The *Pesticides Monitoring Journal* is published quarterly under the auspices of the Federal Working Group on Pest Management (responsible to the Council on Environmental Quality) and its Monitoring Panel as a source of information on pesticide levels relative to humans and their environment.

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

The 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 Monitoring Panel which participate in operation of the national pesticides monitoring network, are expected to be the principal sources of data and articles. However, pertinent data in summarized form, together with 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. Publication of scientific data, general information, trade names, and commercial sources in the *Pesticides Monitoring Journal* does not represent endorsement by any Federal agency.

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. For further information on Journal scope and manuscript preparation, see Information for Contributors at the back of this issue.

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EDITORIAL

Journal Enters Tenth Year; Expands Information for Contributors

Scanning the first nine volumes of the *Pesticides Monitoring Journal,* the researcher is struck by two traditions: that the publication has honored its primary goal of disseminating findings of the National Pesticides Monitoring Program, and that those findings have been presented intelligibly. It is appropriate that this, the tenth volume of the Journal, should introduce a revised Information for Contributors (see back page of this issue). A periodical in its tenth year of publication should be able to draw on its own history in refining subject matter and editorial policy.

In 1967 the scope of the Journal was described as "qualified data and interpretive information which contribute to the understanding and evaluation of pesticides and their residues in relation to man and his environment." Since that first issue authors, reviewers, advisors, and editors have proved this to be a workable definition for a specialized technical journal with worldwide distribution. As each contributor projected his/her interpretation of the scope in the varied studies published here, certain refinements emerged. These refinements are reflected in the definition of monitoring which appears in this issue: "repeated sampling and analysis of environmental components to obtain reliable estimates of levels of pesticide residues and related compounds in these components and the changes in these levels with time. It can include the recording of residues at a given time and place, or the comparison of residues in different geographic areas."

No less significant than the scope of a publication is the manner of its presentation. The most dramatic findings in the scientific world are valuable only so far as they are understood by the reader. Thus the revised Information for Contributors contains expanded instructions for authors in the preparation of manuscripts. The Journal staff consulted numerous style manuals, technical publications, and Federal and private-industry editors to achieve a consensus on controversial points. Style policies are listed in sometimes scrupulous detail, as befits a publication striving to present technical findings consistently and lucidly to an international audience. Appropriate idiosyncrasies appear: recycled paper, for example, is acceptable in original manuscripts if it does not degrade the quality of reproduction. The manner of citing literature references has been simplified to meet author demand: sources are numbered in alphabetical order rather than in order of their appearance in the text.

Criteria established by the Journal staff and the Editorial Advisory Board and approved by the Monitoring Panel are the fruits of a decade of author/editor communication. We are fortunate. Almost unanimously our authors have been cooperative. They are ripe for ideas which render their papers readable and credible, and eager to offer their own suggestions on scope and delivery of monitoring studies. Such cooperation among professionals has served us well. Throughout the world the *Pesticides Monitoring Journal* is considered an authoritative source of information on the monitoring of pesticide residues.

BRIEF

Residues of DDT and DDE in Livers of Waterfowl, Northeastern Louisiana—1970-71 [1]

Donald H. White [2]

ABSTRACT

A study was conducted to determine the levels of DDT and DDE in the livers of 10 species of waterfowl collected in Louisiana from 1970 to 1971. Livers of 48 of 50 specimens contained detectable levels of DDT and/or DDE. DDT residues ranged from 0.01 to 10.90 ppm; DDE levels ranged from 0.02 to 38.69 ppm.

Introduction

Residues of DDT and its metabolites are commonly found in tissues and eggs of waterfowl species (*9*). DDE is by far the most persistent metabolite and occurs most frequently in nature; residues may range from barely detectable levels to hundreds of ppm in certain tissues (*7*). DDE has impaired reproductive success of mallards (*Anas platyrhynchos*) and black ducks (*Anas rubripes*) in experimental studies, resulting in thin shells, cracked eggs, and poor hatchability (*3,5*).

Because organochlorines are highly fat-soluble, residues concentrate in adipose tissues. The extent of this concentration depends upon the exposure and the physiological condition of the organism determined by biological demands such as migration, feeding activity, and reproduction (*9*). When analyzed for organochlorines, adipose tissues or whole bodies of organisms give some indication of their past history of pesticide exposure.

Studies of Japanese quail (*Coturnix coturnix japonica*) showed that DDE reached peak levels in the liver about 3 weeks after initial exposure and then rapidly declined (*6*). In another study, a known concentration of radiolabeled DDT was applied to a fenced 4-acre marsh (*2*). Wild mallards and lesser scaup (*Aythya affinis*) were released intermittently into the area. Ducks were collected and their tissues were analyzed for DDT and/or its metabolites. Residues in duck livers generally peaked about 2 weeks after application and then declined. Thus the avian liver does not appear to be a major accumulator of organochlorine residues. However, high residues in the liver may reflect recent ingestion of contaminated food items when the animal is not exposed to a continuous level of toxicant.

Collection and Analytical Procedures

Waterfowl were shot at several locations within Ouachita Parish in northeastern Louisiana during the fall and winter of 1970-71. The ducks were frozen soon after collection and maintained in a freezer until analysis. Five livers from each of 10 species of duck were analyzed for residues of DDT and DDE.

DDT and DDE were extracted from the livers following essentially the methods of Boyle et al. (*1*). Each duck was thawed and the liver was dissected from the body and weighed. The liver was homogenized in a Waring blendor with 5 g Na_2SO_4 and 175 ml hexane. The supernatant was decanted, the process was repeated, and the combined supernatants were filtered to remove large particles of liver tissue. The hexane solution was evaporated to near dryness on a steam bath, diluted to 25 ml with hexane, and transferred to a 125-ml separatory funnel. Four 25-ml volumes of acetonitrile were added to the separatory funnel and each volume was drained off as it layered on the bottom of the hexane solution. The acetonitrile fractions were combined, evaporated to dryness on a steam bath, and diluted to 10 ml with hexane.

The sample was placed on a column of previously standardized florisil and eluted with 500 ml of a 9:1 hexane : petroleum ether solution. After florisil cleanup the eluate was evaporated to dryness on a steam bath and diluted to 2 ml with hexane. This final extract was analyzed for DDT and DDE residues.

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Determinations were made by injecting 1 μl of the sample solutions into a Hewlett-Packard model 402 gas chromatograph with an electron-capture detector. The column was glass, 4 ft by 4 mm, packed with 4 percent SE-30 80/100 mesh chromosorb W-AWDMCS. Temperatures for column, injector, and detector were 180°, 225°, and 255°C, respectively. Carrier gas was 5 percent methane in argon at 80 ml/min.

DDT and DDE in the samples were tentatively identified by comparing retention times with those of standard solutions. All residues then were confirmed by thin-layer chromatography (TLC) according to the method of Morley and Chiba (*4*). Some PCB interference may be reflected in the DDT results, although TLC did not indicate any.

All residues are expressed as ppm wet weight. Limits of sensitivity were 0.01 ppm for both DDT and DDE. Recovery percentages from spiked samples averaged 94 percent for DDT and 90 percent for DDE. Analytical results were not corrected for recovery.

Results and Discussion

Table 1 shows the means, standard errors, and ranges of DDE and DDT residues in livers of ducks collected in Louisiana during the fall and winter months of 1970-71. Forty-eight of the 50 livers analyzed had detectable levels of DDE, DDT, or both. There was wide variation in concentrations of the two compounds among species and individuals. Detectable residues of DDE in livers ranged from 0.02 to 38.69 ppm; DDT levels ranged from 0.01 to 10.90 ppm. Four samples contained trace residues of dieldrin.

Livers from northern shovelers (*Anas clypeata*), blue-winged teal (*Anas discors*), and green-winged teal (*Anas crecca carolinensis*) contained the highest mean residues of DDE and/or DDT. These species commonly feed in very shallow water and are often found together (*8*). Although the ducks were collected in northeastern Louisiana, findings should not be interpreted on a local basis since waterfowl are highly mobile species and may cover a wide range of habitats. The data do suggest however, that some of the ducks may have eaten highly contaminated food items.

LITERATURE CITED

(*1*) *Boyle, H. W., R. H. Burtschell, and A. A. Rosen. 1966.* Infrared identification of chlorinated insecticides of poisoned fish. Org. Pestic. Environ. 60:207-218.

(*2*) *Dindal, D. L. 1970.* Accumulation and excretion of Cl^{36} DDT in mallard and lesser scaup ducks. J. Wildl. Manage. 34(2):74-92.

(*3*) *Heath, R. G., J. W. Spann, and J. F. Kreitzer. 1969.* Marked DDE impairment of mallard reproduction in controlled studies. Nature 224(5214):47-48.

(*4*) *Morley, H. V., and M. Chiba. 1964.* Thin-layer chromatography for chlorinated pesticide residue analysis without cleanup. J. Ass. Offic. Anal. Chem. 47(2): 307-309.

(*5*) *Longcore, J. R., F. B. Samson, and T. W. Whittendale. 1971.* DDE thins eggshells and lowers reproductive success of captive black ducks. Bull. Environ. Contam. Toxicol. 6(6):485-490.

(*6*) *Ludke, J. L. 1974.* Interaction of dieldrin and DDE residues in Japanese quail (*Coturnix coturnix japonica*). Bull. Environ. Contam. Toxicol. 11(4):297-302.

(*7*) *Stickel, L. F. 1968.* Organochlorine Pesticides in the Environment. Spec. Sci. Rep.—Wildl. No. 119. Washington, D.C. 32 pp.

(*8*) *White, D. H. 1975.* Environments of Fresh Water Feeding Sites of Waterfowl in Autumn on the Welder Wildlife Refuge in Southern Texas. Ph.D. thesis, Univ. Ark., Fayetteville, Ark. 62 pp.

(*9*) *White, D. H., and L. F. Stickel. 1975.* Impacts of chemicals on waterfowl reproduction and survival. Trans. First Int. Waterfowl Symp., St. Louis. Pp. 132-142.

TABLE 1. *Residues of DDE and DDT in livers of waterfowl, northeastern Louisiana—1970-71*

Species	Residues, ppm Wet Weight [1]			
	DDE		DDT	
	$\bar{X} \pm$ S.E.	Range	$\bar{X} \pm$ S.E.	Range
Mallard (*Anas platyrhynchos*)	0.76 ± 0.20	0.33 — 1.37	0.59 ± 0.52	TR — 2.95
Pintail (*Anas acuta*)	0.47 ± 0.14	0.13 — 1.06	1.28 ± 0.46	TR — 2.40
Gadwall (*Anas strepera*)	0.56 ± 0.09	ND — 0.56	0.32 ± 0.29	ND — 1.64
American Wigeon (*Anas americana*)	0.36 ± 0.21	ND — 1.21	0.39 ± 0.35	ND — 1.95
Northern Shoveler (*Anas clypeata*)	8.63 ± 4.14	0.35 — 26.67	0.03 ± 0.03	TR — 0.19
Blue-Winged Teal (*Anas discors*)	12.47 ± 6.50	1.68 — 38.69	0.16 ± 0.11	TR — 0.65
American Green-Winged Teal (*Anas crecca carolinensis*)	1.32 ± 0.30	0.55 — 2.55	4.54 ± 2.03	TR — 10.90
Wood Duck (*Aix sponsa*)	0.16 ± 0.03	0.02 — 0.22	2.26 ± 0.86	TR — 4.41
Ring-Necked Duck (*Aythya collaris*)	1.26 ± 0.82	0.06 — 4.94	0.92 ± 0.65	TR — 3.80
Lesser Scaup (*Aythya affinis*)	0.17 ± 0.03	0.09 — 0.31	0.03 ± 0.02	ND — 0.10

NOTE: ND = not detected.
TR = trace residues detected below limit of quantification, 0.01 ppm.
S.E. = standard error.

[1] Results represent residues in livers of five birds of each species.

Uptake of the Mosquito Larvicide Temefos by the Salt Marsh Snail, New Jersey—1973-74 [1,2]

George Fitzpatrick [3] and Donald J. Sutherland [4]

ABSTRACT

Uptake of the mosquito larvicide temefos (Abate) by the salt march snail (Melampus bidentatus *Say*) *in New Jersey was measured by gas-chromatographic analysis. Measurable quantities of temefos were found in the snails within 1 day after the first treatment with a 2 percent granular formulation but 3 weeks elapsed before uptake occurred following treatment with a temefos emulsion. Residues in the snails exposed to the granular formulation were generally more than 10 times higher than those in snails exposed to the emulsion although application rates of the granular formulation were only about three times higher than those of the emulsion.*

Residues in snails exposed to the emulsion fell below detectable levels less than 3 weeks after cessation of treatments although measurable amounts were found in snails exposed to the granular formulation for more than 5 weeks after the last treatment. The persistence of temefos in M. bidentatus *suggests the potential for its movement through food webs exposed to the granular formulation.*

Introduction

Since the decline in use of persistent insecticides, the role of relatively nonpersistent organophosphorous compounds in mosquito control programs has been increasing (*10*). At present, the organophosphorous insecticide temefos, also known as Abate, is the larvicide most frequently used in New Jersey for salt marsh mosquito control (*12*).

The salt marsh snail (*Melampus bidentatus* [Basommatophora: Melampidae]), which is generally less than 10 mm long, occurs in large numbers in the high littoral zone, areas of salt marshes flooded infrequently by high tides (*1,9*). Coincidentally, the high littoral zone is the habitat most suitable for salt marsh mosquito breeding (*8*). Therefore, insecticides for control of salt marsh mosquito larvae are frequently applied to marshes harboring large populations of *M. bidentatus*, an important food source for a number of animals (*3,7*). Measurable residues of DDT have been detected in *M. bidentatus* from treated marshes (*3,5*).

The objectives of the present study were to determine the magnitude and rate of temefos uptake by *M. bidentatus* in salt marshes subjected to multiple treatments, and the persistence of temefos residues in snails after cessation of treatments.

Materials and Methods

Treatments with a 2 percent granular formulation at 0.112 kg actual insecticide/ha. (0.10 lb/acre) included four applications to a *Spartina alterniflora* salt marsh plot at approximately 2-week intervals in 1973 and 10 applications to an *S. patens* salt marsh plot at approximately 2-week intervals in 1973. In 1974 an *S. patens* salt marsh plot was treated approximately every other week for 8 weeks, then once again in approximately 6 weeks. All granular formulations were applied to a salt marsh plot near Tuckerton, N.J. Treatments with a temefos emulsion at 0.037 kg actual insecticide/ha. (0.032 lb/acre) consisted of four applications at approximately 2-week intervals to an *S. patens* salt marsh plot near Manahawkin, N.J., in 1974. All applications were made by a Bell 47G4 helicopter, flying at 96.5 km/h (60 mph) at an altitude of 3.0-6.1 m (10-20 ft). The working swath width was 10.7 m (35 ft) for the granular formulations and 15.2 m (50 ft) for the emulsion. The treated areas have been described previously (*4*).

Samples of *M. bidentatus* were collected from the treated plots, placed on ice, and frozen within 2.5 hours after collection. Each sample was a composite of at least 15 snails; differences in weights of various samples reflect differences in snail sizes and availability of snails.

[1] Paper of the Journal Series, New Jersey Agricultural Experiment Station, Rutgers, The State University of New Jersey, New Brunswick, N.J.

[2] Presented in part to the Entomological Society of America, Eastern Branch, Philadelphia, Pa., October 13, 1975.

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Before extraction, the snails were washed to remove grass, mud, or granular particles, then blotted dry on paper towels.

Temefos was extracted three times in methylene chloride from whole-snail homogenate which included the shell. Extracts were washed twice in distilled water and cleaned with hexane and acetonitrile. Final preparations were dissolved in acetone for injection into the gas chromatograph. Further details of the extraction and cleanup have been published elsewhere (*4*). Recovery was 97 percent.

The gas chromatograph used was a Micro-Tek model 220 with a flame photometric detector utilizing the phosphorous mode. The glass column was 6 mm (0.25 in.) OD, 4 mm ID, and 40.6 cm (16.0 in.) long. It was packed with 2 percent OV-101 on 80-100 mesh Gas-Chrom Q. Off-column injections were made utilizing a glass insert containing silanized glass wool approximately 1.3 cm (0.5 in.) from the point of release of the sample from the injection needle. Inlet temperature was 270°C, column temperature was 230°C, and detector temperature was 220°C. The carrier gas was prepurified nitrogen and the flow rate was 100 ml/min.

Residues in the snails including shells are expressed in ppm wet weight. Average water content was 29 percent of the total wet weight including shells.

Results and Discussion

M. bidentatus samples from untreated salt marsh plots and snail samples taken in the test plots before the first treatment were free of temefos. The limits of detectability varied with the weight of the sample and day-to-day fluctuations in the sensitivity of the gas chromatograph; for samples weighing between 1 and 2 g, the sensitivity was about 0.01 ppm.

Measurable uptake of temefos was observed in samples of *M. bidentatus* from the plots treated with either the emulsion or granular formulations. In 1974 snails from the *S. patens* plot treated with the granular formulations contained 0.09 ppm temefos residue 1 day after the first treatment (Table 1). In 1973 samples were taken 9 days after the first treatment; the residue was 0.44 ppm in the *S. patens* plot (Table 2), and 1.10 ppm in the *S. alterniflora* plot (Table 3). In contrast, uptake of temefos did not occur in *M. bidentatus* from the *S. patens* plot treated with the emulsion in 1974 until 6 days after the second treatment and 20 days after the first. At that time a residue of 0.038 ppm was detected (Table 4). In the first 17 days of this 20-day period, the three samples taken contained no measurable residues of temefos.

In general, levels of temefos were much lower in snails exposed to the emulsion than in those exposed to the granular formulation. The highest residue in snails from the emulsion-treated plot was 0.059 ppm after four treatments; the highest residue found in snails exposed to the granular formulation was 8.75 ppm after nine treatments. Moreover, there were eight samples from granu-

TABLE 1. *Temefos residues in* Melampus bidentatus *sampled from a* Spartina patens *salt marsh plot treated five times with a 2 percent granular formulation, Tuckerton, N.J.—1974*

Treatment Date	Sampling Date	Sample Weight, g	Temefos residue, ppm wet weight
July 9	July 10	2.8	0.09
July 23	July 26	2.7	0.82
Aug. 6	Aug. 8	2.7	0.50
Aug. 20	Aug. 21	2.8	0.46
	Oct. 3	3.1	0.19
Oct. 7	Oct. 29	2.5	0.16
	Nov. 19	1.3	0.38

TABLE 2. *Temefos residues in* Melampus bidentatus *sampled from a* Spartina patens *salt marsh plot treated 10 times with a 2 percent granular formulation, Tuckerton, N.J.—1973*

Treatment Date	Sampling Date	Sample Weight, g	Temefos residue, ppm wet weight
	Apr. 23	1.4	<0.06
Apr. 25	May 2	2.3	0.44
	May 7	0.8	0.54
May 10	May 11	1.3	0.63
	May 21	1.5	0.83
May 23	May 27	0.9	6.67
	June 4	1.2	0.78
June 6	June 7	1.9	0.06
June 18	July 3	1.3	0.80
July 5	July 6	1.5	2.14
	July 17	2.1	0.77
July 18	July 19	1.1	0.69
	Aug. 3	2.1	1.05
Aug. 4	Aug 15	0.7	0.64
Aug. 17	Aug. 20	0.5	8.75
	Aug. 30	2.3	1.04
Sept. 4	Sept. 5	1.6	1.35

TABLE 3. *Temefos residues in* Melampus bidentatus *samples from a* Spartina alterniflora *salt marsh plot treated five times with a 2 percent granular formulation, Tuckerton, N.J.—1973*

Treatment Date	Sampling Date	Sample Weight, g	Temefos residue, ppm wet weight
Apr. 25	May 2	0.7	1.101
	May 7	0.2	1.336
May 10	May 11	0.4	0.386
May 23			
June 6	June 15	1.1	0.443

TABLE 4. *Temefos residues in* Melampus bidentatus *sampled from a* Spartina patens *salt marsh plot treated four times with an emulsion, Manahawkin, N.J.—1974*

Treatment Date	Sampling Date	Sample Weight, g	Temefos residue, ppm wet weight
July 2	July 3	4.6	<0.01
	July 11	4.7	<0.01
July 16	July 17	1.9	<0.02
	July 22	2.5	0.038
July 31	Aug. 1	4.1	0.013
Aug. 14	Aug. 15	2.7	0.031
	Aug. 27	2.6	0.059
	Sept. 5	6.5	<0.01
	Sept. 13	2.7	<0.03

lar-treated plots that had residues greater than 1.0 ppm, illustrating the general trend of higher residues in snails treated with this formulation.

