproductive performance represents single years, and residue levels are not related to reproduction at the specific aeries from which the eggs were collected, a tentative conclusion can be formed: namely, that the critical level of DDE in egg content is about 15 to 20 ppm wet weight. This value corresponds with the suggested critical value of 20 ppm DDE, wet weight, derived from consideration of the eggshell-thinning data. These lines of evidence indi-

cate that peregrines should continue to maintain normal population levels in the Aleutians where wet-weight means of egg content are 5 to 7 ppm, but not in the Alaskan interior populations where wet-weight means are 20 to 40 ppm. This hypothesis agrees with published observations of peregrines in the Aleutians (8) and interior Alaska (10,12,21) on reproductive success and population changes. As shown in Table 4, this relationship is particularly dramatic for peregrines nesting on the Colville River. If the present rate of reproductive failure is not drastically reversed soon, the last young falcons will fledge from the Colville aeries in 1975, and the remaining adult population will slowly disappear by 1980.

The use of DDT in the United States has decreased almost linearly from a peak of 78 million pounds in

1959 to essentially zero in 1973 (22). Various monitoring surveys have clearly indicated decreased levels of DDT and its metabolites over this period. Residue levels in estuarine mollusks surveyed from 1965 to 1972 showed a clear trend toward decreased levels of DDE beginning in 1969-70 (2). In 1970 Martin and Nickerson found that residue levels in starlings (*Sturus vulgaris*) had decreased from 1967-68 levels at 35 of 38 sampling points (4); overall reduction of total DDT was 53 percent. Henderson et al. found that total DDT residues in fish had decreased at 33 of 50 sampling points from 1968 to 1969 (3). Ware et al., while studying the effect of a 2-year moratorium on the agricultural use of DDT in Arizona, found that levels in alfalfa and beef fat decreased significantly, but soil levels changed only negligibly (5). The rate of clearance indicated by these studies appears to be more rapid than had been predicted by Harrison et al. in 1970 (6); they estimated that the half-life of DDT for a given trophic level would be four times the average life span of the longest-lived species.

TABLE 4. Number of breeding pairs and productivity of peregrines, Colville River, Alaska

YEAR	TOTAL NO. PAIRS	NO. PAIRS PRODUCING YOUNG ¹	NO. YOUNG PRODUCED ¹
1952-59 ²	32-36	20-25	40-50
1967 ³	27	18	34
1968 ³	32	16	34
1969	33	13	26
1971 ⁴	25	9	14
1973	14	4	9

¹ Ranges are estimated. The entire river was not monitored every year.

² Refer to Literature Cited, reference 26.

³ Refer to Literature Cited, reference 12.

⁴ Refer to Literature Cited, reference 10.

Samples of a few flickers (*Colaptes auratus*) killed by migrating falcons in Maryland and Virginia had residue levels of only a trace to a few tenths of a ppm. Flickers, which migrate the same time as the falcons, are an important food source for peregrines. The fact that levels of organochlorines in arctic peregrine eggs remain high suggests that these residues are obtained largely in Central and South American countries where their use has not been banned.

Although the use of DDT in the United States, Canada, and many European countries has decreased considerably, there is no clear evidence that use is decreasing on a global scale. United States production of DDT remained between 100 and 180 million pounds from 1955 to 1970 and a steadily increasing proportion of the DDT was exported (22). Many countries in Central and South America, Africa, and Asia now manufacture DDT. Monitoring levels of organochlorines in ocean plankton would trace the concentration of total DDT in the world's ultimate sink.

Findings of the current study cause little optimism about the ultimate fate of North American peregrines. Residue levels remain high and reproduction low in mainland Alaskan peregrines. There is little to suggest that the 1970 forecast of extinction within a decade (21) was incorrect for some of the northern populations, and the same bleak picture applies to the remaining Rocky Mountain population (23). The situation in Greenland, fortunately, appears more encouraging (24).

The first major success in artificial breeding occurred in 1973 when 20 young peregrines were raised; two females from the Colville River mothered 13 of those 20 hatchlings (25). This was more than the entire natural productivity from the Colville River in 1973. Authors' findings suggest that reintroduction of captivity-produced peregrines will be successful only if the released falcons do not migrate south of the United States.

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LITERATURE CITED

- (1) Hickey, J. J., editor. 1969. The peregrine falcon populations: their biology and decline. University of Wisconsin Press, Madison, Wisc.
- (2) Butler, P. A. 1972. Organochlorine residues in estuarine mollusks, 1965-72. Pestic. Monit. J. 6(4):238-362.
- (3) Henderson, C., A. Inglis, and W. L. Johnson. 1971. Organochlorine insecticide residues in fish—fall 1969. Pestic. Monit. J. 5(1):1-11.
- (4) Martin, W. E., and P. R. Nickerson. 1972. Organochlorine residues in starlings—1970. Pestic. Monit. J. 6(1):33-40.
- (5) Ware, G. W., B. J. Estes, and W. P. Cahill. 1971. DDT moratorium in Arizona—agricultural residues after 2 years. Pestic. Monit. J. 5(3):276-280.
- (6) Harrison, H. L., O. L. Loucks, J. W. Mitchell, D. F. Parkhurst, C. R. Tracy, D. G. Watts, and V. J. Yannacone, Jr. 1970. Systems studies of DDT transport. Science 170(3957):503-508.
- (7) White, C. M., W. B. Emison, and F. S. L. Williamson. 1971. Dynamics of raptor populations on Amchitka Island, Alaska. BioScience 21(12):623-627.
- (8) White, C. M., W. B. Emison, and F. S. L. Williamson. 1973. DDE in a resident Aleutian Island peregrine population. Condor 75(3):306-311.
- (9) Cade, T. J., C. M. White, and J. R. Haugh. 1968. Peregrines and pesticides in Alaska. Condor 70(2):170-178.
- (10) White, C. M., and T. J. Cade. 1971. Cliff-nesting raptors and ravens along the Colville River in arctic Alaska. Living Bird 10:107-150.
- (11) Racliffe, D. A. 1967. Decrease in eggshell weight of certain birds of prey. Nature 215(5097):208-210.
- (12) Cade, T. J., J. L. Lincer, C. M. White, D. G. Roseneau, and L. G. Swartz. 1971. DDE residues and