The differences in uptake can be attributed to a number of factors. Chemical monitoring of the emulsion-treated plot revealed that the first treatment was applied at a very low actual rate: 26 percent of that expected (W. F. Carey, 1975. Analytical Chemist, Department of Entomology and Economic Zoology, Rutgers, The State University of New Jersey, New Brunswick, N.J.: personal communication). This could have been at least partly responsible for the absence of measurable uptake until after the second treatment. The actual amount of active ingredient applied per unit area with emulsion was approximately one third (37 g/ha.) the amount applied with the 2 percent granular formulation (112 g/ha.). Another factor to consider is the chance of a snail's ingesting a granule. If this occurred in only one snail in a sample, the influence on the total residue could be considerable. Highest residues occurred in snails collected during the 1973 tests when there were 10 granular treatments. Because there were fewer treatments in the 1974 tests, there was less temefos available for absorption by the snails.

There was generally a great deal of variability in residue levels in all time periods, especially in the 1973 tests which involved more samples. This may be attributed to an uneven deposition of the insecticide on the marsh. Granular formulations applied aerially often do not cover the target area uniformly (*11*). If the temefos applications did generate sporadic aggregations of granules, randomly selected samples of snails could have varied considerably in temefos residue levels.

Table 4 shows that temefos residues in snails exposed to four emulsifiable concentrate formulation treatments rose gradually as the number of treatments increased and then decreased to levels below the limits of detection after the last treatment. During this same treatment schedule the population density of *M. bidentatus* in the treated plot declined steadily as the number of treatments increased. After the last treatment snail density increased to pretreatment levels (*4*). There were no significant changes in population density in the untreated plots or in the plots treated with other insecticides. This material is to be presented elsewhere (*6*). Data indicate that the temefos residues in snails may be related to a significant but reversible decline in population density. Laboratory toxicity data suggest that these levels of temefos are not acutely toxic to *M. bidentatus* (*4*). It can be surmised, therefore, that treatments of temefos emulsion resulting in residues in *M. bidentatus* to levels approaching 0.059 ppm are likely to affect populations through an interaction involving some other component of the salt marsh community. The mechanism of the overall population decline is unknown.

Residues of temefos in *M. bidentatus* exposed to the granular formulation persisted for more than 5 weeks after the last of a series of treatments. This raises some serious questions concerning the longevity of this formulation in the environment. Recovery of temefos residues from *Spartina* roots and salt marsh mud more than 4 months after the last of a series of granular treatments has been reported (*2*). If toxicant release were to be protracted over a long period, the effects could be similar in some ways to those of a persistent insecticide, with potential for passage through food webs. However, temefos residues in samples taken from the plot treated with the emulsion were undetectable less than 3 weeks after the last treatment (Table 4).

Further research is necessary to determine the extent of temefos movement through food webs which might be exposed to multiple treatments of the granular formulation.

Acknowledgments

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LITERATURE CITED

(*1*) *Apley, M. L. 1970.* Field studies on life history, gonadal cycle, and reproductive periodicity in *Melampus bidentatus* (Pulmonata: Ellobiidae). Malacologia 10 (2):381-397.

(*2*) *Carey, W. F. 1974.* Initial studies of Abate® in a salt-marsh ecosystem—chemical studies. Proc. 61st Ann. Meet. N. J. Mosq. Exterm. Assoc. 61:129-137.

(*3*) *Ferrigno, F., L. G. MacNamara, and D. M. Jobbins. 1969.* Ecological approach for improved management of coastal meadowlands. Proc. 56th Ann. Meet. N. J. Mosq. Exterm. Assoc. 56:188-203.

(*4*) *Fitzpatrick, G. 1975.* Impact of Temefos and Other Mosquito Larvicides on the Salt Marsh Snail *Melampus bidentatus* Say (Basommatophora: Ellobiidae). Ph. D. thesis, Rutgers, The State University of New Jersey. 120 pp.

(*5*) *Foehrenbach, J. 1972.* Chlorinated pesticides in estuarine organisms. J. Water Poll. Cont. Fed. 44(4): 619-624.

(*6*) *Fitzpatrick, G., and D. J. Sutherland.* Impact of the mosquito larvicides temefos and chlorpyrifos on populations of the salt marsh snail *Melampus bidentatus* Say. In preparation.

(*7*) *Hausmann, S. A. 1932.* A contribution to the ecology of the salt marsh snail (*Melampus bidentatus*). Am. Nat. 66(707):541-545.

(*8*) *Headlee, T. J. 1945.* The Mosquitoes of New Jersey and Their Control. Rutgers University Press, New Brunswick, N.J. 326 pp.

(*9*) *Kerwin, J. A. 1972.* Distribution of the salt marsh snail (*Melampus bidentatus* Say) in relation to marsh plants in the Poropotank River area, Virginia. Chesapeake Sci. 13(2):150-153.

(*10*) *McDuffie, W. C., and D. E. Weidhaas. 1965.* The future outlook for new and improved materials and methods for mosquito control. Mosq. News 25(2): 85-91.

(*11*) *Sutherland, D. J., R. F. Schmidt, and G. Fitzpatrick. 1974.* Distribution patterns of Abate granules applied by helicopter. Mosq. News 34(3):320-324.

(*12*) *Ward, D. V. 1973.* Studies on environmental impact of organophosphorous pesticides on salt marshes. Proc. 60th Ann. Meet. N. J. Mosq. Exterm. Assoc. 60:28-34.

Mercury in Eggs of Aquatic Birds, Lake St. Clair—1973

Rey C. Stendell,[1] Harry M. Ohlendorf,[1] Erwin E. Klaas,[1,2] and James B. Elder [3]

ABSTRACT

Eggs from four species of aquatic birds inhabiting waterways of the Lake St. Clair region were collected in 1973 and analyzed for mercury. Species analyzed were mallard ducks (Anas platyrhynchos), *common terns* (Sterna hirundo), *black-crowned night herons* (Nycticorax nycticorax), *and great egrets* (Casmerodius albus). *Mallard eggs contained relatively low residue levels, <0.05-0.26 ppm, and common tern eggs contained the highest residues, ranging up to 1.31 ppm. Mercury levels in the eggs were appreciably lower than those in the same species in 1970. The declines are attributed to the 1970 restrictions placed on industrial discharges of mercury into the St. Clair and Detroit Rivers.*

Introduction

The discovery of high mercury levels in fish of Lake St. Clair in 1970 focused attention upon the possible hazard that this element poses to fish and wildlife in the United States. Subsequent studies showed that birds and other aquatic animals in the area also contained high levels of the toxic metal (*3*). Elevated levels in flora and fauna of the area have been attributed to mercury in effluents from industrial sites along the St. Clair and Detroit Rivers (*15*). Subsequent action curtailed mercury discharges into the rivers in 1970, but it was predicted (*14*) that a substantial period would be required for natural degradative processes to reduce the level of contamination. In 1973, 3 years after the apparent source of contamination had been identified and curtailed, authors arranged for eggs to be collected from four species of birds that inhabit the waterways and had them analyzed for mercury.

Methods

Authors collected eggs of mallard ducks (*Anas platyrhynchos*) and common terns (*Sterna hirundo*) near the St. Clair River inlet of Goose Bay, which is west of Dickinson Island in the St. Clair Flats Public Hunting Grounds. Eggs of black-crowned night herons (*Nycticorax nycticorax*), greater egrets (*Casmerodius albus*), and mallards were taken from Stony Island in the Detroit River near its confluence with Lake Erie. Eggs of mallards, night herons, and terns were collected May 15-16, 1973, from the same sites sampled May 21-23, 1970 (*3*). Egret eggs were not collected in 1970. Complete clutches of eggs usually were taken and the eggs were analyzed individually, making it possible to measure the variation in mercury residues within and between clutches. Variances were calculated from expected mean squares in a nested analysis of variance for each species. The significance of the differences in mercury contamination between 1970 and 1973 for each species was determined with Wilcoxon rank sum tests (*19*). To compare residues of 1973 with those of 1970, authors analyzed one randomly selected egg from each clutch collected in 1973 because only one egg from each clutch collected in 1970 had been analyzed.

Analyses for total mercury were performed with cold vapor atomic absorption spectrophotometry (*7*) by WARF Institute, Inc., Madison, Wis. A 3-g aliquot from each uniformly prepared egg sample was digested by refluxing it with a mixture of sulfuric and nitric acids. A mixture of hydroxylamine, stannous chloride, and sulfuric acid was added to the digest to reduce the mercury ions to mercury metal. Samples were aerated at a rate of 3 liter/min and passed through the absorption cell of the spectrophotometer. The recovery efficiency was evaluated by analyzing aliquots from three egg samples spiked with known quantities of mercury. All results are expressed on a wet-weight basis. Mean recovery was 101 percent; the limit of detection was 0.05 ppm. For computational purposes values less than 0.05 ppm were entered as 0.025 ppm.

An atomic absorption spectrophotometer with a boat modification was used by WARF Institute for the mercury determinations of the 1970 samples (*3*). Tests have

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shown that results from determinations by this method are comparable to those obtained by the cold vapor method; there is less than 10 percent variation in bird tissues (R. E. Christensen, 1974, WARF Institute, Inc., Elemental Chemistry Department: personal communication).

Results and Discussion

Mercury was detected in all eggs of black-crowned night herons, great egrets, and common terns, and in 47 of 64 (73.4 percent) mallard eggs. Eggs of the night herons, egrets, and terns contained noticeably higher levels of mercury than did mallard eggs (Table 1). These differences probably reflect the species' relative positions in the food chain (*2,5,16,17*), indicating that mercury is being concentrated at higher trophic levels and that birds feeding at the higher trophic levels ingest greater amounts of mercury. Mallards' diet consists of about 90 percent plant material (*10*), black-crowned night herons feed extensively on fish and aquatic arthropods (*13*), and common terns feed almost exclusively on small fish (*1*).

TABLE 1. *Mercury in eggs from complete clutches of aquatic birds, Lake St. Clair, Michigan—1973*

Species	Clutch	No. eggs	Mercury Residues, ppm wet weight: Arithmetic Mean	Median	Range
Mallard	1[1]	8	0.200	0.20	0.18-0.26
	2[2]	7	0.034	<0.05	<0.05-0.06
	3[2]	5	0.096	0.08	0.08-0.14
	4[2]	8	<0.050	<0.05	<0.05
	5[2]	6	0.068	0.07	0.05-0.08
	6[2]	4	0.050	0.05	0.05-0.06
	7[2]	10	0.055	0.06	<0.05-0.08
Black-crowned night heron[1]	1	3	0.730	0.76	0.67-0.76
	2	5	0.386	0.39	0.35-0.40
	3	4	0.322	0.32	0.31-0.34
	4	4	0.610	0.61	0.60-0.63
	5	4	0.308	0.26	0.20-0.51
	6	4	0.485	0.48	0.46-0.53
	7	3	0.363	0.36	0.33-0.40
Great egret[1]	1	3	0.243	0.23	0.21-0.29
	2	4	0.430	0.44	0.40-0.45
Common tern[2]	1	2	1.090	1.09	0.87-1.31
	2	2	0.730	0.73	0.69-0.77

[1] Samples collected from Stony Island
[2] Samples collected from St. Clair flats

The concentration of contaminents in the eggs of these four species is below 6 ppm, a level shown to impair reproduction in captive mallards (*8*). However, ring-necked pheasants (*Phasianus colchicus*) with low dietary levels of mercury laid eggs containing 0.5-1.5 ppm mercury and had significantly lower hatchability than had control specimens (*4*). Eggs from night herons and terns collected from the Lake St. Clair area in 1973 contained mercury levels within this range.

The coefficients of variation show that differences in residue levels occur between clutches rather than within clutches (Table 2). Mercury levels in eggs from the same clutch were quite similar. Differences between clutches are significant and probably reflect differences in the extent of exposure to mercury by individual females. Mercury contamination varied only slightly within clutches of field-collected eggs of herring gulls (*Larus argentatus*) and California gulls (*Larus californicus*) (*16*); the same was true of eggs of black ducks (*Anas rubripes*) when the adults had been fed low levels of methylmercury (*6*).

TABLE 2. *Summary of mercury residues in eggs of four species of birds, Lake St. Clair, Michigan—1973*

	Species: Mallard	Black-crowned night heron	Great egret	Common tern
No. eggs analyzed	41	27	7	7
No. clutches represented	6	7	2	5
Arithmetic mean mercury residue, ppm wet weight	0.05	0.45	0.35	1.15
Range, ppm wet weight	<0.05-0.14	0.20-0.76	0.21-0.45	0.69-2.16
Coefficient of variation:				
Among clutches	32.4	28.3	33.8	40.4
Within clutches	15.5	19.3	8.9	19.4

NOTE: Analyses based on complete clutches

Mercury levels apparently declined in eggs of two of the three species between 1970 (*3*) and 1973 (Table 3). The decline was most dramatic in the mallard ($P < 0.01$) whose level of contamination in 1973 was only about 10 percent of that in 1970. A significant

TABLE 3. *Comparison of 1970 and 1973 mercury contamination of aquatic bird eggs from the Lake St. Clair area*

	Mercury Residues, ppm wet weight: 1970				1973			
Species	No. clutches	Arithmetic mean	Median	Range	No. clutches	Arithmetic mean	Median	Range
Mallard[1]	7	0.99	0.74	0.23-2.7	14	0.07	0.06	<0.05-0.14
Night heron[2]	5	0.77	0.74	0.46-1.1	7	0.44	0.40	0.19-0.67
Common tern[2]	5	2.73	1.5	0.63-6.25	5	1.30	1.31	0.77-2.16

NOTE: See Literature Cited, reference 1, for 1970 study.
Analyses based on one egg randomly selected from each clutch. For 1973 mallards, 7 whole clutches and 2 eggs from each of 7 additional clutches were collected.
[1] Samples collected from St. Clair flats
[2] Samples collected from Stony Island

decline also occurred in eggs of the black-crowned night heron ($P < 0.05$) although mercury levels in common terns showed only a slight reduction ($P > 0.05$). It is noteworthy that the greatest decline in mercury contamination occurred in eggs of the mallard, the species that feeds most extensively on lower trophic level organisms. Available mercury may be retained longer in the higher levels of the food chain.

Mercury poisoning of Swedish wildlife, particularly seed-eating birds and certain avian predators, was attributed to the use of mercurial seed dressings. The use of these dressings was restricted in 1966 and within 2-3 years significant declines occurred in mercury contamination of certain Swedish birds (*11,12*).

In 1970, discharges from chlor-alkali plants were recognized as one of the major industrial sources of mercury pollution in the United States (*18*). Resulting legal actions forced many manufacturers to reduce their mercury discharge.

Mercury introduced into water systems by industrial effluents is primarily incorported into bottom sediments, and mercury may be exchanged between these sediments and the overlying water for a period of 10-100 years (*9*). However, mercury-contaminated sediments may be naturally separated from the overlying water when they are covered with clean silt deposits following curtailment of the discharge. At Lake St. Clair this may have contributed to the rapid decline of mercury residues in eggs of aquatic birds. The St. Clair River flows rapidly and is laden with sediments at its confluence with Lake St. Clair.

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LITERATURE CITED

(*1*) *Bent, A. C. 1921.* Life Histories of North American Gulls and Terns. U.S. Natl. Mus. Bull. No. 113. 345 pp.

(*2*) *Berg, W., A. Johnels, B. Sjostrand, and T. Westermark. 1966.* Mercury content in feathers of Swedish birds from the past 100 years. Oikos 17(1):71-83.

(*3*) *Dustman, E. H., L. F. Stickel, and J. B. Elder. 1972.* Mercury in wild animals, Lake St. Clair, 1970. Pp. 46-52 *in* Hartung and Dinman, eds. Environmental Mercury Contamination. Ann Arbor Science Publishers, Ann Arbor, Mich.

(*4*) *Fimreite, N. 1971.* Effects of dietary methylmercury on ring-necked pheasants. Can. Wildl. Serv. Occasional Paper No. 9. 37 pp.

(*5*) *Fimreite, N. 1974.* Mercury contamination of aquatic birds in northwestern Ontario. J. Wildl. Manage. 38(1):120-131.

(*6*) *Finley, M. T., and R. C. Stendell. 1975.* Unpublished results. Fish and Wildlife Service, U.S Department of Interior, Patuxent Wildlife Research Center, Laurel, Md.

(*7*) *Hatch, W. R., and W. L. Ott. 1968.* Determination of sub-microgram quantities of mercury by atomic absorption spectrophotometry. Anal. Chem. 40(14): 2085-2087.

(*8*) *Heinz, G. 1974.* Effects of low dietary levels of methyl mercury on mallard reproduction. Bull. Environ. Contam. Toxicol. 11(4):386-392.

(*9*) *Jernelov, A. 1969.* Conversion of mercury compounds. *In* Miller and Berg, eds. Chemical Fallout. Charles C. Thomas, Springfield, Ill. 531 pp.

(*10*) *Kortright, F. H. 1953.* The Ducks, Geese and Swans of North America. Wildlife Management Institute, Washington, D.C. 476 pp.

(*11*) *Ljunggren, L. 1971.* Mercury in the liver of the wood pigeons *Columba p. palumbus* in 1964 and 1967. Ornis Scand. 2(1):13-15.

(*12*) *Malmberg, T. 1973.* Pesticides and the rook *Corvus frugilegus* in Scania, Sweden between 1955 and 1970. Oikos 24(3):377-387.

(*13*) *Palmer, R. S. 1962.* Handbook of North American Birds, Vol. 1. Yale University Press, New Haven, Conn. 557 pp.

(*14*) *Parker, C. E. 1970.* Mercury—major new environmental problem. The Conservationist 25(1):6-9.

(*15*) *Turney, W. G. 1972.* The mercury pollution problem in Michigan. Pp. 29-31 *in* Hartung and Dinman, eds. Environmental Mercury Contamination. Ann Arbor Science Publishers, Ann Arbor, Mich.

(*16*) *Vermeer, K. 1971.* Survey of mercury residues in aquatic bird eggs in the Canadian prairie provinces. Trans. N. Am. Wildl. Nat. Resour. Conf. 36:138-152.

(*17*) *Vermeer, K., F. A. J. Armstrong, and D. R. M. Hatch. 1973.* Mercury in aquatic birds at Clay Lake, Western Ontario. J. Wildl. Manage. 37(1):58-61.

(*18*) *Wallace, R. A., W. Fulkerson, W. D. Shults, and W. S. Lyon. 1971.* Mercury in the environment, the human element. ORNL-NSF-EP-1. Nat. Tech. Inf. Serv., Springfield, Va.

(*19*) *Wilcoxen, F., and R. A. Wilcox. 1964.* Some Rapid Approximate Statistical Procedures. Lederle Laboratories, New York. 60 pp.

Nationwide Residues of Organochlorines in Starlings, 1974 [1]

Donald H. White

ABSTRACT

Organochlorine residues in starlings (Sturnus vulgaris) *from 126 collection sites were monitored during the fall of 1974. DDE, DDT, polychlorinated biphenyls (PCB's), and benzene hexachloride were present in all samples. Dieldrin, heptachlor expoxide, hexachlorobenzene, and oxychlordane were present in approximately 97 percent of the samples. DDE, dieldrin, and PCB residues in starlings were significantly lower than they had been in 1972.*

Introduction

The Fish and Wildlife Service, U.S. Department of Interior, began nationwide monitoring of organochlorine residues in starlings (*Sturnus vulgaris*) in 1967-68 as part of the National Pesticides Monitoring Program. Residue data from these original collections were to serve as baseline readings from which future trends in residue levels might be detected. Monitoring was scheduled for 2-year intervals thereafter. Starlings were selected because their range is the continental United States, they are considered expendable, and their omnivorous feeding habits should reflect residues from a wide range of food sources (*3*). This paper presents the results of the analyses of the 1974 starling collection including residue levels from each collection site; a comparison of nationwide averages of DDE, dieldrin, and polychlorinated biphenyls (PCB's) in the four collection periods since 1967-68; and the distribution of 1974 residues by frequency of occurrence at collection sites.

Collection Methods

Earlier papers (*3-5*) discuss collection procedures in detail. The sample area lies within the contiguous 48 States and consists of 40 blocks of 5° latitude and longitude. During the initial study, 139 collection sites were randomly selected within these blocks; these sites were to be used for each biannual collection. In 1974, samples were obtained from 126 of these sites. Table 1

TABLE 1. *Starling collection sites listed by State and county, 1974*

State	County	Site
Alabama	Marion	3-H-1
	Talladega	4-H-3
Arizona	Navajo	3-C-3
	Yavapai	3-C-4
	Maricopa	4-C-1
	Graham	4-C-2
Arkansas	Yell/Pope	3-G-2
	Lonoke/Pulaski	3-G-3
California	Colusa	2-A-1
	Shasta	2-A-2
	Modoc	2-A-3
	Ventura	3-A-1
	Stanislaus	3-A-2
	Monterey	3-A-3
	Inyo	3-B-1
	Kern	3-B-4
	Imperial	4-B-1
Colorado	Weld	2-D-4
	Montrose	3-D-1
	Crowley	3-D-2
Connecticut	New London	2-K-2
Florida	Bay	4-H-1
	Madison	4-H-3
	Polk	5-I-1
	Hardee	5-I-2
Georgia	Pike	4-H-4
	Wayne	4-I-2
Idaho	Nez Perce	1-B-1
	Owyhee	2-B-1
	Franklin	2-C-3
	Minidoka	2-C-4
Illinois	Stephenson	2-G-1
	Adams	2-G-3
	Kane	2-H-2
Indiana	Hendricks	2-H-3
Iowa	Fremont	2-F-3
	Jasper	2-G-2
	Marshall	2-G-4
Kansas	Phillips	2-E-2
	Kearny	3-E-1
	Nemaha	2-F-4
	Marion	3-F-2

(*Continued next page*)

Fish and Wildlife Service, U.S. Department of Interior, Patuxent Wildlife Research Center, Laurel, MD 20811

TABLE 1 (contd.). *Starling collection sites listed by State and county, 1974*

State	County	Site
Kentucky	Ohio	3-H-2
	Hopkins	3-H-4
Louisiana	Jefferson	4-G-3
	Rapides	4-G-4
Maine	Penobscot	1-K-2
Michigan	Chippewa	1-H-1
	Grand Traverse	1-H-2
	Kent	2-H-1
	Ingham	2-H-4
Minnesota	Swift	1-F-2
Mississippi	Leake	4-G-1
	Harrison	4-G-2
	Jackson	4-H-2
Missouri	Butler	3-G-1
	Bollinger	3-G-4
Montana	Meagher	1-C-1
	Missoula	1-C-4
	Richland	1-D-1
	Yellowstone	1-D-4
Nebraska	Keith	2-E-3
	Brown	2-E-4
	Lancaster	2-F-1
	Clay	2-F-2
Nevada	White Pine	2-B-3
	Humboldt	2-B-4
	Nye	3-B-2
	Clark	3-B-3
New Mexico	Bernalillo	3-D-3
	Torrance	3-D-4
	Luna	4-D-1
	Otero	4-D-2
	Chaves	4-D-3
	Quay	3-E-2
New York	Jefferson	2-J-4
	Rensselaer	2-K-1
North Carolina	Wilkes	3-I-1
	Union	3-I-2
	Macon	3-I-3
	Pender	3-J-1
North Dakota	McLean	1-E-3
	Grand Forks	1-F-1
	Ransom	1-F-4
Ohio	Pickaway	2-I-1
	Wood	2-I-2
	Noble	2-I-3
Oklahoma	Greer	3-E-4
	Canadian	3-F-1
	Nowata	3-F-3
	Okmulgee	3-F-4
Oregon	Yamhill	1-A-3
	Lane	1-A-4
	Klamath	2-A-4
	Baker	1-B-4
	Harney	2-B-2
Pennsylvania	Somerset	2-J-2
	Luzerne	2-J-3
South Carolina	Aiken	4-I-1
South Dakota	Potter	1-E-1
	Butte	1-E-2
	Hughes	1-E-4
	Brown	1-F-3
Tennessee	Davidson	3-H-3
Texas	Kinney	4-E-3
	Cochran	4-E-4
	Comal	4-F-1
	Clay	4-F-3
	San Patricio	5-F-1
Utah	Weber	2-C-1
	Duchesne	2-C-2
	Sevier/Millard	3-C-1
Vermont	Addison	1-K-1
Virginia	Amherst	3-I-4
	Prince George	3-J-2
	Caroline	3-J-3
Washington	Pierce	1-A-1
	Yakima	1-A-2
	Spokane	1-B-2
	Whitman	1-B-3
Wisconsin	Trempealeau	1-G-3
	Clark	1-G-2
Wyoming	Big Horn	1-D-2
	Crook	1-D-3
	Goshen	2-D-1
	Washakie	2-D-2

lists the collection sites for 1974 by State and county; Figure 1 shows their actual locations within sampling blocks.

Normally a starling sample consists of a pool of 10 birds taken by trapping or shooting, although a few samples may be smaller. Each pool is wrapped in aluminum foil, placed in a polyethylene bag, frozen as soon as possible, and shipped to WARF Institute, Madison, Wis., for analysis.

Analytical Procedures

Prior to analysis the feet, beaks, wing tips, and skins were removed from birds in each composite sample and the sample was weighed and ground in a food grinder. A 20-g portion of the homogenate was ground with 100 g Na_2SO_4 and dried at room temperature for 72 hours. The dried sample was placed in a 43-by-123-mm Whatman extraction thimble and extracted for 8 hours on a Soxhlet extractor using 150 ml ethyl ether and 150 ml petroleum ether. The solvent extract was evaporated to 10-15 ml on a steam bath and diluted to 50 ml with petroleum ether. A 15-ml aliquot of the sample was placed on previously standardized florisil and eluted with 150 ml of 3 percent ethyl ether in petroleum ether, followed by 240 ml of 15 percent ethyl ether in petroleum ether. After florisil cleanup the resulting solutions were evaporated on a steam bath to 10-15 ml and diluted to 25 ml with petroleum ether. The Armour-Burke method (*1*) was used for PCB separation on those samples with high concentrations of DDT and/or its metabolites. This method is to be used on all samples in future starling monitoring efforts because of speculation that PCB interference may have influenced past results.

Determinations were made by injecting 10 μl or less of the sample solutions into a Barber-Coleman Pesticide

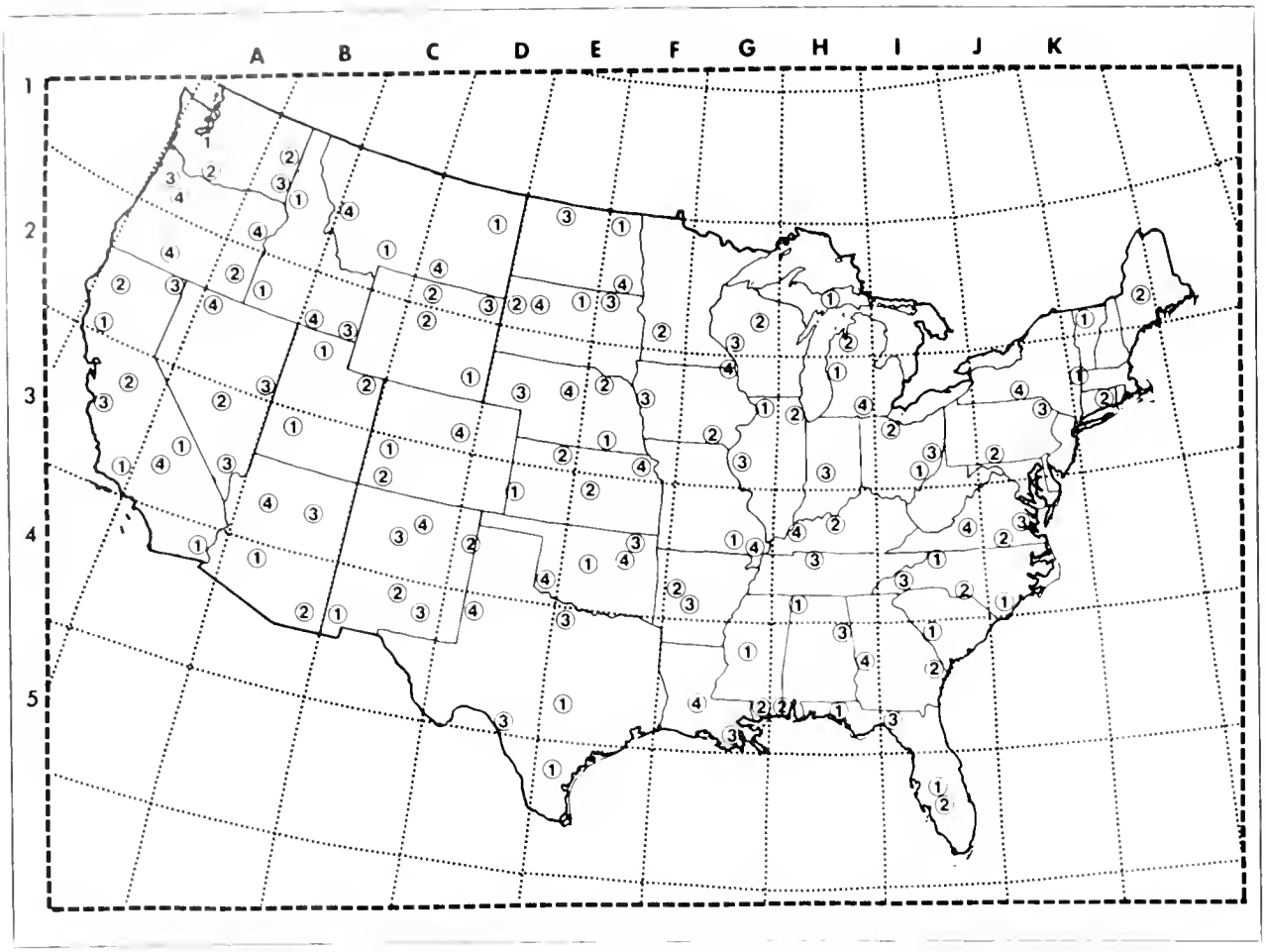

FIGURE 1. *Starling collection sites, 1974*

Analyzer model 5360. Instrument conditions for DDE, TDE, DDT, dieldrin, and PCB's were:

Column	1219 mm by 4 mm glass packed with 5 percent DC 200 on 80/100 Gas-Chrom Q	
Temperatures	Column	200 C
	Injector	217 C
	Detector	238 C
Carrier gas	Nitrogen at 80 ml/min	

Instrument conditions for HCB, BHC, heptachlor epoxide, and oxychlordane were

Column	1219 mm by 4 mm glass packed with 11 percent mixed phase OV-17/QF-1 on 80/100 Gas-Chrom Q	
Temperatures	Column	200 C
	Injector	225 C
	Detector	200 C
Carrier gas	Nitrogen at 80 ml/min	

Residues in 10 percent of the samples were confirmed by mass spectrometry.

All residues are expressed as ppm wet weight. They may be converted to dry or lipid weight by dividing a given wet-weight value by 0.29 or 0.05, the mean proportions, respectively, of dry and lipid material in the samples. Limits of sensitivity were 0.005 ppm for organochlorine pesticides and 0.01 ppm for PCB's. Recoveries ranged from 54 to 120 percent. Analytical results were not corrected.

Results and Discussion

Table 2 lists residues of DDE, TDE, DDT, dieldrin, PCB's, heptachlor epoxide, BHC, HCB, and oxychlordane by State and collection site of 1974 samples. Since some starlings are migratory, findings should not be interpreted on a statewide basis. Residues do not necessarily reflect year-round levels because collections were made only in the fall. DDE, DDT, PCB's, and BHC were present in all 126 pooled samples at levels equal to or exceeding limits of analytical sensitivity. Dieldrin, heptachlor epoxide, HCB, and oxychlordane were present in approximately 97 percent of the samples. Endrin was detected in nine samples (0.006-0.065 ppm) and mirex was detected in 14 samples (0.054-4.47 ppm).

TABLE 2. *Organochlorine residues in starlings, continental United States—1974*

State	Site No.	Residues, ppm Wet Weight								
		DDE	TDE	DDT	Dieldrin	PCB's	Heptachlor Epoxide	BHC	HCB	Oxychlordane
Alabama	3-H-1	1.20	TR	0.025	0.005	0.042	0.006	0.009	TR	TR
	4-H-3	0.027	0.013	0.13	0.008	1.88	ND	0.016	TR	ND
Arizona	3-C-3	0.13	ND	0.011	TR	0.083	TR	0.021	ND	TR
	3-C-4	0.52	ND	0.013	0.079	0.042	0.007	0.010	TR	0.008
	4-C-1	9.11	0.023	0.038	0.035	0.017	0.028	0.017	0.052	0.027
	4-C-2	1.48	ND	0.008	TR	0.063	TR	0.012	TR	TR
Arkansas	3-G-2	0.26	0.006	0.035	0.005	0.25	0.010	0.056	ND	0.007
	3-G-3	9.11	ND	0.040	ND	0.042	0.005	0.008	ND	TR
California	2-A-1	0.39	TR	0.005	0.021	0.025	TR	0.005	0.040	0.008
	2-A-2	0.52	TR	0.008	0.20	0.058	0.008	0.005	0.230	TR
	2-A-3	0.43	TR	0.008	0.013	0.021	TR	0.007	TR	TR
	3-A-1	3.65	0.013	0.033	0.042	0.13	0.008	0.012	TR	0.012
	3-A-2	1.82	TR	0.018	0.13	0.042	0.005	0.012	0.038	0.006
	3-A-3	1.04	0.008	0.021	0.042	0.10	0.021	0.006	0.042	0.013
	3-B-1	1.30	TR	0.023	0.017	0.071	0.014	0.005	0.006	0.007
	3-B-4	1.04	TR	0.021	0.019	0.042	0.005	0.005	0.007	0.013
	4-B-1	2.71	0.005	0.019	0.042	0.042	0.008	0.008	0.017	0.015
Colorado	2-D-4	0.81	0.006	0.021	0.025	0.063	0.012	0.014	TR	0.012
	3-D-1	0.16	TR	0.005	0.038	0.038	TR	0.006	0.006	TR
	3-D-2	0.12	0.041	0.006	0.063	0.029	TR	TR	0.006	TR
Connecticut	2-D-2	0.04	TR	0.017	0.008	0.083	ND	TR	TR	ND
Florida	4-H-1	0.73	0.014	0.029	0.26	0.15	0.069	0.019	TR	0.071
	4-I-3	0.42	TR	0.023	0.005	0.10	TR	TR	TR	0.023
	5-I-3	0.007	TR	0.023	0.13	0.13	0.007	0.009	ND	0.021
	5-I-2	0.18	TR	0.015	0.017	0.083	TR	TR	ND	0.008
Georgia	4-H-4	0.29	TR	0.015	TR	0.033	TR	TR	ND	TR
	4-I-2	0.10	0.008	0.017	TR	0.20	TR	0.006	ND	0.005
Idaho	1-B-1	0.33	TR	0.007	0.18	0.013	TR	0.039	9.11	TR
	2-B-1	0.23	ND	TR	0.02	0.013	0.012	0.014	TR	TR
	2-C-3	0.60	TR	0.042	0.021	0.27	0.013	0.012	TR	0.007
	2-C-4	0.34	0.012	0.025	0.048	0.013	0.038	0.052	TR	0.017
Illinois	2-G-1	0.22	TR	0.021	0.22	0.15	0.071	0.026	TR	0.027
	2-G-3	0.096	TR	0.025	0.17	0.23	0.083	TR	0.17	0.046
	2-H-2	0.40	TR	0.025	0.10	0.19	0.061	TR	0.006	0.031
Indiana	2-H-3	0.075	0.010	0.029	0.083	0.25	0.013	TR	0.14	0.007
Iowa	2-F-3	0.085	ND	0.013	0.22	0.021	0.075	0.019	TR	0.079
	2-G-2	0.096	TR	0.010	0.23	0.021	0.079	TR	TR	0.046
	2-G-4	0.20	TR	0.009	0.60	0.025	0.18	TR	TR	0.10
Kansas	2-E-2	0.063	TR	0.038	0.042	0.029	0.012	TR	TR	0.017
	3-E-1	0.096	ND	0.005	0.017	0.008	0.31	TR	0.009	0.083
	2-F-4	0.077	ND	0.006	0.10	0.033	0.031	0.021	TR	0.025
	3-F-2	0.10	TR	0.008	0.042	0.050	TR	TR	TR	0.011
Kentucky	3-H-2	0.10	TR	0.021	0.023	0.15	0.005	TR	TR	0.007
	3-H-4	0.62	TR	0.006	0.033	0.042	TR	TR	ND	TR
Louisiana	4-G-3	0.27	0.005	0.065	0.007	0.47	0.027	TR	TR	0.012
	4-G-4	1.67	0.013	0.044	0.015	0.033	0.013	0.021	TR	TR
Maine	1-K-2	0.21	TR	0.015	0.010	0.10	0.007	TR	TR	0.005
Michigan	1-H-1	0.060	0.017	0.048	0.096	0.46	TR	TR	0.006	TR
	1-H-2	0.27	0.011	0.029	TR	0.33	0.005	TR	TR	0.010
	2-H-1	0.29	0.010	0.022	TR	0.17	0.010	0.023	TR	0.011
	2-H-4	0.36	TR	0.018	TR	0.15	0.014	TR	TR	0.007
Minnesota	1-F-2	0.042	TR	0.006	0.017	0.063	TR	TR	ND	0.006
Mississippi	4-G-1	2.24	ND	0.021	0.017	0.042	TR	0.035	ND	TR
	4-G-2	0.52	0.017	0.017	0.73	0.10	0.092	0.012	ND	0.15
	4-H-2	0.57	0.015	0.025	1.01	0.063	0.29	0.023	TR	0.18
Missouri	3-G-1	0.73	ND	0.031	0.050	0.12	0.054	0.014	0.038	0.016
	3-G-4	0.10	ND	0.023	0.083	0.063	0.054	0.012	TR	0.021
Montana	1-C-1	0.096	0.019	0.033	0.013	0.31	0.016	0.030	0.006	0.008
	1-C-4	0.070	0.013	0.067	0.021	0.74	0.010	0.007	TR	TR
	1-D-1	0.007	TR	0.008	TR	0.050	ND	0.007	0.007	ND
	1-D-4	0.035	ND	TR	TR	0.025	0.008	0.009	TR	TR
Nebraska	2-E-3	0.11	0.008	0.019	0.013	0.054	0.012	0.029	TR	ND
	2-E-4	0.097	ND	0.011	0.057	0.067	0.17	0.057	0.26	0.13
	2-F-1	0.077	0.006	0.027	0.120	0.140	0.023	0.025	0.007	0.013
	2-F-2	0.077	TR	TR	0.027	0.013	0.011	0.014	TR	0.006

(Continued next page)

TABLE 2 (cont'd.). *Organochlorine residues in starlings, continental United States—1974*