- eggshell changes in Alaskan falcons and hawks. *Science* 172(3986):955-957.
- (13) *Stickel, L. F., W. H. Stickel, and R. Christensen. 1966.* Residues of DDT in brains and bodies of birds that died on dosage and in survivors. *Science* 151(3717): 1549-1551.
- (14) *Anderson, D. W., and J. J. Hickey. 1972.* Eggshell changes in certain North American birds. *Proc. 15th Int. Ornithol. Congr.* pp. 514-540.
- (15) *Dewitt, J. B. 1956.* Chronic toxicity to quail and pheasants of some chlorinated insecticides. *J. Agr. Food Chem.* 4(8):863-866.
- (16) *Lillie, R. J., C. A. Denton, H. C. Cecil, J. Bitman, and G. F. Fries. 1972.* Effect of *p,p'*-DDT, *o,p'*-DDT and *p,p'*-DDE on the reproductive performance of caged white leghorns. *Poultry Sci.* 50(5):1597-1598.
- (17) *Peakall, D. B., and M. L. Peakall. 1973.* Effect of the polychlorinated biphenyl on the reproduction of artificially and naturally incubated dove eggs. *J. Appl. Ecol.* 10(3):863-868.
- (18) *Ratcliffe, D. A. 1972.* The peregrine population of Great Britain in 1971. *Bird Study* 19(3):117-156.
- (19) *Haegele, M. A., and R. H. Hudson. 1973.* DDE effects on reproduction of ring doves. *Environ. Pollut.* 4(1): 53-56.
- (20) *Lockie, J. D., D. A. Ratcliffe, and R. Balharry. 1969.* Breeding success and organo-chlorine residues in golden eagles in west Scotland. *J. Appl. Ecol.* 6(3): 381-389.
- (21) *Cade, T. J., and R. Fyfe. 1970.* The North American peregrine survey, 1970. *Can. Field Nat.* 84(3):231-245.
- (22) *U.S. Department of Agriculture. 1972.* Pesticide Review 1972.
- (23) *Walker, W., W. G. Mattox, and R. W. Risebrough. 1973.* Pollutant and shell thickness determinations of peregrine eggs from West Greenland. *Arctic* 26(3): 255-256.
- (24) *Enderson, J. H., and J. Craig. 1974.* Status of the peregrine falcon in the Rocky Mountains in 1973. *Auk.* 91(4):727-736.
- (25) *Laboratory of Ornithology Newsletter. Summer 1973.* No. 69. Cornell University, Ithaca, N.Y.
- (26) *Cade, T. J. 1960.* Ecology of the peregrine and gyrfalcon populations in Alaska. *Univ. Calif. Publ. Zool.* 63(2):151-290.

GENERAL

Comparison Between Two Methods of Subsampling Blubber of Northern Fur Seals for Total DDT Plus PCB's¹

Raymond E. Anas and Donald D. Worlund

ABSTRACT

*Samples of 100 g blubber were collected from each of twelve 8- to 13-year-old fur seals (*Callorhinus ursinus*) taken off the coast of Washington State in March 1972. Two methods of subsampling the blubber were compared. The mean level of total DDT (DDE, DDD, and DDT) plus polychlorinated biphenyls (PCB's) from a 5-g chunk of blubber taken from a 100-g sample was significantly less than the mean level from a 5-g subsample taken from the remainder of the blubber sample after it had been thoroughly ground. Total DDT plus PCB residues ranged from 5.66 to 72.17 ppm, with a mean of 23.69 ppm in the chunks, and from 5.33 to 95.70 ppm, with a mean of 28.64 ppm in the homogenized blubber.*

Introduction

Northern fur seals (*Callorhinus ursinus*) breed each summer on islands in the Bering and Okhotsk Seas, where they are harvested for their furs. Small breeding colonies are found on the Kuril Islands, Japan, and the Channel Islands off southern California. Fur seals are pelagic except during the breeding season. Their range extends from California to Japan.

In the sampling of marine mammals for pesticide residues the size of some organs and the blubber layer makes it necessary to take not only a relatively small sample from each animal, but also a subsample. Methods of subsampling tissues from marine mammals for pesticide residues have varied widely. Holden and Marsden (1) used 5-g aliquots of tissue from an original sample of unspecified weight. Anas and Wilson (2) and Aucamp et al. (3) collected and analyzed 10 g

tissue; Arndt (4) collected 15-100 g tissue and analyzed 10-g subsamples. Wolman and Wilson (5) collected 100 g tissue and analyzed subsamples of unspecified weight. The present report compares total DDT (DDE, DDD, and DDT) plus PCB (polychlorinated biphenyl) residues from two methods of subsampling northern fur seal blubber to see whether the subsampling method affects results.

Analytical Methods

Two methods of subsampling the blubber were used: removing and analyzing a random 5-g chunk of frozen blubber from a 100-g sample; and grinding the remainder of the 100-g sample while frozen, stirring thoroughly, and removing and analyzing a random 5-g subsample. The 100-g sample of blubber consisted of a cross section taken from the belly area near the midline and anterior to the mammarys of 12 adult female northern fur seals taken off the coast of Washington State in March 1972. Samples were kept frozen at -23°C .

Ages of the seals, determined by counting lines of dentine in longitudinally sectioned upper canine teeth (6,7), ranged from 8 to 13 years. Both parous and nonparous seals were included. Unpublished data by the authors on 51 adult female northern fur seals ranging from 8 to 13 years have shown that mean organochlorine residues are not associated with age or parous condition ($P > 0.05$), so pregnant and nonpregnant seals from 8 to 13 years were pooled for the current study.

Organochlorine residues were determined by WARF Institute, Inc., Madison, Wisc. Methodology has been described previously; total DDT and PCB's were summed to reduce possible errors (8).

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Results and Conclusions

Total DDT plus PCB's ranged from 5.66 to 72.17 ppm, with an average of 23.69 ppm in the chunks, and 5.33 to 95.70 ppm with an average of 28.64 ppm in the homogenized blubber (Table 1). A paired t-test indicated that the average total DDT plus PCB level for samples from homogenized blubber was significantly greater than the level for chunks ($P < 0.05$). Comparison of values in Table 1, however, suggests that the difference in results between the two sampling methods increases with increasing residue levels. The average difference of 4.95 ppm, therefore, may not be strictly applicable to the range of residue levels observed in this sample of 12 individuals.

TABLE 1. Total DDT plus PCB's in blubber from 12 adult female fur seals, Washington State, March 1972

SAMPLE NO.	TYPE OF SAMPLE		DIFFERENCE	RATIO
	CHUNKS	HOMOGENIZED		
1	5.66	5.33	-0.33	1.08
2	8.40	11.79	+3.39	0.71
3	14.78	16.68	+1.90	0.89
4	17.15	17.34	+0.19	0.99
5	15.05	17.93	+2.88	0.84
6	17.60	17.96	+0.36	0.98
7	20.90	25.27	+4.37	0.83
8	25.86	28.04	+2.18	0.92
9	26.55	28.96	+2.41	0.92
10	16.73	29.78	+13.05	0.56
11	43.47	48.89	+5.42	0.89
12	72.17	95.70	+23.53	0.75
AVERAGE	23.69	28.64	+4.95	0.83

NOTE: Data expressed in ppm; mg/kg wet weight. Ages ranged from 8 to 12 years.