State	Site No.	Residues, ppm Wet Weight								
		DDE	TDE	DDT	Dieldrin	PCB's	Heptachlor Epoxide	BHC	HCB	Oxychlordane
Nevada	2-B-3	0.89	TR	0.006	0.020	0.033	0.005	0.010	TR	0.006
	2-B-4	0.26	0.011	0.028	0.029	0.013	0.009	0.015	0.005	0.012
	3-B-2	0.067	TR	0.005	0.045	0.042	0.012	0.007	TR	0.007
	3-B-3	0.30	TR	0.008	0.040	0.042	0.013	0.009	TR	0.009
New Mexico	3-D-3	0.17	TR	0.005	0.015	0.042	0.012	0.024	TR	0.008
	3-D-4	0.52	ND	0.010	0.008	0.10	0.005	0.007	TR	TR
	4-D-1	0.89	TR	0.006	TR	0.10	ND	TR	TR	TR
	4-D-2	0.94	ND	0.006	0.010	0.13	0.023	0.012	TR	0.005
	4-D-3	3.70	0.006	0.015	0.008	0.042	TR	0.007	ND	TR
	3-E-2	0.12	ND	0.006	TR	0.13	0.006	0.018	TR	0.005
New York	2-J-4	0.62	TR	0.010	ND	0.006	0.005	TR	TR	TR
	2-K-1	0.56	0.006	0.013	0.010	0.13	TR	0.010	TR	TR
North Carolina	3-I-1	0.23	TR	0.011	TR	0.096	0.007	0.008	TR	0.009
	3-I-2	0.40	0.006	0.025	0.11	0.22	0.011	0.009	TR	0.015
	3-I-3	0.33	TR	0.010	0.015	0.063	TR	0.010	TR	0.005
	3-J-1	0.65	ND	0.021	ND	0.13	0.023	0.010	TR	0.019
North Dakota	1-E-3	0.017	TR	TR	TR	0.021	TR	0.033	TR	TR
	1-F-1	0.097	ND	TR	0.010	0.017	0.038	0.094	TR	0.012
	1-F-4	0.038	TR	0.012	0.005	0.083	0.007	0.017	TR	0.007
Ohio	2-J-1	0.098	0.010	0.035	0.058	0.19	0.010	0.010	0.029	0.009
	2-I-2	0.025	TR	0.021	0.092	0.13	0.009	TR	0.013	0.008
	2-I-3	0.072	0.006	0.006	0.006	0.075	TR	TR	TR	TR
Oklahoma	3-E-4	0.18	ND	0.007	0.014	0.042	TR	TR	0.006	TR
	3-F-1	0.18	TR	0.013	0.063	0.058	0.006	0.009	TR	0.010
	3-F-3	0.10	TR	0.006	0.017	0.063	0.005	TR	0.005	TR
	3-F-4	0.085	ND	0.007	0.013	0.063	0.007	TR	TR	TR
Oregon	1-A-3	0.52	0.012	0.031	0.038	0.083	TR	0.014	0.13	TR
	1-A-4	0.15	TR	0.013	0.052	0.042	0.013	0.020	0.038	TR
	2-A-4	0.45	TR	0.006	TR	0.063	0.008	0.007	TR	0.007
	1-B-4	0.094	TR	0.006	0.017	0.042	0.006	0.007	0.007	TR
	2-B-2	0.28	0.021	0.021	0.040	0.042	0.007	0.007	0.031	0.010
Pennsylvania	2-J-2	0.11	TR	0.023	0.081	0.16	0.023	0.022	TR	0.021
	2-J-3	0.11	TR	0.010	0.029	0.063	0.017	0.021	TR	0.030
South Carolina	4-I-1	1.88	TR	0.021	0.008	0.063	0.010	0.018	ND	0.012
South Dakota	1-E-1	0.07	ND	0.008	TR	0.063	0.006	0.023	TR	0.008
	1-E-2	0.035	ND	0.005	TR	0.083	0.007	0.025	TR	ND
	1-E-4	0.090	TR	0.015	TR	0.10	TR	0.008	TR	TR
	1-F-3	0.046	ND	0.006	TR	0.054	0.005	0.015	TR	TR
Tennessee	3-H-3	0.11	TR	0.023	0.010	0.15	TR	0.005	TR	0.013
Texas	4-E-3	0.49	ND	0.007	0.006	0.063	TR	0.005	TR	TR
	4-E-4	5.47	0.008	0.013	0.013	0.063	0.13	0.015	0.038	0.021
	4-F-1	0.20	ND	0.006	TR	0.063	0.015	0.014	0.010	0.011
	4-F-3	0.47	ND	0.010	0.005	0.17	0.017	0.013	0.015	0.007
	5-I-1	1.04	ND	0.015	0.005	0.021	0.006	0.009	0.012	0.006
Utah	2-C-1	0.13	TR	0.017	0.019	0.10	0.006	0.017	0.009	0.007
	2-C-2	0.11	TR	0.008	0.015	0.033	0.007	0.005	TR	TR
	3-C-1	0.69	TR	0.021	0.094	0.042	0.033	0.017	0.017	0.013
Vermont	1-K-1	0.56	0.015	0.021	0.035	0.42	0.050	0.11	TR	0.090
Virginia	3-I-4	0.15	TR	0.010	TR	0.063	0.013	0.013	TR	0.008
	3-J-2	0.10	0.010	0.035	0.007	0.27	0.013	0.007	0.24	0.017
	3-J-3	0.19	0.005	0.025	0.005	0.13	0.006	TR	TR	TR
Washington	1-A-1	0.054	TR	0.010	0.006	0.10	0.006	0.019	0.005	0.009
	1-A-2	2.29	TR	0.010	0.019	0.021	TR	0.005	0.19	ND
	1-B-2	0.098	TR	0.010	0.007	0.083	0.008	0.009	0.55	ND
	1-B-3	0.21	TR	0.006	0.067	0.042	TR	0.031	0.36	TR
Wisconsin	1-G-3	0.055	TR	0.006	0.008	0.092	TR	0.010	TR	TR
	1-G-2	0.062	0.006	0.021	ND	0.13	TR	0.010	TR	0.007
Wyoming	1-D-2	0.026	ND	TR	0.008	0.013	TR	TR	TR	TR
	1-D-3	0.046	TR	0.013	0.008	0.096	TR	0.007	TR	TR
	2-D-1	0.46	TR	0.010	0.17	0.042	TR	0.009	TR	0.009
	2-D-2	0.11	0.009	0.019	0.006	0.17	0.017	0.013	TR	0.021

NOTE: Limits of sensitivity were 0.005 ppm for organochlorine pesticides and 0.01 ppm for PCB's.
TR = trace residues detected at levels below limits of quantification
ND = not detected

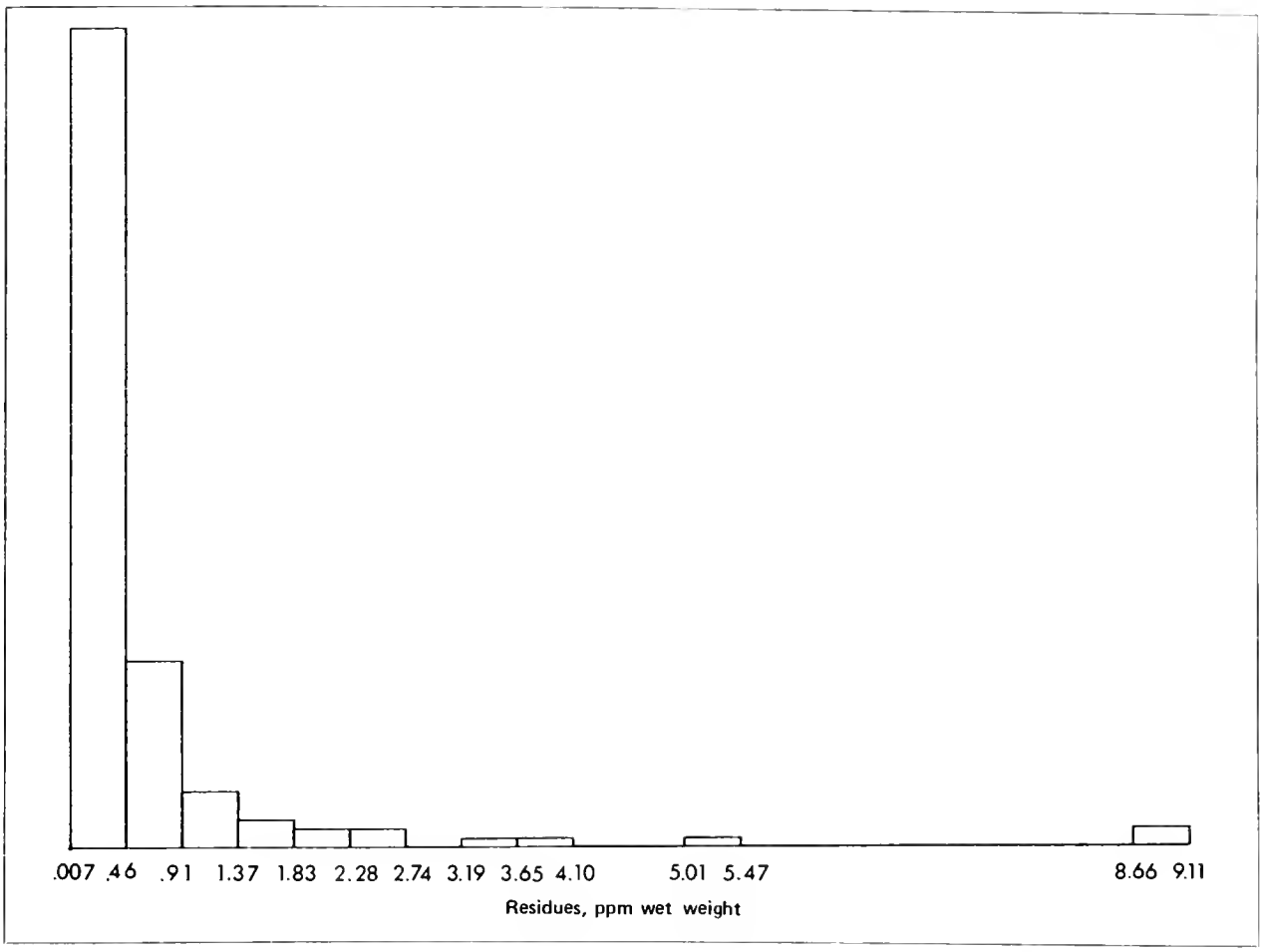

FIGURE 2. *Distribution of DDE residues in starlings, continental United States—1974*

Table 3 lists the arithmetic means, ranges, and geometric means of DDE, dieldrin, and PCB residues in starlings from each collection period from 1967-68 through 1974. The geometric mean is an approximation of the median. Therefore, about 50 percent of the values for a given compound fall above the geometric mean and about 50 percent fall below it. Statistical comparisons were made between DDE, dieldrin, and PCB residues from 1972 and 1974 to detect trends. Because of skewness, data were log transformed and then subjected to analysis of variance. Mean residues of DDE, dieldrin, and PCB's were significantly lower ($P < 0.001$) in 1974 than in 1972. DDE residues decreased 22 percent, dieldrin decreased 42 percent, and PCB's decreased 74 percent nationwide. It is conceivable that the decline in usage of DDT and dieldrin are reflected in a decline of residues in animal populations. Longcore and Mulhern (*2*) found that levels of DDE in eggs of the black duck (*Anas rubripes*) had decreased between 1964 and 1971, and White and Heath (*7*)

TABLE 3. *Arithmetic means, ranges, and geometric means of DDE, dieldrin, and PCB's in starlings, continental United States—1967-74*

		Residues, ppm Wet Weight								
		DDE			Dieldrin			PCB's [2]		
Year	No. Pools	$\bar{X} \pm$ S.E.	Range	Geom. $\bar{X}$	$\bar{X} \pm$ S.E.	Range	Geom $\bar{X}$	$\bar{X} \pm$ S.E.	Range	Geom $\bar{X}$
1967-68	360	1.637 ± 0.270	0.037 – 48.20	0.579	0.139 ± 0.016	TR – 1.18	0.084	–	–	–
1970	125	0.839 ± 0.148	0.047 – 14.80	0.355	0.117 ± 0.038	0.005 – 3.59	0.036	0.663 ± 0.196	0.09 – 24.30	0.358
1972	130	0.788 ± 0.124	0.023 – 11.70	0.387	0.098 ± 0.018	TR – 1.56	0.035	0.425 ± 0.153	0.037 – 19.90	0.215
1974 [1]	126	0.617 ± 0.118	0.007 – 9.11	0.229	0.057 ± 0.011	ND – 1.01	0.019	0.112 ± 0.016	0.006 – 1.88	0.068

[1] Mean residues of DDE, dieldrin, and PCB's significantly lower in 1974 than in 1972. $P < 0.001$.
[2] PCB's were not analyzed in 1967-68.

reported declines of DDE, dieldrin, and PCB's in black ducks and mallards (*Anas platyrhynchos*) between 1969 and 1972.

Table 4 shows the distribution of DDE, dieldrin, and PCB residues by frequency of occurrence at collection sites for 1974. Residues are generally low, between 0 and 1.0 ppm for most compounds. For all three compounds the data are skewed to the left. Figure 2 further illustrates this skewness in 1974 DDE residues. Statistical comparisons using a parametric test should not be made with these raw data (6). Figure 3 shows the distribution of the same data after log transformation. Data are normally distributed and may be tested for differences by parametric methods.

TABLE 4. *Distribution of residues in starlings by frequency of occurrence at collection sites, continental United States—1974*

	DDE	Dieldrin	PCB's
Range, ppm	No. Sites with Residues	No. Sites with Residues	No. Sites with Residues
ND - 0.01	2	50	2
>0.01 - 0.1	39	61	89
>0.1 - 1.0	67	14	34
>1.0 - 10.0	18	1	1

NOTE: ND = not detected

Conclusions

Residues of DDE, dieldrin, and PCB's in starlings have declined nationwide since 1972. This decrease corresponds to a decline in environmental levels of organochlorines, indicating that starlings can provide information on residue trends over a period of time.

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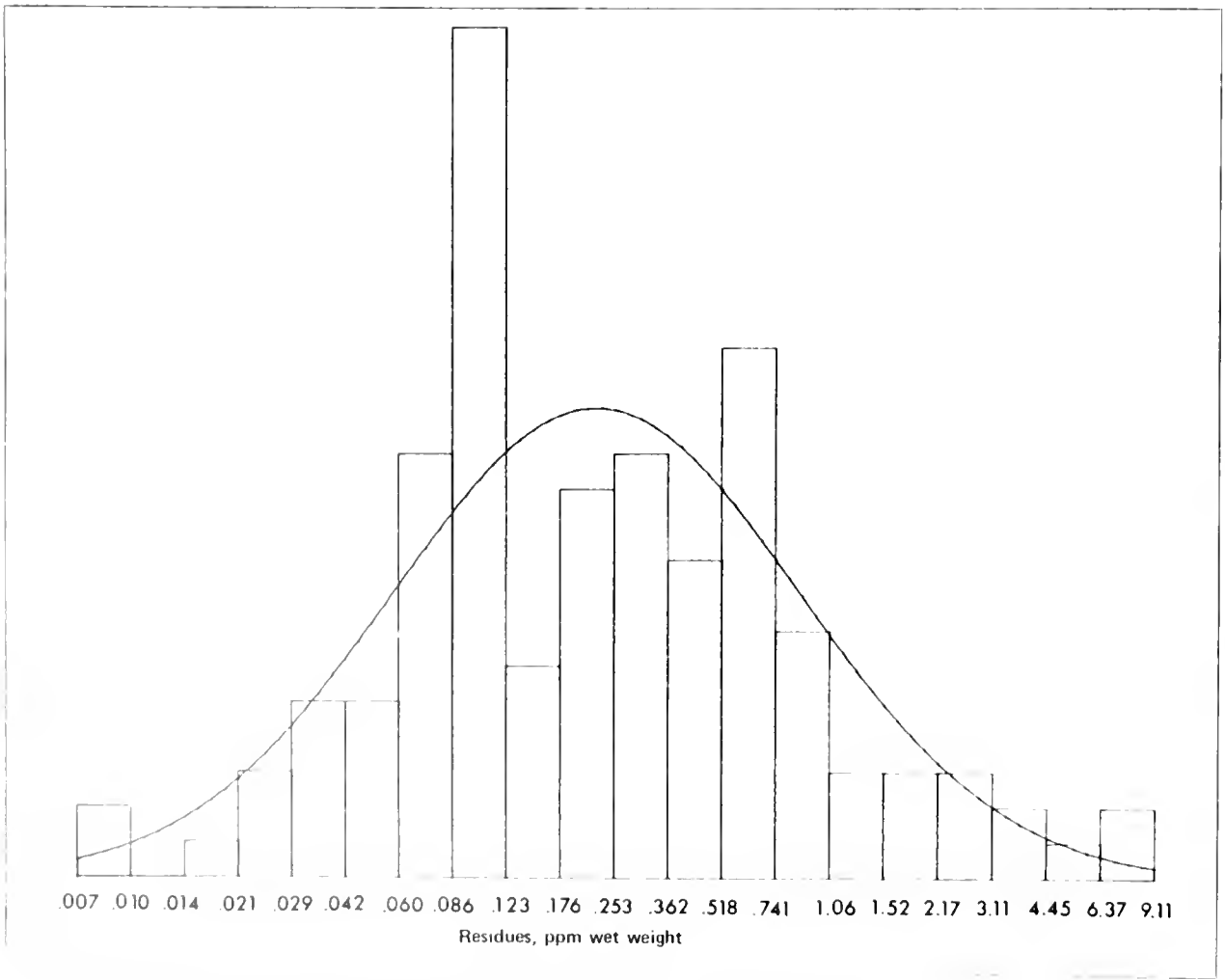

FIGURE 3. *Distribution of DDE residues in starlings after log transformation, continental United States—1974*

LITERATURE CITED

(1) *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.

(2) *Longcore, J. R., and B. M. Mulhern. 1973.* Organochlorine pesticides and polychlorinated biphenyls in black duck eggs from the United States and Canada—1971. Pestic. Monit. J. 7(1):62-66.

(3) *Martin, W. E. 1969.* Organochlorine insecticide residues in starlings. Pestic. Monit. J. 3(2):102-114.

(4) *Martin, W. E., and P. R. Nickerson. 1972.* Organochlorine residues in starlings—1970. Pestic. Monit. J. 6(1):33-40.

(5) *Nickerson, P. R., and K. R. Barbehenn. 1975.* Organochlorine residues in starlings, 1972. Pestic. Monit. J. 8(4):247-254.

(6) *Snedecor, G. W., and W. G. Cochran. 1967.* Statistical Methods. Iowa State University Press, Ames, Iowa. 593 pp.

(7) *White, D. H., and R. G. Heath. 1976.* Nationwide residues of organochlorines in wings of adult mallards and black ducks, 1972-73. Pestic. Monit. J. 9(4):176-185.

RESIDUES IN FOOD AND FEED

Pesticide Residues in Total Diet Samples, Spain—1971-72 [1,2]

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ABSTRACT

Average pesticide residue levels were determined for the 17 main food groups in the average Spanish diet. Using these levels and the estimated average intake of these foods, authors computed an individual's average daily consumption of pesticides from each of these food groups and her his total diet.

Foods were acquired over a 1-year period from the market of Valencia, a city that gets supplies from an agricultural area where pesticide consumption is appreciably higher than that of the rest of the country. Thus average residue levels found must be higher than the national average.

Except for fruits and vegetables, the different items composing each food group were sampled in proportion to the amount consumed in the average Spanish diet. Foods forming each group were homogenized into composite samples. All foods were analyzed raw.

The most frequently detected pesticides were DDT and BHC. Malathion was detected at levels less than 0.10 ppm in some samples of vegetable oils, pears, and apples. DDT and BHC levels varied from undetectable to amounts less than 1.0 ppm. Highest levels were found in lard.

An individual's average daily intake of pesticides was calculated to be 78 μg DDT, a sum which includes residues of o,p'-DDT, p,p'-DDT, and p,p'-DDE, and 13.8 μg γ-BHC. These levels are much lower than the maximum acceptable daily limits established by the United Nations Food Agricultural Organization and World Health Organization.

Introduction

Part of a series of studies on pesticide contamination in agricultural products (*3,4,5,11*), the present paper represents authors' attempts to determine the extent of pesticide contamination of the various food groups composing the average Spanish diet (*9*) and compute an individual's average daily intake of pesticides from these foods and her/his diet. Pesticide residue levels are also being determined for the average diet in the U.S., Canada, and England (*1,6,7,12*). Results of these studies and the present study are evaluated by comparing them with the maximum daily levels of pesticide intake from foods established by the United Nations Food Agricultural Organization (FAO) and World Health Organization (WHO) (*13*).

Sampling

Constituent foods of the average Spanish diet were classified into 17 groups. Table 1 lists the foods which

TABLE 1. *Average per capita yearly food consumption, Spain—1969* [9]

Food group	Products		Food consumed, Kg/person/year
I Dairy products	Fresh milk		78.94
	Powdered milk		0.25
	Condensed milk		2.51
	Butter		0.35
	Cheese		1.53
		Total	83.58
II Meats	Beef		7.24
	Mutton and goat meat		5.35
	Pork		2.02
	Horse meat		1.31
	Poultry		5.08
	Liver		0.44
	Sausages and giblets		6.37
	Canned meat		0.27
	Meat soups		0.16
		Total	28.44
III Eggs	Eggs		14.22
IV Fish	Fresh sardines		4.10
	Fresh whitebait		1.40
	Fresh pinel		1.90
	Fresh codling		4.70
	Fresh hake		1.10
	Fresh codfish		1.80
	Salted codfish		1.00
	Canned fish		1.60
	Shellfish		0.80
	Other fresh fish		6.30
	Frozen fish		0.50
		Total	25.20

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TABLE 1 (cont'd.). *Average per capita yearly food consumption, Spain—1969* [1]

Food group	Products	Food consumed, Kg/person/year
V. Fats	Lard	4.71
	Margarine	0.14
	Total	4.85
VI. Vegetable oils	Olive oil	24.10
	Other vegetable oils	0.66
	Total	24.76
VII. Bakery goods	Bread	134.50
	Flour	5.80
	Italian pastry	4.50
	Biscuits	2.30
	Rolls	4.10
	Total	151.20
VIII. Grains	Rice	9.70
	Other (except wheat)	0.20
	Total	9.90
IX. Vegetables	Tomatoes	18.50
	Lettuce	3.30
	Green beans	3.60
	Cabbages and sprouts	4.40
	Peppers	3.30
	Artichokes	1.90
	Beets	2.20
	Peas	0.70
	Spinach	0.80
	Onions, leeks, tender onions	5.60
	Cauliflower	1.10
	Other vegetables	8.90
	Total	54.30
X. Tubers	Potatoes	109.50
	Carrots	0.30
	Total	109.80
XI. Legumes	Beans	5.90
	Chick peas	6.90
	Lentils	2.10
	Other legumes	0.10
	Total	15.00
XII. Fruits	Oranges	20.60
	Lemons	0.60
	Other sour fruits	0.30
	Bananas	7.30
	Apples	5.90
	Pears	3.20
	Peaches	1.50
	Apricots	0.20
	Cherries and berries	0.60
	Plums	0.70
	Melons	7.40
	Grapes	5.00
	Other fresh fruits	3.60
	Chestnuts	0.20
	Nuts	0.10
	Other dried fruits	0.27
	Total	57.47
XIII. Canned foods	Vegetables	1.31
	Legumes	0.03
	Olives	0.96
	Marmalade	0.13
	Quince	0.37
	Juices	0.40
	Other fruits	0.38
	Total	3.58
XIV. Sweets and condiments	Sugar	14.10
	Chocolate	2.14
	Cacao	0.43
	Honey	0.05
	Turron (Spanish confectionery)	0.21
	Other sweets	0.30
	Salt	3.92
	Vinegar	1.20
	Garlic	0.52
	Other dressings	0.22
	Total	23.09
XV. Water	Tap water	200.00
	Mineral water	2.90
	Soda and seltzer	15.30
	Total	218.20
XVI. Alcoholic drinks	Wine	47.90
	Beer	2.00
	Other	3.20
	Total	53.10
XVII. Beverages	Coffee	1.46
	Malts	0.81
	Other	11.00
	Total	13.27

[1] See Literature Cited, reference 9.

compose each group and the average amount of each food an individual consumes each year (*9*).