Ratios of residue values (chunk:homogenized) in Table 1 do not exhibit a trend with increasing residue levels. This hypothesis was indirectly tested by computing a weighted regression of residue values from chunks on those from homogenized samples and comparing the estimated intercept with zero. The variance about the line was assumed proportional to the residue level, so weights used in the regression were constructed from reciprocals of residue values for homogenized samples and adjusted to sum to the sample size of 12. The intercept and its standard error were estimated to be 1.60 and 3.98, respectively. Because the standard error of the intercept is nearly 2.5 times larger than the intercept itself, there is little reason to reject the hypothesis that the intercept is zero. Therefore it appears that residue values from chunks are a constant fraction of those from homogenized samples and that a regression through the origin adequately describes the relationship between results from the two sampling methods.

Again, assuming the variance proportional to the residue level, the slope of the above regression is best estimated from the ratio of the average for chunks to the average for homogenized samples. This value, 0.83, is significantly less than 1 ($P < 0.05$) and indicates, as did the paired t-test, that significantly different residue values were obtained from the two subsampling methods used in this experiment (9). Analyses of residue levels expressed on a fat basis rather than a wet-weight basis produced the same results.

The reason for the differences in pesticide levels by the two methods is not known. Obviously, one or both of the methods was not random. Differences could be caused by uneven distribution of organochlorine compounds or lipids in the blubber, or unequal separation of these compounds during subsampling. It is known, for example, that in finback whales (*Balaenoptera physalus*), the percent lipids in three sections of blubber is highest in the outer section and lowest in the inner section (10). Whatever the reason for the differences, this study demonstrates that careful consideration should be given to the way in which subsamples are taken for pesticide analyses.

LITERATURE CITED

- (1) Holden, A. V., and K. Marsden. 1967. Organochlorine pesticides in seals and porpoises. *Nature* 216(5122): 1274-1276.
- (2) Anas, R. E., and A. J. Wilson, Jr. 1970. Organochlorine pesticides in nursing fur seal pups. *Pestic. Monit. J.* 4(3):114-116.
- (3) Aucamp, P. J., J. L. Henry, and G. H. Stander. 1971. Pesticide residues in South African marine animals. *Mar. Pollut. Bull.* 2(12):190-191.
- (4) Arndt, D. P. 1973. DDT and PCB levels in three Washington State harbor seal (*Phoca vitulina richardii*) populations. M.S. Thesis, Univ. Washington, Seattle, Wash. 65 pp.
- (5) Wolman, A. A., and A. J. Wilson, Jr. 1970. Occurrence of pesticides in whales. *Pestic. Monit. J.* 4(1): 8-10.
- (6) Scheffer, V. B. 1950. Growth layers on the teeth of Pinnipedia as an indication of age. *Science* 112 (2907):309-311.
- (7) Fiscus, C. H., G. A. Baines, and F. Wilke. 1964. Pelagic fur seal investigations, Alaska waters, 1962. U.S. Fish Wildl. Serv. Spec. Sci. Rept. Fish. 475. 59 pp.
- (8) Anas, R. E. 1974. DDT plus PCB's in blubber of harbor seals. *Pestic. Monit. J.* 8(1):12-14.
- (9) Cochran, W. C. 1953. Sampling techniques. John Wiley and Sons, Inc. New York. 330 pp.
- (10) Ackman, R. G., C. A. Eaton, and P. M. Jangaard. 1965. Lipids of the fin whale (*Balaenoptera physalus*) from North Atlantic waters. *Canad. J. Biochem.* 43(9):1513-1520.

Degradation of Parathion Applied to Peach Leaves

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ABSTRACT

Parathion was applied to peach trees in three different formulations 70 days before harvest. Leaf samples were taken periodically through the 70-day period and gas-liquid chromatographic analyses were conducted for dislodgable and penetrated residues. Analyses were also conducted for paraoxon and the s-ethyl isomer of parathion. Punched samples were compared to whole-leaf samples; generally residue levels for both types corresponded closely. A new experimental formulation, encapsulated parathion, produced highest levels of total parathion throughout the 70-day study, but even this formulation resulted in low total residue levels around 1 ppm at time of harvest. Degradation of the s-ethyl isomer of parathion was generally very rapid in all formulations studied. Dislodgable residues of paraoxon may be significant in some formulations and should be included in parathion degradation studies. Much of the parathion found on peach leaves throughout the growing season was dislodgable residue, but this depended considerably on the formulation used.

Introduction

Recent reports (1-6) have shown that foliage and other plant parts may accept and retain deposits of pesticide residues in much greater quantities and for longer times than does fruit, and that foliage may be a very important factor in considering worker reentry into insecticide-treated orchards. Gunther et al. (7) observed that a freestone peach tree about 10 years old has a leaf-to-fruit surface area ratio approximating 53:1; the

same ratio for a clingstone peach tree is 28:1. Because foliage appears to be the greatest source of exposure of potentially toxic insecticides to farm workers, authors of the present study aimed to ascertain leaf residue levels of parathion and its toxic degradation products.

Formulations can have an appreciable effect on deposit and penetration levels as well as toxicity of insecticides (3,8,9). This study compares residue levels of two commonly used formulations, emulsifiable concentrate (EC) and wettable powder (WP), and an experimental formulation, encapsulated parathion (Enc.). Both dislodgable and penetrated residues were measured periodically for 70 days following application of each formulation. EC and Enc. formulations were applied July 10, 1971, and the WP formulation was applied August 3, 1971.

El-Rafai and Hopkins (10) reported that paraoxon and possibly the s-ethyl isomer of parathion accumulated on both grass and leaf surfaces and were principal metabolites within the plant. The first few days after treatment, according to these investigators, paraoxon accumulated faster on leaf surfaces than it did internally. The adverse was true several days later, however: surface paraoxon degraded more rapidly. Both paraoxon and the s-ethyl isomer are stronger cholinesterase inhibitors than parathion, which in accumulated amounts could pose a threat to workers through dislodgable deposits. Therefore, the study reported here includes both these products as well as their parent compound, parathion.

Analyses were conducted on punches taken at or near the center of leaves and on the whole leaf. Results

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were compared on a weight basis. This portion of the study was designed to determine whether punched grape leaves would be representative for expressing dislodgable residue in $\mu\text{g}/\text{cm}^2$ without sacrificing accuracy to sampling.

Volunteer workers were permitted to enter the fields a few days following parathion application; samples of blood and urine were taken before and after their entrance into the fields. Because this study involves only residues on peach foliage, findings involving human subjects will be reported elsewhere (11).

Materials and Methods

FIELD APPLICATION AND SAMPLING

A 60-acre orchard of freestone peaches southwest of Modesto, Calif., was subdivided into three 20-acre plots. Parathion was applied to each plot in one of the three formulations mentioned above: WP, EC, or Enc. The latter formulation encloses parathion in a porous microplastic capsule. This permits parathion to be released more slowly, over a longer period of time, than are most conventional insecticide formulations.