Samples were acquired at random between March 1971 and March 1972 in different markets in Valencia. They were mixed into composite samples according to their proportion in the average diet.

Because they are seasonal, some foods, especially those in the fruit and vegetable groups, were studied individually. Because residue levels in foods from these groups are similar (*3*), authors studied only the foods which are eaten in greatest volume and considered their residue levels representative of all foods in the group.

Analytical Procedures

All foods were analyzed raw. Unless specified otherwise, samples were composed of 100-g mixtures of foods from the designated group and pesticide residues were extracted and purified as delineated in the *Pesticide Analytical Manual* of the Food and Drug Administration, U.S. Department of Health, Education, and Welfare (*14*).

Samples of dairy products were homogenized in a blendor and shaken at high speed for 2 minutes. Fifty g of this mixture was weighed in a 400-ml glass and analyzed according to the method expounded by Faubert et al. (*8*).

Samples of meat and fish products were diced into 0.5- to 1-g pieces and ground in a glass mortar with 100 g washed sand and 200 g anhydrous sodium sulfate. According to Faubert's method (*8*), pesticide residues were extracted from 40 g of this homogenized mixture, which is equivalent to 10 g of the sample.

The whites and yolks of three eggs were homogenized by shaking for 3 minutes. This mixture was added to sufficient anhydrous sodium sulfate (45-50 g) to make it dusty and dry. Then it was extracted by Soxhlet for 6 hours with 250 ml 2:1 n-hexane:acetone. The extract was dried by shaking for 10 minutes with 25 g an-

hydrous sodium sulfate, filtered, concentrated in a Kuderna-Danish evaporator to 25 ml, and purified by partition with acetonitrile according to the method outlined by Onley and Mills (*10*). Purified extracts were then chromatographed in an alumina column (*8*) and eluted with 100 ml hexane and 100 ml hexane mixed with 6 percent ethyl ether.

White rice samples were ground until they could pass through a 1-mm sieve. Fifty g cereal was added to 350 ml 65:35 acetonitrile:water for 30 minutes, ground at a high speed for 3 minutes, and centrifuged for 10 minutes at 2,000 rpm. Floating liquid was poured into a 1-liter separatory funnel and 100 ml bidistilled petroleum ether was added.

Fifty-g samples of dry legumes were moistened for 30 minutes with 350 ml of a 65:35 mixture of acetonitrile: water, ground for 5 minutes at a high speed, and filtered. The resulting mixture was centrifuged for 10 minutes at 2,000 rpm.

Samples of sweets and condiments weighing 50 g were placed in a 400-ml glass with 100 ml bidistilled water, shaken for 15 minutes, poured into a mixer with 200 ml acetonitrile, and ground for 5 minutes.

Potable water samples were acidified with 2 ml of 1N HCl and extracted with three portions of 100 ml n-hexane. Samples were added to 10 g anhydrous sodium sulfate, shaken for 5 minutes, poured through filter paper, and concentrated in a rotory evaporator to 10 ml in a vacuum and to 2 ml in an airstream.

Alcoholic drinks were extracted as the potable water except that 10 ml ethanol was added at the aqueous phase to break up the emulsions formed during the extraction with n-hexane. Extracts were concentrated to 10 ml in a rotary evaporator in vacuum and chromatographed in an alumina column according to the method used for meat products.

A 1-liter sample of beverages was placed in a separatory 2-liter funnel. Pesticide residues were extracted according to the procedures described for water.

Fat and vegetable oil samples weighed 3 g and tuber samples consisted of peeled and washed potatoes. Bakery samples were ground in a blendor for 3 minutes with a 65:35 mixture of acetonitrile:water and poured through filter paper before extraction.

Analyses were performed on a Perkin-Elmer model F-11 gas chromatograph according to the methods recommended by FDA (*14*) or those used by the authors in earlier work (*2*). Electron-capture and sodium thermionic detectors were used. Columns were glass packed with either 10 percent DC-200 or 10 percent DC-200 and 15 percent QF-1 on Gas-Chrom Q. All results are reported on a whole-product basis.

One of every four samples was checked for recovery, which varied from 80 to 110 percent for DDT, lindane, α-BHC, aldrin, dieldrin, and endrin. Results have not been corrected.

To confirm the identity of pesticide residues, thin-layer chromatography was used implementing either the FDA method (*14*) or the authors' earlier procedures (*3*). DDT residues were also confirmed by alkaline degradation to DDE (*2*).

Results and Discussion

Table 2 shows the average organochlorine pesticide residue level in each food group. Average contamination by BHC varies from undetectable levels in tubers and fruits to 0.4 ppm in lard. DDT levels vary from undetectable to 0.8 ppm in meats and fats. These results agree with the well-known fact that all chlorinated insecticides accumulate in the fat tissues of animals because they are liposoluble.

Residues of other chlorinated insecticides were not found. Malathion was the only organophosphorous in-

TABLE 2. *Average pesticide residue in 17 food groups, Spain—1971-72*

Food group	Residues, ppm				
	α-BHC	γ-BHC	*p,p'*-DDE	*o,p'*-DDT	*p,p'*-DDT
I. Dairy Products	0.005	0.004	0.006	ND	0.004
II. Meats	0.033	0.070	0.167	0.023	0.186
III. Eggs	0.019	0.019	0.151	ND	0.198
IV. Fish	0.011	0.009	0.078	ND	0.106
V. Fats	0.150	0.268	0.218	0.061	0.160
VI. Vegetable oils	0.016	0.009	0.012	ND	0.012
VII. Bakery Goods	0.005	0.003	0.003	0.002	0.016
VIII. Grains	0.004	0.003	0.002	ND	0.013
IX. Vegetables	0.002	0.001	0.001	0.002	0.004
X. Tubers	ND	ND	0.001	ND	0.001
XI. Legumes	0.005	0.003	ND	ND	0.004
XII. Fruits	ND	ND	ND	0.001	0.002
XIII. Canned vegetables	0.008	0.005	ND	0.001	0.004
XIV. Sweets and condiments	0.005	0.004	0.003	0.008	0.009
XV. Water	ND	ND	ND	ND	ND
XVI. Alcoholic drinks	0.001	ND	ND	ND	ND
XVII. Beverages	ND	ND	ND	ND	ND

NOTE: ND = residue levels < 0.001 ppm.

ɜecticide detected. It was found in several samples of vegetable oils, pears, and apples at levels less than 0.1 ppm.

Kelthane (dicofol) and Tedion (tetradifon) residues were detected in some samples of fruits and greens. The highest level found was 0.2 ppm.

Table 3 presents a sample distribution according to the contamination levels of every pesticide detected. It also shows the maximum content of every compound found for each food group. The percentage of samples in each food group without any detectable residues is shown in Table 4. Table 5 shows the average contamination of fruits and vegetables.

TABLE 3. *Distribution of food samples according to contamination by different pesticides*

Food groups [1]	Pesticides [2]	Distribution according to contamination due to different pesticides, %				Highest level, ppm
		Not detectable	Trace: 0.001-0.010 ppm	0.011-0.050 ppm	Greater than 0.050 ppm	
I. Dairy products	α-BHC	20	75	5	0	0.015
	γ-BHC	35	55	10	0	0.018
	p,p'-DDE	50	20	30	0	0.026
	o,p'-DDT	95	5	0	0	0.004
	p,p'-DDT	50	40	10	0	0.018
II. Meats	α-BHC	15	30	50	10	0.200
	γ-BHC	0	0	60	40	0.160
	p,p'-DDE	25	15	20	40	0.635
	o,p'-DDT	65	20	10	5	0.230
	p,p'-DDT	15	10	25	50	0.845
III. Eggs	α-BHC	40	15	40	5	0.105
	γ-BHC	25	35	35	5	0.100
	p,p'-DDE	10	10	35	45	0.469
	o,p'-DDT	100	0	0	0	ND
	p,p'-DDT	20	10	25	35	0.566
IV. Fish	α-BHC	55	15	30	0	0.050
	γ-BHC	70	15	15	0	0.050
	p,p'-DDE	15	25	15	45	0.250
	o,p'-DDT	90	0	5	5	0.120
	p,p'-DDT	15	0	25	60	0.231
V. Fats	α-BHC	0	0	10	90	0.260
	γ-BHC	0	0	0	100	0.390
	p,p'-DDE	0	0	10	90	0.510
	p,p'-DDT	30	0	10	60	0.410
VI. Vegetable oils	α-BHC	75	5	10	10	0.125
	γ-BHC	90	0	5	5	0.090
	p,p'-DDE	90	0	0	10	0.160
	p,p'-DDT	90	0	0	10	0.160
	Malathion	80	0	20	0	0.040
VII. Bakery goods	α-BHC	25	65	10	0	0.023
	γ-BHC	45	55	0	0	0.010
	p,p'-DDE	50	35	15	0	0.015
	o,p'-DDT	55	35	10	0	0.016
	p,p'-DDT	25	30	45	0	0.050
VIII. Grains	α-BHC	35	60	5	0	0.015
	γ-BHC	40	55	5	0	0.012
	p,p'-DDE	75	20	5	0	0.012
	p,p'-DDT	40	20	40	0	0.044
IX. Vegetables	α-BHC	68	30	2	0	0.017
	γ-BHC	71	29	0	0	0.007
	p,p'-DDE	80	19	0	0	0.016
	o,p'-DDT	73	25	2	0	0.024
	p,p'-DDT	71	20	9	0	0.043
	Kelthane	82	5	9	4	0.130
	Tedion	87	10	1	2	0.110
X. Tubers	*p,p'*-DDE	75	25	0	0	0.004
	p,p'-DDT	75	25	0	0	0.004
XI. Legumes	α-BHC	35	55	10	0	0.016
	γ-BHC	40	50	10	0	0.012
	p,p'-DDT	55	35	10	0	0.025
XII. Fruits	α-BHC	71	28	1	0	0.018
	γ-BHC	78	19	3	0	0.013
	p,p'-DDE	72	28	4	0	0.005
	o,p'-DDT	72	14	14	0	0.024
	p,p'-DDT	57	19	23	1	0.103
	Kelthane	87	3	5	5	0.200
	Tedion	92	1	4	3	0.200
XIII. Canned vegetables	α-BHC	45	50	0	5	0.100
	γ-BHC	85	10	0	5	0.100
	p,p'-DDE	85	15	0	0	0.010
	p,p'-DDT	60	30	10	0	0.021

(Continued next page)

TABLE 3. (cont'd.). *Distribution of food samples according to contamination by different pesticides*

Food groups [1]	Pesticides [2]	Distribution according to contamination due to different pesticides, %: Not detectable	Trace: 0.001-0.010 ppm	0.011-0.050 ppm	Greater than 0.050 ppm	Highest level, ppm
	α-BHC	45	45	10	0	0.015
	γ-BHC	50	40	10	0	0.014
XIV. Sweets and condiments	*p,p'*-DDE	80	15	5	0	0.029
	o,p'-DDT	50	35	15	0	0.045
	p,p'-DDT	50	15	30	5	0.066
	α-BHC	50	50	0	0	0.006
XV. Alcoholic drinks	γ-BHC	70	30	0	0	0.008
	p,p'-DDT	10	90	0	0	0.005

[1] There were no detectable residues in groups XV and XVI, water and beverages, respectively.
[2] Pesticides not listed were not detected in the specified food group.

TABLE 4. *Food samples not contaminated by pesticides, Spain—1971-72*

Food group		Samples with no detectable residues, %
I	Dairy Products	20
II.	Meats	0
III	Eggs	10
IV.	Fish	10
V.	Fats	0
VI	Vegetable Oils	50
VII.	Bakery Goods	10
VIII	Grains	25
IX.	Vegetables	38
X	Tubers	60
XI	Legumes	20
XII	Fruits	39
XIII	Canned vegetables	30
XIV.	Sweets and condiments	15
XV	Water	100
XVI	Alcoholic drinks	90
XVII	Beverages	100

Based on the pesticide residue levels in each food group and an individual's average yearly intake of these foods (Table 1), authors have estimated the average amount of pesticides an individual in Spain consumes daily from each food group and her/his diet: 78.4 μg DDT, including *p,p'*-DDT, *o,p'*-DDT, and *p,p'*-DDE, and 13.8 μg γ-BHC (Table 6).

These levels are much lower than the daily maximum acceptable concentrations established by FAO and WHO: 250 μg DDT and 625 μg γ-BHC for persons who weigh 50 kg (110 lb). DDT and BHC levels calculated in this study are similar to, but a bit higher than, comparable levels found in the U.S. (55 μg DDT and 3 μg γ-BHC per day) and England (44 μg DDT and 6.6 μg γ-BHC per day) according to Smith (*12*) and Abbott et al. (*1*). Highly toxic pesticides such as dieldrin, which are common in the other countries mentioned, were not detected in Spain.

Acknowledgment

Authors are grateful to Jose Alberola Matoses for his collaboration in the analysis of pesticide residues by gas-liquid chromatography.

TABLE 5. *Average pesticide residue levels in fruits and vegetables, Spain—1971-72*

Product	Residues, ppm: α-BHC	γ-BHC	*p,p'*-DDE	*o,p'*-DDT	*p,p'*-DDT
Oranges	0.001	ND	ND	ND	ND
Bananas	ND	ND	0.001	0.001	0.002
Apples	ND	ND	ND	0.001	0.001
Pears	0.001	0.004	ND	ND	0.009
Peaches	0.001	0.001	ND	0.001	0.007
Melons	0.002	ND	ND	ND	ND
Grapes	ND	ND	0.006	0.015	0.045
Tomatoes	0.001	ND	0.001	0.002	0.001
Lettuce	0.003	0.002	0.002	0.002	0.007
Green beans	0.002	0.001	0.001	0.001	0.004
Onions	ND	ND	ND	ND	ND

NOTE: ND = 0.001 ppm

LITERATURE CITED

(1) *Abbott, D. C., D. C. Holmes, and J. O'G. Tatton. 1969.* Pesticide residues in the total diet in England and Wales, 1966-1967. II. Organochlorine pesticide residues in the total diet. J. Sci. Food Agr. 29(4):245-249.

(2) *Carrasco, J. M., P. Cunat, M. Martinez, and E. Primo. 1972.* Pesticide contamination of average Spanish diet food constituents. Rev. Agroquim. Tecnol. Aliment. 12(3):463-476.

(3) *Carrasco, J. M., J. Cunat, M. Martinez, E. Primo, and J. Alberola. 1971.* Contamination of agricultural products with pesticides. IV. Contamination levels of fruits and vegetables. Rev. Agroquim. Tecnol. Aliment. 11(2):236-248.

(4) *Carrasco, J. M., R. M. Martinez, and P. Cunat. 1969.* Contamination of agricultural products with pesticides. III. Fate of hydrocyanic residues in oranges after fumigation. Rev. Agroquim. Tecnol. Aliment. 9(4): 574-577.

(5) *Cunat, P., J. M. Carrasco, and M. Martinez. 1968.* Contamination of agricultural products with pesticides. II. Pesticide residues in tomatoes. Rev. Agroquim. Tecnol. Aliment. 8(4):472-477.

(6) *Duggan, R. E., and P. E. Corneliussen. 1972.* Dietary intake of pesticide chemicals in the United States (III) June 1968—April 1970. Pestic. Monit. J. 5(4):331-341.

(7) *Duggan, R. E., and J. R. Weatherwax. 1967.* Dietary intake of pesticide chemicals. Science 157(3792): 1006-1010.

(8) *Faubert, M. J., H. Egan, E. W. Godly, E. W. Hammond, J. Roburn, and J. Thomson. 1964.* Clean-up of animal fats and dairy products for the analysis of chlorinated pesticide residues. Analyst 89(1056): 168-174.

(9) *National Institute of Statistics. 1969.* Survey of family budgets. II. Food consumption. Madrid. 360 pp.

(10) *Onley, J. A., and P. A. Mills. 1962.* Detection and estimation of chlorinated pesticides in eggs. J. Ass. Offic. Anal. Chem. 45(4):983-987.

(11) *Primo, E., J. M. Carrasco, and R. M. Martinez. 1967.* Contamination of agricultural products with pesticides. I. Residues of malathion, ziram, lebaycide, kelthane, and Tedion on fruits and its fate before harvest. Rev. Agroquim. Tecnol. Aliment. 7(1):98-104.

(12) *Smith, D. C. 1971.* Pesticide residues in the total diet in Canada. Pestic. Sci. 2(2):92-95.

(13) *United Nations. Food Agricultural Organization/ World Health Organization. 1969.* Residues of Pesticides in Foods. WHO Technical Report No. 525. 50 pp.

(14) *U.S. Department of Health, Education, and Welfare. Food and Drug Administration. 1969.* Pesticide Analytical Manual. Vol. 1.

TABLE 6. *Estimated per capita daily intake of pesticides from food, Spain—1971-72*

Food groups [1]	Residues, μg				
	α-BHC	γ-BHC	*p,p'*DDE	*o,p'*-DDT	*p,p'*-DDT
I. Dairy Products	1.14	0.91	1.37	ND	0.91
II. Meats	2.57	5.45	13.01	1.79	14.99
III. Eggs	0.74	0.74	5.88	ND	7.71
IV. Fish	0.76	0.62	5.38	ND	7.31
V. Fats	1.99	3.56	2.90	0.82	2.13
VI. Vegetable oils	1.09	0.61	0.81	ND	0.81
VII. Bakery goods	2.07	1.24	1.24	0.82	6.62
VIII. Grains	0.11	0.08	0.06	ND	0.19
IX. Vegetables	0.29	0.15	0.15	0.30	0.59
X. Tubers	ND	ND	0.30	ND	ND
XI. Legumes	0.20	0.12	ND	ND	0.16
XII. Fruits	ND	ND	ND	0.15	0.31
XIII. Canned vegetables	0.08	0.05	ND	ND	0.04
XIV. Sweets and condiments	0.31	0.25	0.19	0.50	0.57
XVI. Alcoholic drinks	0.15	ND	ND	ND	ND
TOTAL	11.52	13.78	31.29	4.46	42.66

NOTE: ND = not detectable (< 0.01 μg).
[1] There were no detectable residues in groups XV and XVII, water and beverages, respectively.

GENERAL

Organochlorine Pesticides in the Hawaii Kai Marina, 1970-74

Russell Tanita,[1] Jerry M. Johnson,[2] Michael Chun,[2] and John Maciolek [3]

ABSTRACT

Sediments, water, and oysters from the receiving waters of the Hahaione Valley, a suburban development in southeastern Oahu, Hawaii, were analyzed for organochlorine pesticidal compounds. The insecticides dieldrin, α- and γ-chlordane, and p,p'-DDT were found in the study site environment. Levels were in the low parts per billion range for oysters and sediments and in the low parts per trillion range for water.

During the past several years dieldrin residues in the marina study site have increased, even though the only activity known to influence pesticide levels in the valley is the chronic treatment for subterranean and dry wood termites. If present trends continue, dieldrin may pose a threat to biota of the aquatic environment. Findings have shown that residue levels of dieldrin and p,p'-DDT in the sediments are within the LD_{50} (median lethal dose) range for estuarine fish and thus may have a deleterious effect on bottom-feeding organisms. According to present standards of the Food and Agriculture Organization/World Health Organization, pesticide residue levels within the study site do not appear to constitute a health hazard to humans.