The formulations were applied with a ground sprayer at rates of 1 lb active parathion per acre for both the EC and Enc., and 2 lb per acre for WP. Parathion was applied at 400 gallon/acre for each of the three 20-acre plots, which is a standard application for peaches in most counties of California. In all three applications, sulfur was also mixed with the formulations and applied at a rate of 20 lb active sulfur per acre. Each 20-acre plot was subdivided into four replicate plots. Ten trees near the center of each replicate were selected for sampling. Whole-leaf and 2.5 cm^2 leaf-punch samples were taken one day before application, the day of application, and 3, 7, 14, 21, 28, and 70 days afterward. Twenty leaves and punches were taken from each tree selected at random in a circular fashion at approximately 18° intervals, 5 feet above ground. Samples from each 10-tree plot were combined, labeled, and frozen immediately in dry ice. Samples were soon transferred to a walk-in freezer where they were kept frozen at subzero temperatures until analyzed.

EXTRACTION AND ANALYSIS

Samples of punched leaves were weighed and the grams per sample were recorded with the total number of punches. Whole-leaf samples were handled on a weight basis only and no attempt was made to measure leaf area. Each sample was extracted for dislodgable residue and for remaining residue according to the method of Gunther (7). Using this procedure, 200 leaf punches were transferred to a heavy-walled 500-ml Erlenmeyer flask. To each flask was added 200 ml of a 1:25,000 dilution of Sur-Ten wetting agent, also called aerosol OT 75 (trimethyl laurel ammonium chlo-

ride). Contents of the flask were shaken for 60 minutes on a Gyrotory shaker at 180 rpm. The aqueous solution was decanted into a 1-liter separatory funnel and another 200 ml diluted wetting agent was added. The solution was shaken for 30 minutes. The second portion of the wash liquid was combined with the first portion and a final 25 ml of wash solution was added to the leaves and shaken for 5 seconds. All Sur-Ten wash solutions were combined and extracted for 30 seconds with four 200-ml portions of chloroform. After filtering through sodium sulfate the organic solvent extracts were combined and stored in the dark until analyzed.

The remainder residue, that which had penetrated, was extracted by transferring leaf contents remaining from Sur-Ten washings to a Waring blender container with 200 ml chloroform. Forty g sodium sulfate was added and the contents were blended for 2 minutes. The solvent was filtered through Whatman No. 1 filter paper into a storage bottle containing 20 g sodium sulfate. An additional 200 ml chloroform was added to the blender cup and the contents were blended for 30 seconds and filtered. The extraction was repeated for 30 seconds with 200 ml chloroform, filtered, and the combined chloroform extracts were stored in the dark until analyzed.

Whole-leaf samples were handled as the punched samples had been. A 50-g portion of leaves was washed twice with 450 ml Sur-Ten solution in a 1-liter flask, then washed again with a 100-ml solution. The solvent extraction was carried out by transferring 100 ml Sur-Ten wash solution representing 5 g leaves into a 250-ml separatory funnel and extracting four times with 50 ml chloroform. The remaining residue was handled in the same manner as the punches except that a larger quantity of sodium sulfate was added to the blending operation: 100 g instead of 20 g.

To remove residues from fruit samples, four peaches were selected, weighed, and measured, taking the diameter of each peach through three mutually perpendicular axes. Surface area was calculated by averaging the diameters and assuming the peach was a sphere. The four peaches were transferred to a 1-gallon can, sealed with 500 ml Sur-Ten solution, and rolled for 1 hour. The wash solution was decanted and the peaches were given a final wash with 500 ml Sur-Ten solution for 30 minutes. Washes were combined and an aliquot equivalent to 50 g was extracted as described for leaf samples. Remainder or penetrated residues were extracted by chopping only the edible portion of the fruit in a Hobart food cutter. Fifty-g chopped peaches were transferred into a blender containing 50-g sodium sulfate. Two hundred ml chloroform was added to the blender and the contents were blended for 2 minutes. The extraction process was then handled according to the procedure discussed for remaining residue in leaf tissue.

LABORATORY ANALYSIS

Because leaf samples contained high levels of sulfur, which interferes with the analysis of parathion, paraoxon, and the s-ethyl isomer of parathion, the extract had to be cleaned for detection by gas-liquid chromatography (GLC). It was also desirable to develop a procedure by which paraoxon and the s-ethyl isomer could be separated from parathion prior to gas chromatography. Most GLC columns do not satisfactorily separate these materials, particularly when parathion has considerably more residue than the other two products. As a result there is an overlapping of GLC peaks which prevents satisfactory quantitative results.

The cleanup procedure involved column chromatography using florisil as the adsorbant. A glass column, 2 cm in diameter and 12 cm long with a 150-ml reservoir, was packed with 8 g PR grade florisil and pre-washed with 50 ml benzene. An extract of the sample in chloroform was evaporated to dryness and redissolved in 5 ml benzene. The sample was quantitatively transferred to the column and eluted with 50 ml benzene; the eluate caused an interfering sulfur response which was discarded. Eighty ml 5 percent ethyl ether by volume in benzene was transferred to the column; this fraction contained the parathion that was collected. The column was then eluted with 75 ml 8 percent acetone in benzene; this fraction contained paraoxon and the s-ethyl isomer of parathion. Depending on the quantity of residue present, the sample was evaporated to dryness and the volume was adjusted to facilitate gas chromatographic analysis.

Analyses were carried out with a Varian Aerograph Model 204 gas chromatograph equipped with a cesium bromide thermionic detector. Two gas chromatographic columns satisfactorily separated the three products. One column was a 2-ft-by- $\frac{1}{8}$ -in.-OD pyrex glass column packed with 5 percent (w/w) Dexsil 300 on 80/100 mesh Gas Chrom Q; the other column was a 2-ft-by- $\frac{1}{8}$ -in.-OD pyrex glass column packed with 5 percent Apiezon L on Gas Chrom Q, 80/100 mesh. Both columns were operated at 225° C with a slightly higher injection and detector temperature. Gas flow conditions were 19 cc/min for nitrogen, the carrier gas; 16 cc/min for hydrogen; and 150 cc/min for air.

Recovery studies for parathion, paraoxon, and the s-ethyl isomer of parathion were performed before and during the study. Samples of control leaves were taken from plots prior to application and were fortified on leaf tissues during extraction before addition of surfactant solution. Samples of control peaches were taken at harvest from trees not sprayed with parathion. Two levels of fortification at 0.1 and 1.0 ppm were made for each chemical analyzed. All recovered residues were based on total residue; that found in the surfactant

solution plus the remainder found in the chloroform extract.

Results and Discussion

The method employed to separate and detect parathion, paraoxon, and the s-ethyl isomer of parathion on and in peach leaves and fruit is reproducible and can detect residues as low as 0.01, 0.02, and 0.02 ppm, respectively, for each of the three chemicals. Fortified control studies at the 0.1 and 1.0 ppm level ranged between 90 and 100 percent, 85 and 95 percent, and 70 and 85 percent, respectively, for parathion, paraoxon, and the s-ethyl isomer. None of the data reported were based on or corrected for percent recovery. Residues found were frequently confirmed by repeated analysis and by using both the Apiezon L and the Dexsil 300 columns. Further confirmation would have been desirable through gas-liquid chromatography/mass spectrometry and other detection systems; however, such instrumentation was not available.