Introduction

Nearly 50 organochlorine compounds are being used in Hawaii as pesticidal agents. The insecticides dieldrin, aldrin, and chlordane are particularly important because of their high application levels (*7*). DDT, although no longer in use, has been included in the present study because it was found by Bevenue (*1*) to be widely distributed in estuarine sites on the island of Oahu, Hawaii.

Studies indicate that organochlorine pesticides have had a detrimental effect on the environment. DDT, for example, has been responsible for a number of fish and bird kills (*3*). Toxicity studies on estuarine fishes by Eisler (*4*) showed LC_{50} (median lethal concentration) levels 96 hours after application ranging from 0.4 to 89 ppb for *p,p'*-DDT and from 0.9 to 34 ppb for dieldrin. Further studies by Eisler (*5*) have shown that these toxicity values were highly dependent upon physical and chemical parameters such as temperature and pH.

The extent to which suburban pesticide usage pollutes the environment is particularly significant to Hawaii with its rapidly expanding suburban population. This problem is compounded in marine waters which serve as popular recreational centers and sources of food. An earlier study (*10*) showed that ground-applied organochlorine pesticides disappear rapidly from Hawaiian coralline soil, the type found in the study area. Only 0.7, 2.3, and 1.8 percent, respectively, of baseline aldrin, chlordane, and dieldrin concentrations in test plot soil remained after 7 years. Retreatment for control of subterranean termites occurs about every 5-10 years. The current study was conducted to assess the contamination of a marine environment by adjacent suburban pesticide use.

The Hahaione Valley, Oahu, receiving waters were selected as the study site. The area was free of industrial and agricultural pesticidal influence from 1964 to 1973. An Epidemiologic Studies Program survey (*7*) of the valley showed that dieldrin, aldrin, and chlordane were being used by households and pest control operators. Limited monitoring of the Hawaii Kai Marina by the Water Resource Research Center, University of Hawaii, has revealed that these insecticides and DDT are present in the sediments and waters of the marina (Table 1).

The Hawaii Kai development on southeastern Oahu consists of a residential tract and a 268-acre marina with a series of channels separated by fingers of land. The study site is situated in one of the channels (Fig. 1)

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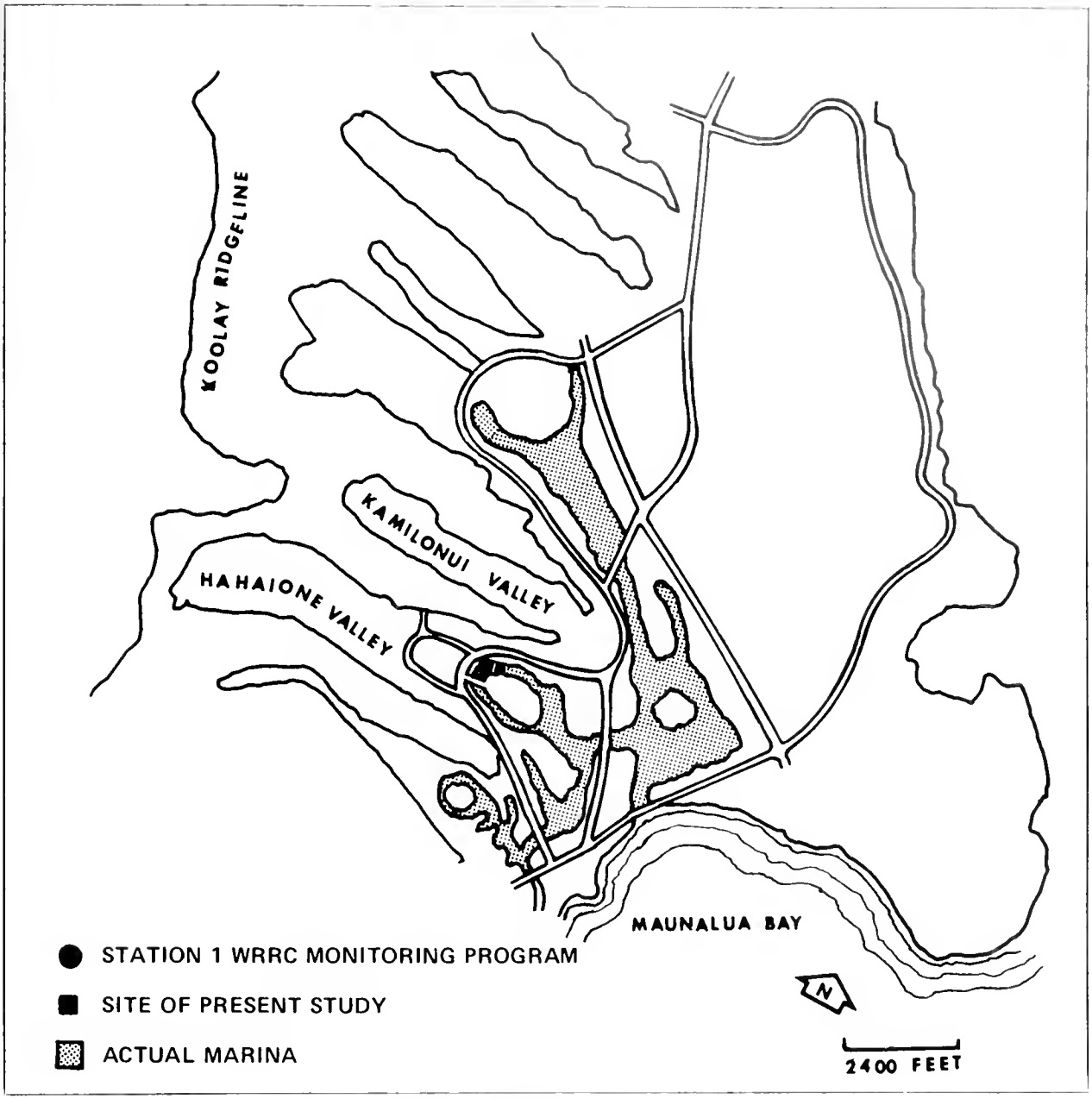

FIGURE 1. *Hawaii Kai suburb and marina*

TABLE 1. *Chlorinated pesticide residue levels in water samples, Hawaii Kai Marina—1972* [1]

Date	Residues, ppbr					
	Dieldrin	Lindane	DDE	DDT	Chlordane α	Chlordane γ
4/27/72	—	—	ND	—	ND	ND
7/15/72	ND	<1	ND	—	<1	<1
11/14/72	—	<1	ND	<1	—	10
10/25/72	—	—	ND	—	—	<1
11/17/72	—	ND	ND	<1	1	<1

NOTE: — = no data.
ND = not detected.

[1] Source: Water Resources Research Center, Hawaii Kai Water Quality Monitoring Program, station 1, University of Hawaii, Honolulu: unpublished data

which serves as the receiving waters for the Hahaione Valley watershed.

The valley has a gently sloping floor from which surface runoff is channeled into a seasonal stream. Surface flow is found only during periods of high rainfall which generally occur during the winter months (*12*). Soils within the watershed range from slightly acidic to moderately alkaline. Permeability is low to moderate. Winds arise from the northeast approximately 70 percent of the time (*10*) but valley ridgelines act as windbreaks, dampening air movement from this direction.

The Hawaii Kai Marina (Fig. 1) has approximately 12 miles of shoreline with an average depth ranging from 5 to 8 feet below mean sea level (*12*). There are two passages on the ocean side between the marina and Maunalua Bay. Each passage is traversed by a bridge. Approximately 90 percent of the shoreline consists of mortared rock walls (*12*), which serve as habitat for oysters and other intertidal organisms in the study area.

Calculated water residence times in the marina vary from 1 to 9 days. The cumulative residence time for the entire marina is 3.5-15 days (*12*). Residence times apparently are directly dependent on tides and wind conditions.

Currents are tide- and wind-induced: tides are primarily responsible for transporting water in and out of the marina (*12*). Surface wind-induced currents are in the direction of the prevailing winds with a subsurface countercurrent. Current velocities vary from 0.1 to 0.2 knots on the surface and from 0.0 to 0.1 knots below the surface.

Construction of the marina began in 1962 and was completed in 1966. Construction of residential dwellings was initiated in 1962 in the Hahaione Valley and is still in progress.

Prior to 1962, the valley consisted primarily of piggeries in the lower stretches and cattle pastures in the interior. Before 1967, the southeastern shores of the marina were under cultivation. Major organochlorine pesticides used at that time were endosulfan, DDT, and dieldrin. Present agricultural activities are now limited to the Kamilonui Valley; no agriculture is practiced in the Hahaione Valley watershed. Pesticide application in the Hahaione Valley is limited to aldrin, chlordane, and dieldrin for ground treatment of termites.

Methods and Procedures

Twelve randomly selected water and sediment samples were obtained from April to July 1974, at the rate of three a month. Sampling was conducted at the seaward boundary of the study site to minimize disturbance of other sites. To avoid possible contamination by the boat or motor, samples were taken from the bow of the boat. Water samples were obtained at a depth of 1 foot below the surface. Only the upper 6 inches of sediment was sampled.

One-gallon glass bottles with aluminum-foil-lined metal covers were used for collecting water samples. One-quart bottles of the same type were used in collecting sediment samples. Before use, bottles and the Soxhlet extraction units were washed with detergent and water and rinsed with a solution of concentrated sulfuric acid and sodium dichromate, followed by a rinsing with water and nanograde hexane. All other glassware was heated for 24 hours at 200°C and rinsed with nanograde hexane.

Oysters were taken from the walls of the sample site over a 3-month period, April-June 1974. Collection began immediately after water and sediment had been sampled. In May 1974 all oysters within a 3-foot grid in the study site were removed to determine wet-weight distribution patterns. Results showed that the distribution was bimodal (Fig. 2).

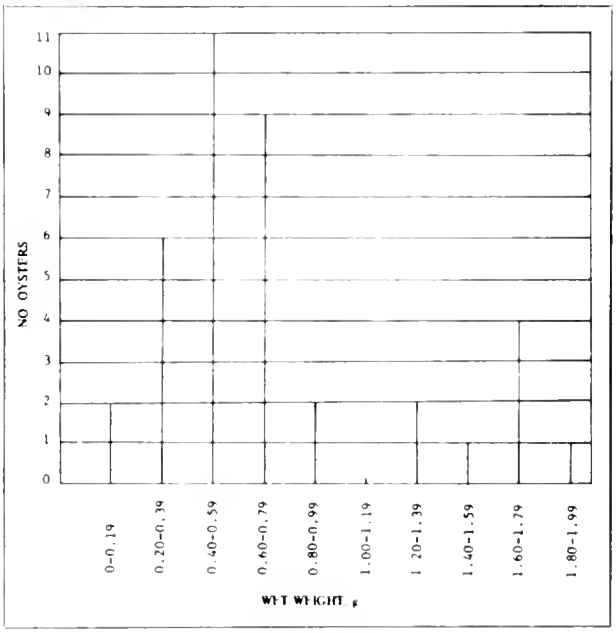

FIGURE 2. *Frequency of distribution of oysters by wet weight, Hawaii Kai Marina—1970-74*

Before extraction, water samples were divided into two 1-liter portions. One portion was filtered through a 0.45-μm-millipore filter. Authors used the partition extraction procedure (Table 1) outlined by the Bureau of Sport Fisheries and Wildlife (*11*) with one modification: a 50:50 mixture of nanograde hexane : nanograde acetone was the solvent. Extracts were cleaned by adsorption chromatography with 6 percent and 15 percent, respectively, purified diethyl ether in nanograde petroleum ether solution (*11*). Resultant fractions were concentrated using a 50°C water bath and a suitable aliquot, usually 5 μl, injected into the gas-liquid chromatograph (GLC).

As a check on the consistency of the procedure described above to extract water samples, triplicate 1-liter portions were processed for the filtered and unfiltered categories. Results are presented in Table 2.

Sediments were air-dried and ground to insure uniformity in size and sample homogeneity. Triplicate 10-g portions were obtained from each sample and extracted with a 50:50 mixture of nanograde hexane : nanograde acetone, using the Soxhlet method (*11*). Extracted

TABLE 2. *Chlorinated pesticide residues in triplicate water samples, Hawaii Kai Marina—July 1974*

	Residues, pptr					
	Filtered Samples			Unfiltered Samples		
Pesticide	1	2	3	1	2	3
γ-Chlordane	1.18	0.15	0.34	1.60	1.20	0.80
α-Chlordane	1.50	0.16	2.50	1.70	1.40	1.84
Dieldrin	9.30	1.00	3.80	6.95	3.33	3.52
p,p'-DDT	1.00	ND	ND	0.62	0.42	ND

NOTE: ND = not detected.

samples were cleaned with the microcolumn silica gel method using a 70:30 mixture of redistilled benzene : nanograde hexane. Resultant fractions were concentrated in a 50°C water bath and aliquots were injected into the GLC.

Oysters were kept frozen until ready for extraction, at which time they were shelled and weighed wet. They were segregated into two groups: large (more than 1 g) and small (less than 1 g), on the basis of the distinctive bimodal frequency distribution noted in a previous sampling of the area (Fig. 2). Large oysters ranged from 1.01 to 2.92 g; average weight was 1.44 g. Small oysters ranged from 0.13 to 0.94 g; average weight was 0.46 g.

Prior to extraction, each oyster was dissected into portions not exceeding a quarter of an inch on each side and extracted with the Soxhlet method followed by microcolumn silica gel cleanup. Fractions were concentrated and injected into the GLC.

Sample analysis was carried out with two Microtek model 220 gas chromatographs with electron-capture detectors. Flow rate was adjusted to insure a minimal retention time of 15 minutes for *p,p'*-DDT. The presence of a residue in the sample was confirmed by the use of two different types of columns: 4 percent SE-30/6 percent OV-210 and 1.5 percent OV-17/195 percent QF-1.

Recovery tests were performed on the three sample categories prior to analysis and after half the samples had been processed. Results ranged from 85 to 95 percent.

Results and Discussion

Results of analyses of water, sediments, and oysters, are given in Tables 3, 4, and 5, respectively.

TABLE 4. *Chlorinated pesticide residues in sediments, Hawaii Kai Marina—April-July 1974*

Pesticide	Range, ppm	Average, ppm	Samples Containing Residue, %
Lindane	90-5,320	1,360	22.2
Aldrin	5,500-11,020	8,260	5.0
p,p'-DDE	110-11,420	2,290	28.7
p,p'-TDE	—	2	2.0
p,p'-DDT	250-6,420	2,165	100.0
Dieldrin	2,000-39,500	8,589	100.0
α-Chlordane	400-5,270	2,966	97.2
γ-Chlordane	1,330-5,120	2,302	92.7

NOTE: — = residue detected in only one sample.

Residue levels in the water samples were in the low parts per trillion (pptr) range (Table 3). Dieldrin, *p,p'*-DDT, and the chlordane isomers were found in a large majority of the samples. Among filtered samples, *p,p'*-DDT occurred three times more frequently than its derivatives, *p,p'*-DDE and *p,p'*-TDE. In the unfiltered samples, the frequency of occurrence of *p,p'*-DDT was 35 percent higher than its derivatives. Average residue levels of filtered and unfiltered samples differed only for *p,p'*-DDE, *p,p'*-TDE, and heptachlor epoxide. Dissimilarities between the filtered and unfiltered samples were also noted in the frequencies of occurrence of *p,p'*-DDE and α-chlordane.

The fact that the unfiltered water had higher average values of *p,p'*-DDE, *p,p'*-TDE, and heptachlor epoxide than had the filtered water indicates that these residues were attached primarily to suspended particulate matter and were not dissolved in the water column. Similar

TABLE 3. *Chlorinated pesticide residues in water samples, Hawaii Kai Marina—April-July, 1974* [1]

	Range, pptr		Average, pptr		Samples Containing Residue, %		Maximum Permissible
Pesticide	Filtered	Unfiltered	Filtered	Unfiltered	Filtered	Unfiltered	Concentration, pptr
α-BHC	0.1-0.3	0.1-0.4	0.2	0.2	33.3	17.7	2,000
Lindane	0.2-0.7	0.1-0.7	0.5	0.4	33.3	25.0	2,000
Aldrin	—	0.9-5.2	1	3	11.1	25.0	40
Heptachlor	—	0.1-0.2	0.2	0.2	22.2	25.0	200
p,p'-DDE	0.4-1.4	0.8-47.1	1	12	22.2	42.7	NS
p,p'-TDE	—	—	1	224	11.1	18.3	NS
p,p'-DDT	1.0-25.9	0.3-21.5	6	5	89.9	83.3	600
Dieldrin	0.8-11.3	0.5-15.0	5	5	89.9	100.0	300
Heptachlor epoxide	—	1.9-127.4	1	65	11.1	17.7	NS
α-Chlordane	NC	NC	NC	NC	89.9	42.7	NS
γ-Chlordane	NC	NC	NC	NC	67.7	67.7	NS

NOTE: NC = residue levels not calculated because of interference from other organic compounds.
— = residue detected in only one sample.
NS = no standards given for these residues.

[1] See Literature Cited, reference 6.

TABLE 5. *Pesticide residues in oysters, Hawaii Kai Marina—April-June 1974* [1]

Pesticide	Range, ppbr		Average, ppbr		Samples Containing Residue, %		Maximum Concentration in/on Food for Human Consumption, mg/kg body weight	FAO/WHO Acceptable Daily Intake, mg/kg body weight
	small	large	small	large	small sample	large sample		
Lindane	1,500-17,870	590-1,260	7,647	925	20.00	18.18	NS	0.0125
Aldrin	—	—	4,830	14,690	6.67	9.09	20,000-100,000	0.0001
Heptachlor	—	ND	4,770	ND	6.67	ND	10,000	0.0005
p,p'-DDE	2,190-7,860	340-4,610	5,025	3,624	13.33	45.45	NS	0.005
p,p'-TDE	ND	3,240-10,550	ND	6,895	ND	18.18	NS	0.005
o,p'-DDT	22,470-50,500	530-4,590	36,485	271	13.33	27.27	NS	0.005
p,p'-DDT	810-27,140	420-17,470	9,337	5,538	46.67	81.82	SD	0.005
Dieldrin	400-94,740	2,870-25,450	34,818	13,472	80.00	100.00	0.200	0.0001
α-Chlordane	2,340-57,640	1,580-22,990	18,640	8,277	33.33	100.00	0.05	0.001
γ-Chlordane	—	1,350-23,380	8,170	7,865	13.33	63.64	0.05	0.001

NOTE: — = residue detected in only one sample.
ND = not detected.
NS = no standards given for these residues.
SD = standard deleted by WHO/FAO.
[1] See Literature Cited, reference 3.

results were obtained in a previous study by Butler (*2*), who showed that the residues were transported primarily on particulate matter. This phenomenon also could account for the higher frequency of occurrence of *p,p'*-DDE in the unfiltered samples.

The filtered fraction had twice as many occurrences of α-chlordane than had the unfiltered fraction. This was probably due to a masking of the α-chlordane peak in chromatographic analysis by organic particulate matter in the water samples. The occurrence of these compounds in the extract made it impossible to accurately quantify chlordane residues in the water samples.

A 1970-71 study by Bevenue (*1*) of selected sites on the island of Oahu reported values of 1.0-14.0 pptr for dieldrin and 0.5-9.0 pptr for *p,p'*-DDT. Results for the Ala Wai Canal, Oahu (*9*), a commercial and industrial receiving channel, are given in Table 6. Levels found by Bevenue are similar to those of the present study.

TABLE 6. *Pesticide data from Ala Wai Canal, Oahu, Hawaii—August 1970-February 1971* [1]

Station	Date Sampled	Residues, ppbr *p,p'*-DDE	*p,p'*-TDE	*p,p'*-DDT	Dieldrin	Chlordane [2]
		Water				
1	8-12-70	1.0	2.0	1.0	5.0	
	2-18-71	ND	1.3	1.6	9.6	9.4
2	8-12-70	ND	3.0	3.0	17.0	
	2-26-71	ND	1.3	1.6	18.6	13.0
3	8-12-70	ND	3.0	2.0	16.0	
	2-18-71	ND	2.6	1.6	0.4	4.8
	Average	0.2	2.2	1.8	11.1	9.1
		Sediment, dry weight				
1	2-18-71	100,000	220,000	150,000	100,000	720,000
2	2-18-71	10,000	100,000	30,000	30,000	290,000
3	2-18-71	10,000	40,000	40,000	100	125,000
	Average	40,000	120,000	73,333	43,366	378,000

NOTE: ND = not detected.
[1] See Literature Cited, reference 9.
[2] Chlordane analyses not conducted in early part of study.