Recent reports (5,7) have shown that dislodgable residue is the principal means by which agricultural workers are exposed to pesticides. There are two means of measuring this dislodgable portion of the pesticide: one uses a weight basis in which data are usually reported in ppm; the other involves surface area only and is expressed as $\mu\text{g}/\text{cm}^2$. Figures 1-3 illustrate the difference between expressing data as ppm and as $\mu\text{g}/\text{cm}^2 \times 10^{-2}$. Taking into consideration normal field and laboratory variability, there appears to be very little difference between the two measurements with peach leaves. This is likely a result of the uniform density of the peach leaves. Once such uniformity has been established, data can be expressed in either form so long as one remembers that ultimately all dislodgable residue data must be understood in terms of surface residue to which a worker may be exposed. Table 1 compares this relationship with a final standard deviation between individual samplings for the ratio of $\text{ppm}/\mu\text{g cm}^2 \times 10^{-2}$. For each formulation the standard deviation did not exceed 0.09.

The most practical way of measuring the dislodgable residue on surface foliage is through a representative punched sample. On the other hand, the punched sample is usually taken near the center of the leaf or foliage. This may not be representative of the total leaf surface because on high-volume applications some investigators have observed that residues on peach leaves appear to have their greatest deposition on the periphery of the leaf, particularly the tip. Therefore this study involved both whole-leaf sampling and punch sampling. Figures 4-6 show total and dislodgable residues expressed on a weight basis (ppm) of the whole-leaf versus the punched samples for each of the three formula-

tions. In all three formulations total residues found were similar in both types of sampling; yet the dislodgable portion of the total residue appeared to differ depending on whether punched or whole-leaf samples had been taken. It is difficult to understand why this difference exists, but current studies indicate that higher dislodgable residues in punched samples are primarily due to the extraction procedure, which is slightly different from that of whole-leaf samples in the ratio of surfac-

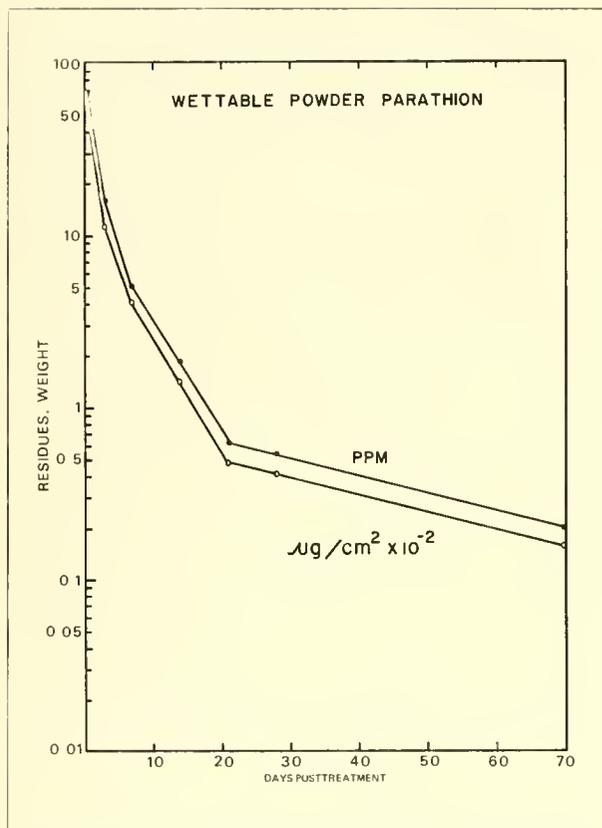


FIGURE 1. Parathion residues from punched peach leaf samples following application of wetttable powder formulation at 2 lb a.i./acre

tant to total crop material. Until this difference can be resolved it is recommended that punched samples be used for analysis of dislodgable residues.

When dislodgable residues are discussed for the encapsulated formulation, they do not indicate residue levels to which a worker may be exposed; the capsule minimizes actual dermal exposure of the worker to the pesticide while extending the residual life of the active ingredient. The extraction procedure in this study removed the microcapsule containing the insecticide and any other residue that might be considered dislodgable from the leaf surface. Once the encapsulated product has been removed, the pesticide contained in the capsule

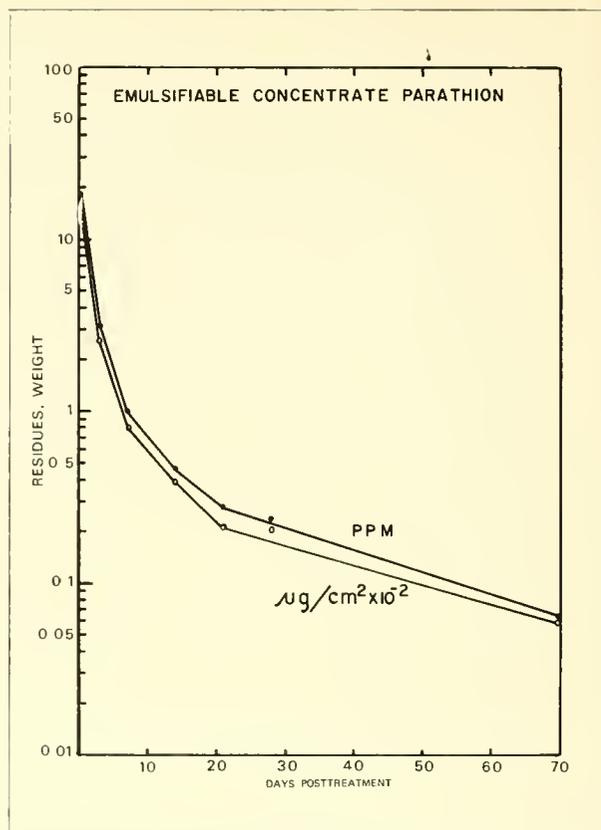


FIGURE 2. Parathion residues from punched peach leaf samples following application of emulsifiable concentrate formulation at 1 lb a.i./acre

is extracted with a soluble organic solvent and nearly all the active pesticide is retrieved. Hence the plastic capsule does not act as a barrier between the pesticide and the solvent.

Formulations played a major role in comparing percents of dislodgable residue removed. The percentage of dislodgable residue in the EC formulation from punched samples ranged between 17 and 33 percent with an average of 25 percent for seven sampling periods. The WP formulation gave a higher percent of dislodgable residue and ranged between 43 and 61 percent with an average of 47 percent for seven sampling periods.

Residue levels throughout the growing season degraded as one might expect with EC and WP parathion. With Enc. parathion the degradation as expressed by the slope was flatter, as anticipated. The percentage of dislodgable parathion compared to the remaining residue was considerably higher; about two-thirds of the total residue was dislodgable. Again it should be emphasized that with this particular formulation dislodgable residues include both capsulated and noncapsulated

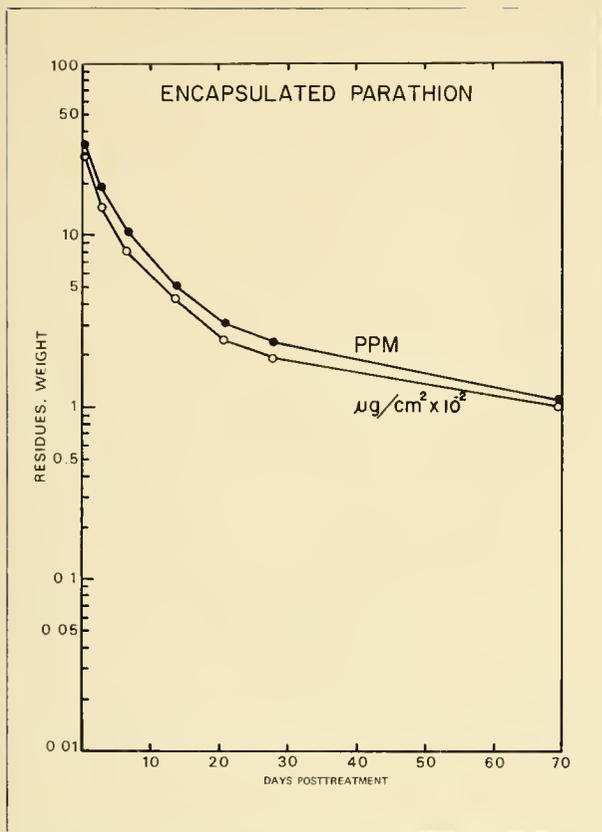


FIGURE 3. Parathion residues from punched peach leaf samples following application of encapsulated formulation at 1 lb a.i./acre

forms. What this means in actual exposure through oral and dermal contact cannot be ascertained from this study; additional work is needed to determine whether the parathion is actually in an exposed form. Enc. parathion resulted in punched-leaf residues of 1.12 ppm or 10 $\mu\text{g}/\text{cm}^2$ at time of harvest. Whole-leaf samples had residues of 0.76 ppm or 7 $\mu\text{g}/\text{cm}^2$ on 70-day harvest samples.

Paraoxon and the s-ethyl isomer, two potentially toxic degradation products of parathion, were also included in the study. Punched samples were limited so all analyses conducted for these two products are reported for whole-leaf samples only. Figure 7 shows the degradation of paraoxon throughout the 70-day study for each of the three formulations. Analyses were also separated according to their total and dislodgeable resi-

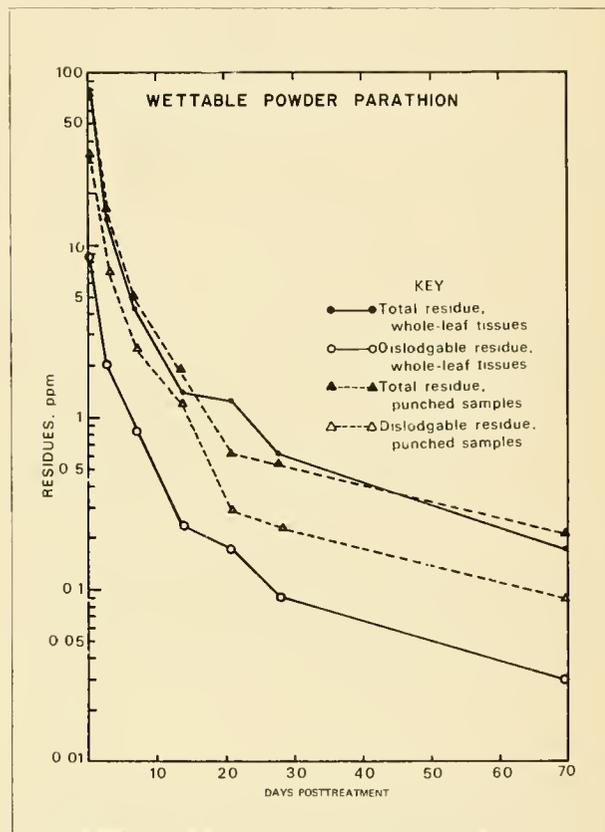


FIGURE 4. Parathion residues on and in whole peach leaf samples following application of wettable powder formulation at 2 lb a.i./acre

TABLE 1. Parathion residues in punched peach leaf samples

DAYS POST-TREATMENT	WETTABLE POWDER			EMULSIFIABLE CONCENTRATE			ENCAPSULATED PARATHION		
	PPM	$\mu\text{G}/\text{CM}^2 \times 10^{-2}$	PPM	PPM	$\mu\text{G}/\text{CM}^2 \times 10^{-2}$	PPM	PPM	$\mu\text{G}/\text{CM}^2 \times 10^{-2}$	PPM
0	69.5	60.8	1.14	18.4	14.7	1.25	34.9	31.5	1.11
3	16.0	11.4	1.41	3.16	2.64	1.20	19.6	14.6	1.34
7	5.12	41.5	1.23	1.00	0.815	1.23	10.4	8.02	1.30
14	1.88	1.45	1.30	0.47	0.387	1.21	5.18	4.27	1.21
21	0.62	0.488	1.27	0.28	0.214	1.31	3.11	2.48	1.25
28	0.54	0.415	1.30	0.24	0.204	1.18	2.40	1.96	1.22
70	0.20	0.157	1.27	0.065	0.060	1.08	1.12	1.03	1.09
Average			1.27			1.21			1.22
Standard deviation			0.0755			0.0653			0.0852

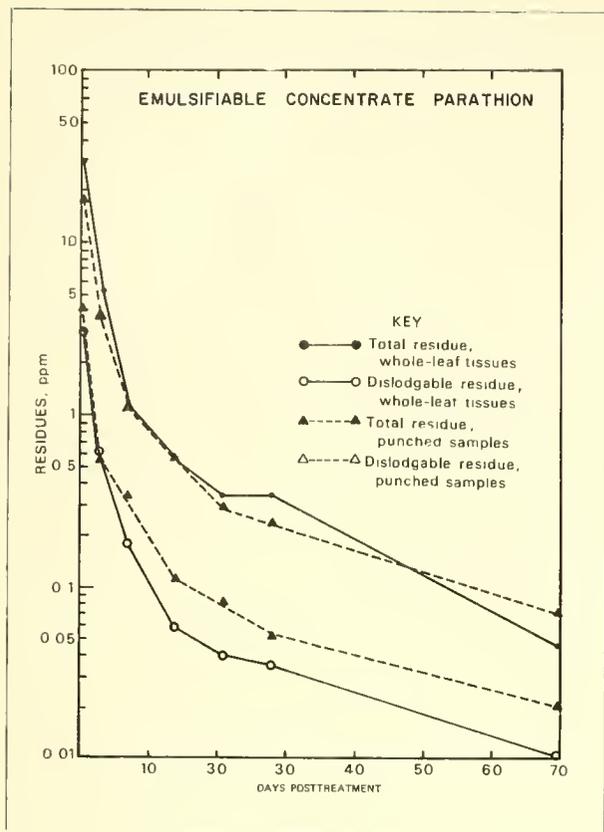


FIGURE 5. Parathion residues on and in whole peach leaf samples following application of emulsifiable concentrate formulation at 1 lb a.i./acre