This may be caused in part by the low solubility of the residues. Since the residues are transported primarily on particulate matter, similar turbidity levels in the Hawaii Kai study site and sites selected by Bevenue could account for the similarities in findings.

The U.S. Department of Interior Committee on Water Quality Criteria (*6*) has recommended pesticide standards for saline waters which are based on the toxicity to marine shrimps, the most sensitive of the marine invertebrates. The criteria levels represent the minimum concentrations at which marine biota would suffer deleterious effects. Levels detected in water samples of the present study were below recommended levels and well below the LD_{50} (median lethal dose) obtained by Eisler (*4*) for bottom-feeding fish.

SEDIMENTS

Detected pesticide levels in the marina sediment samples were in the low parts per billion range (Table 4). Frequencies of occurrence were highest for dieldrin, *p,p'*-DDT, and the chlordane isomers. *P,p'*-DDT and dieldrin levels lie within the LD_{50} range for bottom-feeding fishes reported by Eisler (*4*).

The level of dieldrin detected in the sediments appeared to increase sharply from 1972 to 1974 (Table 7). This apparent trend may be fallacious, resulting from the limited number of samples analyzed during 1972 and 1973. If it is real, however, it is significant. The National Pesticide Monitoring Program considers such a trend to be a potential threat to the affected aquatic environment (*8*).

OYSTERS

Oyster tissues had residue levels in the low parts per billion range (Table 5). Dieldrin, *p,p'*-DDT, and the chlordane isomers were the predominant pesticides, appearing in a large majority of the samples. Dieldrin reached its highest levels in the large oysters; the small oysters had higher levels of *p,p'*-DDT and the chlordane isomers. Residues occurred most frequently in the large oysters. Levels were within the range accepted by the

TABLE 7. *Chlorinated pesticide residues in sediment, Hawaii Kai Marina—1972-74*

Pesticide	1972[1]	Frequency of Occurrence, %	1973[1]	Frequency of Occurrence, %	1974[1]	Frequency of Occurrence, %
Lindane	—	—	—	—	1,360	22
Aldrin	—	—	—	—	8,260	6
p,p'-DDE	303	60	601	67	2,290	28
n,p'-TDE	334	20	ND		2	3
p,p'-DDT	1,518	80	871	100	2,165	100
Σ DDT and derivatives	2,155		1,472		4,456	
Dieldrin	1,332	100	5,950	100	8,589	100
α-Chlordane	3,134	100	2,862	100	2,966	97
γ-Chlordane	2,601	100	2,053	100	2,302	92
Sample size	5		6		36	

NOTE: — = no data.
[1] WRRC monitoring data from station 1, Hawaii Kai Marina.

Food and Agriculture Organization/World Health Organization (FAO/WHO) as safe in food consumed by humans (Table 5).

Conclusions

Results have shown that dieldrin, chlordane, and *p,p'*-DDT were distributed throughout the study site. Because the mountains serve as a windbreak (Fig. 1), drift from outside areas can be considered a negligible influence. So, too, are industrial and agricultural activities since few, if any, operate in the Hahaione Valley.

An Epidemiologic Studies Program survey (*7*) of households in the valley indicated that household use of dieldrin and chlordane was negligible. Other dieldrin sources were confined to treated mill-work and fumigation of homes for dry wood termites. Thus it is doubtful that these uses could account for the levels noted in the present study.

The pest control treatment for subterranean termites was the only activity discovered by the Epidemiologic Studies Program survey that could account for the pesticide levels observed in the marina. Aldrin and chlordane were used in these operations. All home sites within the survey area were treated for subterranean termites prior to construction. Aldrin, which has a half-life of 3½ months (*3*) (Table 8), is readily converted to dieldrin and was the likeliest source of the dieldrin in this study.

TABLE 8. *Persistence of some organochlorine insecticides in soil* [1]

Chemical	Average annual dose, lb/acre	Average annual dose, kg/ha	Half-life, years	Time for 95% disappearance, years: Range	Time for 95% disappearance, years: Average
Aldrin	1-3	1.1-3.4	0.3	1-6	3
Chlordane	1-2	1.1-2.2	1.0	3-5	4
DDT	1-2.5[2]	1.1-2.8	2.8	4-30	10
Dieldrin	1-3	1.1-3.4	2.5	5-25	8
Endrin [3]	1-3	1.1-3.4	2.2	3-20	7
Heptachlor	1-3	1.1-3.4	0.8	3-5	3.5
Lindane	1-2.5	1.1-2.8	1.2	3-10	6.5
Isobenzan	0.25-1	0.3-1.1	0.4	2-7	4

[1] See Literature Cited, reference 3.

Pest control activities were the only apparent source of dieldrin and aldrin within the Hahaione watershed. Water column pesticide levels were in the low pptr range. Oyster pesticide levels were in the low ppb range, well within the range of residues accepted as safe by FAO/WHO in foods consumed by humans.

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—1970-1971. Pestic. Monit. J. 6(1):56-64.

(*2*) *Butler, P. A. 1969.* Monitoring pesticide pollution. Bioscience 19(10):889-891.

(*3*) *Edwards, C. A. 1970.* Persistent Pesticides in the Environment. CRC Uniscience Series. Butterworths, London. 78 pp.

(*4*) *Eisler, R. 1970.* Acute Toxicities of Organochlorine and Organophosphorous Insecticides to Estuarine Fishes. Bureau of Sport Fisheries and Wildlife, U.S. Department of Interior. Technical Paper 46. 12 pp.

(*5*) *Eisler, R. 1970.* Factors Affecting Pesticide Induced Toxicity in an Estuarine Fish. Bureau of Sport Fisheries and Wildlife, U.S. Department of Interior. Technical Paper 45. 20 pp.

(*6*) *Federal Water Pollution Control Administration. 1968.* Report of the Committee on Water Quality Criteria. U.S. Department of Interior. 234 pp.

(*7*) *Hawaii Epidemiological Studies Program. 1975.* Annual Report No. 8—January through December, 1974. Pacific Biomedical Research Center, University of Hawaii. 176 pp.

(*8*) *Panel on Pesticide Monitoring, Working Group on Pesticides. 1971.* Criteria for defining pesticide levels to be considered an alert to potential problems. Pestic. Monit. J. 5(1):36.

(*9*) *Shultz, C. D. 1971.* An Examination of Some Chlorinated Pesticide Residues in the Water, Sediment, and Selected Biota in the Ala Wai Canal, Oahu, Hawaii. Unpublished Master's Thesis. University of Hawaii. 49 pp.

(*10*) *State of Hawaii. 1969.* Evaluation of Pesticide Problems in Hawaii, Department of Agriculture, Honolulu, Hawaii.

(*11*) *Tindle, R. C. 1972.* Handbook of Procedures for Pesticide Residue Analysis. Bureau of Sport Fisheries and Wildlife, U.S. Department of Interior. Sections I-O—VI-O.

(*12*) *U.S. Army Engineer District. 1975.* Draft: Environmental Statement for the Department of the Army Permit Actions in the Hawaii Kai Marina, Oahu, Hawaii. 26 pp.

APPENDIX

Chemical Names of Compounds Discussed in This Issue

ABATE	See temefos.
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
BHC (BENZENE HEXACHLORIDE)	1,2,3,4,5,6-Hexachlorocyclohexane (mixture of isomers). Commercial product contains several isomers of which *gamma* 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
DDD	See TDE.
DDE	Dichlorodiphenyl dichloro-ethylene (degradation product of DDT) *p,p'*-DDE: 1,1-Dichloro-2,2-bis(*p*-chlorophenyl) ethylene *o,p'*-DDE: 1,1-Dichloro-2-(*o*-chlorophenyl)-2-(*p*-chlorophenyl)ethylene
DDT	Main component (*p,p'*-DDT): α-Bis(*p*-chlorophenyl) β,β,β-trichloroethane Other isomers are possible and some are present in the commercial product. *o,p'*-DDT: [1,1,1-Trichloro-2-(*o*-chlorophenyl)-2-(*p*-chlorophenyl) ethane]
DICOFOL	4,4'-Dichloro-α-trichloro-methylbenzhydrol
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-*endo-exo*-5,8-dimethano-naphthalene
ENDRIN	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
HCB	Hexachlorobenzene
HEPTACHLOR EPOXIDE	1,4,5,6,7,8,8-Heptachloro-2,3-epoxy-3a,4,7,7a-tetrahydro-4,7-methanoindane
ISOBENZAN	1,3,4,5,6,7,8,8-Octachloro-1,3,3a,4,7,7a-hexahydro-4,7-methanoisobenzofuran
KELTHANE	See dicofol.
LINDANE	*Gamma* isomer of benzene hexachloride, 1,2,3,4,5,6-hexachlorocyclohexane, of 99+% purity
MALATHION	S-[1,2-bis(ethoxy-carbonyl)ethyl] O,O-dimethyl phosphorodithiate
MIREX	Dodecachlorooctahydro-1,3,4-metheno-2H-cyclobuta[cd]pentalene
OXYCHLORDANE	2,3,4,5,6,6a,7,7-Octachloro-1a,1b,5,5a,6,6a-hexahydro-2,5-methano-2H-indeno(1,2-β)oxirene
PCB'S (POLYCHLORINATED BIPHENYLS)	Mixtures of chlorinated biphenyl compounds having various percentages of chlorine
TDE	2,2 Bis(*p*-chlorophenyl)-1,1 dichloroethane
TEDION	See tetradifon.
TEMEFOS	O,O,O',O'-Tetramethyl O,O'-thiodi-*p*-phenylene phosphorothioate
TETRADIFON	*p*-Chlorophenyl 2,4,5-trichlorophenyl sulfone

ERRATA

Pesticides Monitoring Journal, Volume 9, Number 3, pp. 124-133. In the paper "Mirex Nontarget Organisms after Application of Experimental Baits for Fire Ant Control, Southwest Georgia—1971-72," the Table 1 column caption should read "Components of Bait, % by weight." Table 2 should read:

TABLE 2. *Application patterns of mirex bait in three Georgia counties, 1971-72*

Date	County	Formulation: Mirex, %	Area Treated	Bulk Rate [1,2]
				1.40 kg/ha (4.20 g/ha.)
				1.40 kg/ha. (2.10 g/ha.)
		(Correct as published)		1.12 kg/ha. (1.68 g/ha.)
				1.12 kg/ha. (1.12 g/ha.)
				1.12 kg/ha. (1.12 g/ha.)
				1.40 kg/ha. (4 2 g/ha.)

[1] Numbers in parentheses show amount of actual toxicant, i.e., mirex, applied to each hectare.
[2] 1.40 kg/ha = 1.25 lb/acre; 1.12 kg/ha = 1.0 lb/acre.

The *Pesticides Monitoring Journal* welcomes from all sources qualified data and interpretative information on pesticide monitoring. The publication is distributed principally to scientists, technicians, and administrators associated with pesticide monitoring, research, and other programs concerned with pesticides in the environment. Other subscribers work in agriculture, chemical manufacturing, food processing, medicine, public health, and conservation.

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CONTENTS

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RESIDUES IN FOOD AND FEED

Organochlorine Insecticide Residues in Vegetables of the Kitakyushu District, Japan—1971-74

M. Suzuki,[1] Y. Yamato,[1] and T. Watanabe [2]

ABSTRACT

The residue levels of organochlorine insecticides BHC, DDT, endrin, and dieldrin in the Kitakyushu District, Japan, were monitored from 1971 to 1974. Agricultural uses of these insecticides were banned in 1970. BHC isomers, α-, β-, γ-, and δ-BHC were detected in all vegetable samples taken; β-BHC residue appeared in the highest levels. The proportions of each BHC isomer in total BHC residues were much different from those in the technical product. Average residue levels of α-, β-, γ-, and δ-BHC, dieldrin, endrin, and DDTR (p,p'-DDT+p,p'-DDE+p,p'-TDE+o,p'-DDT) in 1971 were 0.007, 0.042, 0.010, 0.008, 0.021, 0.010, and 0.041 ppm in radishes, and 0.004, 0.007, 0.009, 0.003, 0.087, 0.031, and 0.009 ppm in cucumbers. Levels found in 1974 were 0.002, 0.003, <0.001, <0.001, 0.005, 0.006, and <0.001 ppm in radishes, and <0.001, 0.001, 0.001, <0.001, 0.008, 0.009, and undetectable in cucumbers. These residues were translocated from the insecticide-contaminated field soils to the vegetables through their roots.

Residue levels of dieldrin and endrin frequently exceeded the pesticide tolerance limits of Japan, but DDTR residues were only slightly above the specified levels.

Introduction

Organochlorine insecticides such as BHC, DDT, aldrin, dieldrin, and endrin have been applied extensively to agricultural fields, orchards, and forests in Japan for the past two decades to control pest damage. BHC was sprayed on rice paddies, and aldrin, dieldrin, endrin, and DDT were applied mainly to vegetable fields to control soil worms or orchard pests.

Japan produced 41,742 tons of BHC in 1967 and 45,695 tons in 1968, and 4,936 tons of DDT in 1968. The nation imported 767 tons of cyclodiene insecticide in 1968. The contamination of cows' milk by BHC, mainly β-BHC, was reported in 1969. Agricultural and forest uses of BHC, DDT, aldrin, dieldrin, and endrin were banned in late 1970 because of the public concern with contaminated foods. During 1971, the first year after the ban, only 2,000 tons of BHC were produced. Thereafter the production of BHC and DDT and the importation of cyclodiene insecticides were almost ceased.

Determination of organochlorine insecticides in foodstuffs using a gas-liquid chromatograph with an electron-capture detector in Japan was initially conducted by Nishimoto et al. (*7*) in 1966. Many similar studies were conducted subsequently. Because BHC, one of the most heavily used insecticides in Japan, had been applied to the fields without purifying the insecticidally active γ-BHC(lindane), other isomers such as α-, β-, and δ-BHC have been generally found in vegetables. The composition of technical BHC includes 53-70 percent α-BHC, 3-14 percent β-BHC, 11-18 percent γ-BHC, and 6-10 percent δ-BHC. Residues of dieldrin, endrin, and DDTR (*p,p'*–DDT+*p,p'*–DDE+*p,p'*–TDE+*o,p'*–DDT) were also detected in vegetables.

The main objective of the present study was to monitor organochlorine insecticide residues in vegetables commonly cultivated and consumed in the Kitakyushu District, Japan (Fig. 1).

Sampling Procedures

All the vegetable samples were taken directly from the fields in which they were grown according to the schedule in Table 1. Although sampling procedures varied depending on the sample, approximately 1 kg of each vegetable was collected, wrapped in a polyethylene bag, and immediately taken to the laboratory for analysis. Typical samples were a head of cabbage and Chinese cabbage, a root of radish, or three or four roots of turnips and carrots.

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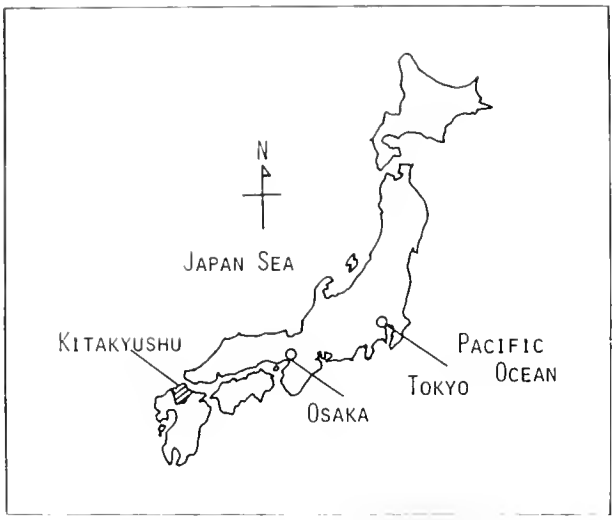

FIGURE 1. *Map of Japan showing the Kitakyushu District*

TABLE 1. *Schedule for sampling vegetables for organochlorine insecticide analyses, Kitakyushu District, Japan—1971-74*

Vegetable	No. Samples Taken	Vegetable	No. Samples Taken
March 21, 1971			
Radish	7	Cabbage	7
Spinach	4		
July 13, 1971			
Cucumber	6	Tomato	5
Eggplant	4	Cabbage	2
September 14, 1971			
Carrot	1	Cabbage	1
Radish	1	Turnip	1
November 5, 1971			
Radish	15	Spinach	6
Chinese Cabbage	8	Turnip	4
Cabbage	7	Carrot	5
July 16, 1972			
Cucumber	8	Radish	1
Eggplant	1	Cabbage	7
November 17, 1972			
Radish	5	Spinach	4
Chinese Cabbage	4	Turnip	4
Cabbage	4		
July 9, 1973			
Cabbage	6	Eggplant	5
Cucumber	5	Carrot	3
December 13, 1973			
Radish	8	Cabbage	5
Chinese Cabbage	6	Turnip	3
September 4, 1974			
Cucumber	4		
November 21, 1974			
Radish	12	Spinach	3
Chinese Cabbage	7	Turnip	5
Cabbage	6		

Analytical Methods

EQUIPMENT AND REAGENTS

Chromatographic columns, 22 x 300 mm

Three-ball Snyder columns with ground glass fittings

5-ml graduated concentrator with ground glass fittings

Shimadzu GC-5AIEE gas chromatograph with dual tritium foil electron-capture detectors

n-Hexane redistilled twice in an all-gas distillation system

Nanograde diethyl ether

Reagent grade anhydrous sodium sulfate heated 2 hours at 625°C to eliminate interferences

Florisil washed thoroughly with distilled water, dried at 110°C, heated at 625°C for 2 hours, deactivated slightly by adding 1 percent distilled water by weight, and mixed well for 30 minutes in a glass-stoppered flask prior to usage

PREPARATION OF SAMPLES

Samples were chopped, mixed thoroughly, and homogenized in a mixer. The root vegetables were washed with cold water to remove adhered soil, and wiped dry. The 100-g homogenized samples were placed in 100-ml beakers, capped with Parafilm, and stored in a refrigerator at –20°C until extraction.

EXTRACTION

All analyses were performed in duplicate and the results represent an average of duplicate analyses. The extraction and partition procedures corresponded to AOAC Official Methods (*1*). However, only 200 ml of 6 percent diethyl ether in n-hexane was used to elute the organochlorine insecticide residues from a florisil column. The eluate was concentrated to approximately 3 ml under a three-ball Snyder column. After addition of heptachlor epoxide as an internal standard, the concentrated eluate was filled up to 5 ml, and 5 μl of the eluate was injected into a gas chromatograph. Recovery was well above 90 percent; results were not corrected.

GAS CHROMATOGRAPHY

Analyses were made with a gas chromatograph equipped with a dual tritium foil electron-capture detector. A multiple column system employing three columns with various polarities was utilized in accordance with the previous report (*12*) to identify and determine residues. The presence of each insecticide was confirmed by comparing the gas-chromatographic retention times of the three columns employed. Operating conditions were:

Column: U-shaped glass, 3 mm ID, 200 cm long
- (i) 2 percent OV-17
- (ii) 2 percent diethylene glycol succinate—0.5 percent phosphoric acid
- (iii) 5 percent Apiezon L grease.

These were coated on 80/100 mesh Gas-Chrom Q.

Carrier gas: prepurified nitrogen at a flow rate of:

(i) 45 ml/min
(ii) 100 ml/min
(iii) 100 ml/min

Temperatures:

Detector: (i) 190°C; (ii) 190°C; (iii) 210°C
Injector: (i) 210°C; (ii) 210°C; (iii) 220°C
Column: (i) 190°C; (ii) 190°C; (iii) 210°C

Retention times of *p,p'*-DDT were approximately 15 minutes on the OV-17 column, 12 minutes on the diethylene glycol succinate–phosphoric acid column, and 12 minutes on the Apiezon L grease column. Twenty-five percent of full-scale deflection was obtained with 0.4×10^{-9} g dieldrin on the Apiezon L grease column. Therefore 0.004 ppm dieldrin in a vegetable sample showed that deflection. Minimum detectable levels of dieldrin, γ-BHC, and *p,p'*-DDT in vegetable samples were 0.0002, 0.0005, and 0.0016 ppm, respectively, through the extraction and gas-chromatographic procedures.

Results and Discussion

The residues detected in vegetable samples are shown in Tables 2-5. BHC isomers were detected in all samples. Insecticide residues in the vegetables might have been transferred from the soil by the roots or taken up from the atmosphere. These insecticides have been prohibited on arable land in Japan since 1970.