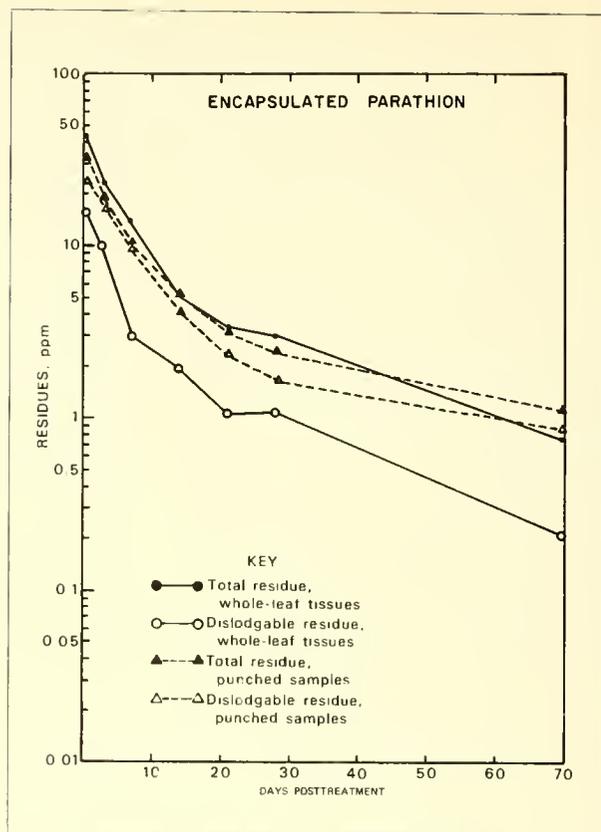


FIGURE 6. Parathion residues on and in peach leaves following application of encapsulated formulation at 1 lb a.i./acre

dues. Paraoxon was lowest with the EC formulation and was below the detectable limit the second day of sampling. Samples sprayed with the WP and Enc. formulations contained considerably higher levels of paraoxon than the EC formulation; the rate of degradation was similar to parathion, particularly after the third post-application day. Paraoxon was barely detectable (0.01 ppm) at harvesttime. The greater percentage of paraoxon residue was found in the dislodgeable form. This could be attributed to either the fact that paraoxon has greater polarity than parathion, which would make it more extractable in the aqueous solvent, or to the difference in rate of surface degradation compared to metabolic degradation.

The *s*-ethyl isomer of parathion was detected in only very small quantities the first few days after application of the WP and Enc. formulations and was not at all detectable after the EC applications. Using the Enc. formulation, the residue declined from 0.11 ppm the day of application to 0.04 ppm the third day following

application. With the WP formulation, the residue declined from 0.28 ppm to 0.05 ppm during this same period. Nearly all residue from the Enc. application was in the dislodgeable form; 50 percent of the WP application was in dislodgeable form. This study indicates that residues of the *s*-ethyl isomer were low enough to be excluded from future studies involving parathion on peach trees.

All dislodgeable and remainder residues on harvested fruit samples were less than 0.01 ppm parathion. Neither paraoxon nor the *s*-ethyl isomer could be found on fruit samples.

Acknowledgment

Authors gratefully acknowledge the assistance of Warren Dow, who supplied the 60 acres of peaches on which this study was conducted. Our thanks go also to Chevron Chemical Company and the Penwalt Corporation, who supplied formulations used in this study.

LITERATURE CITED

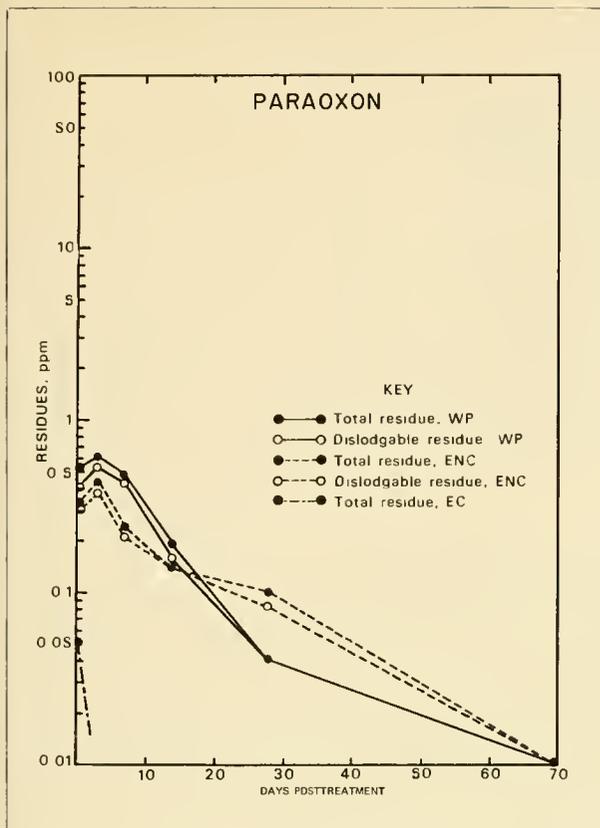


FIGURE 7. Paraoxon on and in peach leaves following parathion application

- (1) Bailey, J. B., D. Mengle, and D. H. Flaherty. 1972. Pesticide residues on grape leaves evaluated for adverse effects on grape pickers as related to worker re-entry periods. Unpublished report.
- (2) Carman, G. E., W. E. Westlake, and F. A. Gunther. 1972. Potential residue problem associated with low volume sprays on citrus in California. Bull. Environ. Contam. Toxicol. 8(1):38-45.
- (3) Gunther, F. A. 1969. Insecticide residues in California citrus fruits and products. Residue Rev. 28:1-119.
- (4) Kilgore, W. W., N. Marei, and W. Winterlin. 1971. Parathion in plant tissues: new considerations. Notes from National Academy of Sciences symposium on degradation of organic molecules in the biosphere, San Francisco, pp. 291-312.
- (5) Westlake, W. E., F. A. Gunther, and G. E. Carman. 1973. Worker environment research. Dioxathion (Delnav) residues on and in orange fruits and leaves, in dislodgable particulate matter, and in the soil beneath sprayed trees. Arch. Environ. Contam. Toxicol. 1(1):60-83.
- (6) Winterlin, W., C. Mourer, and J. B. Bailey. 1974. Degradation of four organophosphate insecticides in grape tissues. Pestic. Monit. J. 8(1):59-65.
- (7) Gunther, F. A., W. E. Westlake, J. H. Barkley, W. Winterlin, and L. Langbehn. 1973. Establishing dislodgable pesticide residues on leaf surfaces. Bull. Environ. Contam. Toxicol. 9(4):243-249.
- (8) Durham, W. F. 1967. The interaction of pesticides with other factors. Residue Rev. 18:21-103.
- (9) Hull, H. 1970. Leaf structure as related to absorption of pesticides and other compounds. Residue Rev. 31:1-151.
- (10) El-Rafai, A., and T. L. Hopkins. 1966. Parathion absorption, translocation and conversion to paraoxon in bean plants. J. Agr. Food Chem. 14(6):588-592.
- (11) Bailey, J. B. 1973. Pesticide residues on peach leaves related to worker reentry periods. 168th Nat. Am. Chem. Soc. Meeting, Los Angeles, Calif., April 3, 1973.

APPENDIX

Chemical Names of Compounds Discussed in This Issue

ALDRIN	Not less than 95% of 1,2,3,4,10,10-Hexachloro-1,4,4a,5,8,8a-hexahydro-1,4- <i>endo-exo</i> -5,8-dimethanonaphthalene
BHC (BENZENE HEXACHLORIDE)	1,2,3,4,5,6-Hexachlorocyclohexane (mixture of isomers). Commercial product contains several isomers of which <i>gamma</i> is most active as an insecticide.
CHLORDANE	1,2,3,4,5,6,7,8-Octachloro-2,3,3a,4,7,7a-hexahydro-4,7-methanoindane. The technical product is a mixture of several compounds including heptachlor, chlordene, and two isomer forms of chlordane.
DDD	See TDE.
DDE	Dichlorodiphenyl dichloro-ethylene (degradation product of DDT) Main component (<i>p,p'</i> -DDE): 1,1-Dichloro-2,2 bis(<i>p</i> -chlorophenyl) ethylene <i>o,p'</i> -DDE: 1,1-Dichloro-2-(<i>o</i> -chlorophenyl)-2-(<i>p</i> -chlorophenyl) ethylene
DDT	Main component (<i>p,p'</i> -DDT): 1,1,1-Trichloro-2,2-bis(<i>p</i> -chlorophenyl) ethane. Other isomers are possible and some are present in the commercial product. <i>o,p'</i> -DDT: [1,1,1-Trichloro-2-(<i>o</i> -chlorophenyl)-2-(<i>p</i> -chlorophenyl) ethane]
DIELDRIN	Not less than 85% of 1,2,3,4,10,10-Hexachloro-6,7-epoxy-1,4,4a,5,6,7,8,8a-octahydro-1,4- <i>endo-exo</i> -5,8-dimethanonaphthalene
ENDRIN	1,2,3,4,10,10-Hexachloro-6,7-epoxy-1,4,4a,5,6,7,8,8a-octahydro-1,4- <i>endo-endo</i> -5,8-dimethanonaphthalene
ETHYLENETHIOUREA	2-Imidazolidinethione
HCB	Hexachlorobenzene
HEPTACHLOR	1,4,5,6,7,8,8-Heptachloro-3a,4,7,7a-tetrahydro-4,7- <i>endo</i> -methanoindene
HEPTACHLOR EPOXIDE	1,4,5,6,7,8,8-Heptachloro 2,3-epoxy-3a,4,7,7a-tetrahydro-4,7-methanoindane
LINDANE	<i>Gamma</i> isomer of benzene hexachloride (1,2,3,4,5,6-hexachlorocyclohexane) of 99+% purity
MALATHION	<i>S</i> -[1,2-Bis(ethoxycarbonyl)ethyl] <i>O,O</i> -dimethyl phosphorodithioate
METHOXYCHLOR	1,1,1-Trichloro-2,2-bis(<i>p</i> -methoxyphenyl) ethane
OXYCHLORDANE	1,2,4,5,6,7,8,8-Octachloro-1,2-epoxy-3a,4,7,7a-tetrahydro-4,7-methanoindan
PCB'S (POLYCHLORINATED BIPHENYLS)	Mixtures of chlorinated biphenyl compounds having various percentages of chloride
TDE	1,1-Dichloro-2,2-bis(<i>p</i> -chlorophenyl) ethane. Technical TDE contains some <i>o,p'</i> -isomer also.
TOXAPHENE	Chlorinated camphene (67-69% chlorine). Product is a mixture of polychlorinated bicyclic terpenes with chlorinated camphenes predominating.

ERRATUM

PESTICIDES MONITORING JOURNAL, Volume 7, Number 3/4, p. 139. In the paper "Levels of Mirex and Some Other Organochlorine Residues in Seafood from Atlantic and Gulf Coastal States," a quotation of P. A. Butler's article "Monitoring Pesticide Pollution" [*Bio-Science*, 19(10)], which stated that mirex was "one of the most abundant of the organochlorine pesticides found in shellfish off the Atlantic, Gulf, and Pacific coasts," was misleading. Butler actually stated, "Although each sample is screened for 10 or more pesticides, DDT (including its metabolites) is the only one commonly present. Dieldrin is next in frequency of occurrence, followed by endrin, toxaphene, and mirex."

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SUBJECT AND AUTHOR INDEXES

Volume 8, June 1974—March 1975

Preface

Primary headings in the subject index consist of pesticide compounds, the media in which residues are monitored, and several concept headings, as follows:

Pesticide Compounds (listed alphabetically by common name or trade name when there is no common name)

Media and Concept Headings

- Air
- Degradation
- Experimental Design
- Factors Influencing Residues
- Food and Feed
- Household Items
- Humans
- Plants (other than those used for food and feed)
- Sediment
- Soil
- Water
- Wildlife

Compound headings are also used as secondary headings under the primary media and concept headings and vice versa.* When a particular paper discusses five or more organochlorines, the compounds are grouped by class under the media or concept headings; in the primary headings, however, all compounds are listed individually. The specific compounds or elements which have

been grouped in various combinations by class for certain papers are as follows:

Organochlorines

- aldrin
- BHC/lindane
- chlordane
- chlorobenzilate
- DDE
- DDMU
- DDT
- dicofol
- dieldrin
- endosulfan
- endrin
- heptachlor
- heptachlor epoxide
- methoxychlor
- mirex
- nonachlor
- oxychlordane
- perthane
- Strobane®
- TDE
- toxaphene

In the author index, the names of both senior and junior authors appear alphabetically. Full citation is given, however, only under the senior author, with a reference to the senior author appearing under junior authors.

* Note: With the exception of 8(2):69-97 and 8(2):110-124 in which no compounds are used as secondary headings.

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