BHC isomers were detected in all samples taken because of the high level of contamination of field soils by BHC, one of the most widely used insecticides in the agricultural fields of Japan (*11*). BHC isomers were relatively well absorbed by the vegetables (*13*); β-BHC was dominant among BHC isomers because it was the most persistent in soil (*15*) and the hydrosphere (*10*). The percentage of β-BHC in total BHC was gradually increased; that of α-BHC has decreased. The percentages of BHC isomers in total BHC in 1973 cabbage samples were 7.8 percent α-BHC, 76.5 percent β-BHC, 5.9 percent γ-BHC, and 9.8 percent δ-BHC. The quantities in 1972 radish samples were 2.8 percent α-BHC, 80.0 percent β-BHC, 11:5 percent γ-BHC, and 5.7 per-

TABLE 2. *Organochlorine insecticide residues in vegetables, Kitakyushu District, Japan—1971*

Vegetable	No. samples	α-BHC	β-BHC	γ-BHC	δ-BHC	Dieldrin	Endrin	DDTR
Radish	22							
Average, ppm wet weight		0.007	0.042	0.010	0.008	0.021	0.010	0.041
Range, ppm wet weight		T-0.076	0.001-0.401	T-0.049	T-0.031	T-0.136	0.001-0.023	0.002-0.083
Positive samples, %		100.0	100.0	100.0	100.0	68.2	40.9	18.2
Chinese Cabbage	8							
Average, ppm wet weight		0.016	0.041	0.025	0.008	0.027	0.003	0.006
Range, ppm wet weight		0.002-0.070	0.002-0.187	0.001-0.142	T-0.031	0.002-0.077	NA	NA
Positive samples, %		100.0	100.0	100.0	100.0	37.5	12.5	12.5
Cucumber	6							
Average, ppm wet weight		0.004	0.007	0.009	0.003	0.087	0.031	0.009
Range, ppm wet weight		0.001-0.006	0.003-0.019	0.002-0.018	0.001-0.011	0.002-0.200	0.012-0.067	NA
Positive samples, %		100.0	100.0	100.0	100.0	50.0	50.0	16.7
Tomato	6							
Average, ppm wet weight		0.003	0.008	0.003	0.001	ND	ND	ND
Range, ppm wet weight		0.002-0.006	0.002-0.030	0.001-0.011	T-0.006	NA	NA	NA
Positive samples, %		100.0	100.0	100.0	100.0	0	0	0
Eggplant	6							
Average, ppm wet weight		0.008	0.010	0.006	0.002	0.006	ND	ND
Range, ppm wet weight		0.003-0.026	0.003-0.036	0.002-0.017	0.001-0.006	0.002-0.009	NA	NA
Positive samples, %		100.0	100.0	100.0	100.0	33.3	0	0
Cabbage	19							
Average, ppm wet weight		0.008	0.014	0.012	0.005	0.005	0.029	0.222
Range, ppm wet weight		0.001-0.037	0.006-0.046	0.002-0.094	T-0.028	0.001-0.009	T-0.076	0.003-0.652
Positive samples, %		100.0	100.0	100.0	100.0	47.4	26.3	15.8
Spinach	10							
Average, ppm wet weight		0.005	0.040	0.007	0.008	0.008	0.063	0.023
Range, ppm wet weight		0.001-0.055	0.001-0.072	0.001-0.016	0.001-0.021	0.001-0.027	0.006-0.121	0.005-0.036
Positive samples, %		100.0	100.0	100.0	100.0	80.0	20.0	30.0
Turnip	5							
Average, ppm wet weight		0.001	0.016	0.002	0.001	0.004	0.002	0.020
Range, ppm wet weight		T-0.003	0.002-0.050	T-0.004	T-0.002	0.003-0.005	NA	0.009-0.031
Positive samples, %		100.0	100.0	100.0	100.0	60.0	20.0	40.0
Carrot	6							
Average, ppm wet weight		0.041	0.134	0.021	0.026	0.035	0.017	0.003
Range, ppm wet weight		0.002-0.192	0.012-0.350	0.001-0.083	0.001-0.068	T-0.110	NA	NA
Positive samples, %		100.0	100.0	100.0	100.0	83.3	16.7	16.7

NOTE: T = trace (<0.001 ppm wet weight).
ND = not detected.
NA = not applicable.

TABLE 3. *Organochlorine insecticide residues in vegetables, Kitakyushu District, Japan—1972*

Vegetable	No. samples	α-BHC	β-BHC	γ-BHC	δ-BHC	Dieldrin	Endrin	DDTR
Radish	6							
Average, ppm wet weight		0.001	0.028	0.004	0.002	0.018	0.008	ND
Range, ppm wet weight		0.001-0.004	0.004-0.072	0.002-0.007	T-0.007	0.009-0.027	0.004-0.010	NA
Positive samples, %		100.0	100.0	100.0	100.0	33.3	50.0	0
Chinese Cabbage	4							
Average, ppm wet weight		0.002	0.010	0.002	0.001	0.003	0.001	ND
Range, ppm wet weight		0.001-0.003	0.004-0.019	T-0.003	T-0.003	0.001-0.005	NA	NA
Positive samples, %		100.0	100.0	100.0	100.0	50.0	25.0	0
Cabbage	11							
Average, ppm wet weight		0.030	0.068	0.010	0.014	0.006	0.004	0.016
Range, ppm wet weight		0.001-0.200	0.003-0.169	0.002-0.043	T-0.088	0.003-0.010	0.002-0.007	0.002-0.045
Positive samples, %		100.0	100.0	100.0	100.0	27.2	18.2	27.2
Spinach	4							
Average, ppm wet weight		0.005	0.009	0.004	0.003	0.068	ND	0.013
Range, ppm wet weight		0.003-0.009	0.013-0.072	0.002-0.010	0.001-0.008	0.014-0.122	NA	0.011-0.015
Positive samples, %		100.0	100.0	100.0	100.0	50.0	0	50.0
Turnip	4							
Average, ppm wet weight		0.001	0.011	0.001	T	0.005	0.016	ND
Range, ppm wet weight		T-0.001	0.007-0.016	NA	T-0.001	0.001-0.008	0.001-0.030	NA
Positive samples, %		100.0	100.0	100.0	100.0	50.0	50.0	0
Cucumber	8							
Average, ppm wet weight		0.014	0.016	0.005	0.003	0.043	0.014	ND
Range, ppm wet weight		0.002-0.031	0.004-0.059	0.002-0.008	0.001-0.005	0.004-0.129	NA	NA
Positive samples, %		100.0	100.0	100.0	100.0	87.5	12.5	0

NOTE: T = trace (<0.001 ppm wet weight).
ND = not detected.
NA = not applicable.

TABLE 4. *Organochlorine insecticide residues in vegetables, Kitakyushu District, Japan—1973*

Vegetable	No. samples	α-BHC	β-BHC	γ-BHC	δ-BHC	Dieldrin	Endrin	DDTR
Radish	8							
Average, ppm wet weight		0.001	0.003	0.001	T	0.003	0.005	0.003
Range, ppm wet weight		T-0.003	T-0.013	T-0.001	NA	T-0.007	T-0.010	T-0.008
Positive samples, %		100.0	100.0	100.0	100.0	50.0	62.5	37.5
Chinese Cabbage	6							
Average, ppm wet weight		0.033	0.009	0.007	0.004	T	0.002	ND
Range, ppm wet weight		T-0.188	T-0.037	T-0.038	T-0.022	T-0.001	0.001-0.003	NA
Positive samples, %		100.0	100.0	100.0	100.0	50.0	50.0	0
Cabbage	11							
Average, ppm wet weight		0.004	0.039	0.003	0.005	0.002	0.003	0.018
Range, ppm wet weight		0.001-0.020	0.002-0.238	0.001-0.012	T-0.036	T-0.006	T-0.005	T-0.078
Positive samples, %		100.0	100.0	100.0	100.0	45.5	54.5	54.5
[illegible]	3							
Average, ppm wet weight		0.001	0.004	T	T	0.002	ND	ND
Range, ppm wet weight		T-0.003	0.002-0.006	T-0.001	T-0.001	0.001-0.003	NA	NA
Positive samples, %		100.0	100.0	100.0	100.0	66.7	0	0
[illegible]	5							
Average, ppm wet weight		0.002	0.003	0.002	0.001	0.043	0.016	0.005
Range, ppm wet weight		0.001-0.004	0.001-0.006	0.001-0.007	0.001-0.002	0.001-0.133	0.005-0.027	0.003-0.007
Positive samples, %		100.0	100.0	100.0	100.0	100.0	80.0	80.0
[illegible]	5							
Average, ppm wet weight		0.001	T	0.001	0.001	0.001	ND	ND
Range, ppm wet weight		T-0.002	T-0.001	T-0.002	T-0.005	NA	NA	NA
Positive samples, %		100.0	100.0	100.0	100.0	20.0	0	0
[illegible]	3							
Average, ppm wet weight		0.013	0.142	0.010	0.013	ND	ND	ND
Range, ppm wet weight		0.004-0.020	0.034-0.275	T-0.021	T-0.024	NA	NA	NA
Positive samples, %		100.0	100.0	100.0	100.0	0	0	0

NOTE: T = trace (<0.001 ppm wet weight).
ND = not detected.
NA = not applicable.

TABLE 5. *Organochlorine insecticide residues in vegetables, Kitakyushu District, Japan—1974*

Vegetable	No. samples	α-BHC	β-BHC	γ-BHC	δ-BHC	Dieldrin	Endrin	DDTR
Radish	12							
Average, ppm wet weight		0.002	0.003	T	T	0.005	0.006	T
Range, ppm wet weight		T-0.004	T-0.015	T-0.001	NA	T-0.021	0.001-0.010	NA
Positive samples, %		100.0	100.0	100.0	100.0	50.0	16.7	16.7
Chinese Cabbage	7							
Average, ppm wet weight		0.712	0.095	0.224	0.054	0.001	0.002	ND
Range, ppm wet weight		T-3.560	0.001-0.348	T-1.200	T-0.198	NA	NA	NA
Positive samples, %		100.0	100.0	100.0	100.0	28.6	14.3	0
Cabbage	6							
Average, ppm wet weight		0.004	0.026	0.002	0.001	0.001	0.001	0.002
Range, ppm wet weight		0.001-0.006	0.001-0.098	0.001-0.002	T-0.002	NA	NA	T-0.007
Positive samples, %		100.0	100.0	100.0	100.0	33.3	16.7	83.3
Spinach	3							
Average, ppm wet weight		0.002	0.128	0.003	0.008	0.012	ND	0.016
Range, ppm wet weight		0.001-0.004	0.003-0.285	0.001-0.008	T-0.022	0.001-0.030	NA	T-0.032
Positive samples, %		100.0	100.0	100.0	100.0	66.7	0	66.7
Turnip	5							
Average, ppm wet weight		T	0.001	0.001	T	0.001	0.001	0.002
Range, ppm wet weight		T-0.001	T-0.004	T-0.003	NA	NA	NA	T-0.005
Positive samples, %		100.0	100.0	100.0	100.0	40.0	20.0	60.0
Cucumber	4							
Average, ppm wet weight		T	0.001	0.001	T	0.008	0.009	ND
Range, ppm wet weight		T-0.001	T-0.002	T-0.001	NA	T-0.025	0.003-0.014	NA
Positive samples, %		100.0	100.0	100.0	100.0	100.0	50.0	0

NOTE: T = trace (<0.01 ppm wet weight).
ND = not detected.
NA = not applicable.

cent δ-BHC. Percentages of BHC isomers in the commercial insecticide in Japan were 53-70 percent α-BHC, 3-14 percent β-BHC, 11-18 percent γ-BHC, and 6-10 percent δ-BHC.

Authors speculate that the percentage of β-BHC increased because of its lower vapor pressure, which is 2.8×10^{-7} mmHg. The vapor pressure of α-, γ-, and δ-BHC are 2.5×10^{-5}, 9.4×10^{-6}, and 1.7×10^{-5} mmHg, respectively (*16*); β-BHC was also the most persistent residue among BHC isomers in the soil (*9,15*). The average BHC residue was composed of 7.5 percent α-BHC, 63.2 percent β-BHC, 12.1 percent γ-BHC, and 17.2 percent δ-BHC 19 months after BHC application to a sandy field (2 kg 3 percent γ-BHC a.i./1000 m^2) (*15*).

Eggplant, tomatoes, and cucumbers, vegetables which grew above ground, had lower residues of the BHC isomers than had the root vegetables. Among root vegetables, carrots had the highest BHC residue levels because of the vegetables' high translocation capability. With slight exceptions, BHC residue levels in the vegetables have gradually decreased during the 4-year period, particularly in radishes and turnips.

Residues of dieldrin and endrin were frequently detected at comparatively high levels. In particular, high dieldrin residue levels were found in cucumbers and carrots, which are known to absorb high quantities of dieldrin (*4*). In Japan the cucumber fields had been heavily treated with cyclodiene insecticides; therefore, dieldrin and endrin residue levels were high in the soil of cucumber fields. Photodieldrin, a photoconversion product (*8*) and microbially degraded metabolite (*5*) of dieldrin, was identified in the cucumber field soils (*14*), but no residue could be found in the cucumbers. During the 4-year survey, residues of dieldrin and endrin were detected in vegetables in the following percentages: 1971, 54.2 and 25.0; 1972, 48.6 and 24.3; 1973, 48.8 and 43.9; 1974, 48.6 and 18.9. These percentages were consistent for dieldrin but a disproportionately high occurrence of endrin was found in 1973. No aldrin residues were detected in any vegetable samples, which suggests that aldrin was converted to dieldrin by plant enzymes such as mixed function oxidases or vapor phase oxidation in the atmospheric environment.

Residues of DDTR were detected in vegetables in the following percentages: 1971, 17.5; 1972, 13.5; 1973, 31.7; 1974, 32.4. These residue levels scarcely exceeded the pesticide residue tolerance (Table 6); DDTR in field soil was generally not translocated into vegetables (*11*).

TABLE 6. *Pesticide residue tolerances set by Japanese government for certain vegetables*

Vegetable	Residues, ppm			
	Total BHC	DDTR	Endrin	Aldrin/Dieldrin
Radish	0.2	0.2	ND	0.02
Chinese Cabbage	0.2	0.2	ND	0.02
Cabbage	0.2	0.2	ND	0.02
Spinach	0.2	0.2	ND	ND
Turnip	0.2	0.2	*	*
Cucumber	0.2	0.2	ND	0.02
Tomato	0.2	0.2	ND	0.02
Eggplant	0.2	0.2	ND	0.02
Carrot	*	*	*	*

NOTE: DDTR = DDT+DDE+TDE.
ND = not detectable.
* = not legislated.

The quantity of samples with insecticide residue levels exceeding the pesticide residue tolerance set by the Japanese government was 25.0 percent in 1971, 35.1 percent in 1972, 36.6 percent in 1973, and 27.0 percent in 1974. Tolerances for carrots and turnips have not yet been set. The percentages of samples exceeding the tolerance limit did not change markedly during the study. A large portion of the excesses are attributed to the high dieldrin and endrin levels. Residues in the vegetables were transported from contaminated field soil through the roots of the vegetables (*4,13*) or absorbed from the atmosphere, or evaporated or codistilled from field soil surface (*6*). Because dieldrin and endrin are two of the most toxic agricultural chemicals, the recommended maximum acceptable daily intake set by the Food and Agricultural Organization/World Health Organization (FAO/WHO) for dieldrin was 0.0001 mg/kg body weight (*18*). Elimination of these insecticides from the environment is desirable.

Uyeta et al. (*17*) reported that the daily intake of dieldrin in total diet by residents of the Kochi Prefecture in Japan was 4.8 μg/day. Daily intakes of 2.6 μg/day in Italy (*2*) and 6.6 μg/day in Great Britain (*3*) have been established. These values range from 37.1 to 94.3 percent of the FAO/WHO maximum acceptable daily intake of a person weighing 70 kg. The daily dieldrin content in the diet of residents of the Kitakyushu District was approximately the same as that of the Kochi Prefecture residents. DDT is less toxic than dieldrin. It has a higher recommended maximum acceptable daily intake (0.01 mg/kg body weight) and a higher maximum daily intake acceptable for a person weighing 70 kg.

Comparing the residue levels in the vegetable samples with those found by Nishimoto et al. (*7*) which were published when organochlorine insecticides were still used, no distinct differences were observed, especially in the residue levels of dieldrin and endrin. For example, Nishimoto et al. reported that 0.007-0.015 ppm endrin was detected in four of five radish samples and 0.006 ppm α-BHC was found in one of five cucumber samples (*7*).

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LITERATURE CITED

(*1*) *Association of Official Analytical Chemists. 1970.* Methods of Analysis. 479 pp.

(*2*) *Del Vecchio, E. V., G. Puccetti, C. Caratozzolo, and A. M. Simeone. 1973.* Chlororganic pesticide content in the total diet in Italy. I. Unprocessed foods. Nuovi Ann. Ig. Microbiol. 24(1):1-41.

(*3*) *Her Majesty's Stationery Office. 1969.* Report of Government Chemist, 1968. London. 79 pp.

(*4*) *Lichtenstein, E. P., K. R. Schulz, T. W. Fuhremann, and T. T. Liang. 1970.* Degradation of aldrin and heptachlor in field soils during a ten-year period. Translocation into crops. J. Agric. Food Chem. 18(1): 100-106.

(*5*) *Matsumura, F., K. C. Patil, and G. M. Boush. 1970.* Formation of photodieldrin by microorganisms. Science 170(963):1206-1207.

(*6*) *Nash, R. G., and M. L. Beall, Jr. 1970.* Chlorinated hydrocarbon insecticides: root uptake versus vapor contamination of soybean foliage. Science 168(935): 1109-1111.

(*7*) *Nishimoto, T., M. Uyeta, and S. Taue. 1966.* Studies on the pesticide residues in food (IV). Analysis of organochlorine pesticide residues by electron capture gas chromatography. J. Food Hyg. Soc. Jpn. 7(2): 152-162.

(*8*) *Robinson, J., A. Richardson, B. Bush, and K. E. Elgar. 1966.* A photoisomerization product of dieldrin. Bull. Environ. Contam. Toxicol. 1(4):127-132.

(*9*) *Stewart, D. K. R., and D. Chrisholm. 1971.* Long-term persistence of BHC, DDT and chlordane in a sandy loam soil. Can. J. Soil Sci. 61(3):379-383.

(*10*) *Suzuki, M., Y. Yamato, and T. Akiyama. 1974.* BHC (1,2,3,4,5,6-hexachlorocyclohexane) residue concentrations and their seasonal variation in aquatic environments in the Kitakyushu District, Japan, 1970-1973. Water Res. 8(9):643-649.

(*11*) *Suzuki, M., Y. Yamato, and T. Watanabe. 1973.* Multiple organochlorine pesticide residues in Japan. Bull. Environ. Contam. Toxicol. 10(3):145-150.

(*12*) *Suzuki, M., Y. Yamato, and T. Watanabe. 1973.* On selection of GLC liquid phases in separation of organochlorine pesticides. J. Agric. Chem. Soc. Jpn. 47(1): 1-6.

(*13*) *Suzuki, M., Y. Yamato, and T. Watanabe. 1973.* On translocation of soil residual organochlorine pesticides into vegetables. J. Food Hyg. Soc. Jpn. 14(2):160-167.

(*14*) *Suzuki, M., Y. Yamato, and T. Watanabe. 1974.* Photodieldrin residues in field soils. Bull. Environ. Contam. Toxicol. 12(3):275-280.

(*15*) *Suzuki, M., Y. Yamato, and T. Watanabe. 1975.* Persistence of BHC (1,2,3,4,5,6-hexachlorocyclohexane) and dieldrin residues in field soils of the Kitakyushu District, Japan. Bull. Environ. Contam. Toxicol. 14(5): 520-529.

(*16*) *Tatsukawa, R., T. Wakimoto, and T. Ogawa. 1970.* BHC in the environment. J. Food Hyg. Soc. Jpn. 11(1):1-8.

(*17*) *Uyeta, M., S. Taue, K. Chikazawa, and T. Nishimoto. 1971.* Pesticides translocated into food. Organochlorine pesticides in total diet. J. Food Hyg. Soc. Jpn. 12(6): 445-450.

(*18*) *World Health Organization. 1969.* Pesticide residues in food. Report of the 1968 Joint FAO WHO Meeting. WHO Tech. Rep. Ser. No. 417. Geneva. 25 pp.

Organochlorine Pesticide Residues in Sugarbeet Pulps and Molasses from 16 States, 1971

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ABSTRACT

Sugarbeet pulp and molasses from 57 processing plants in 16 States were sampled for pesticide residues. No molasses samples contained detectable pesticide residues, but about 15 percent of the pulp samples contained low levels of dieldrin, toxaphene, or DDT and its degradation products. Sugarbeet pulp, when used as animal feed, can be a source of pesticidal contamination of human food.

Introduction

Sugarbeet pulp and molasses are waste products obtained from the processing of sugarbeets and sold directly in large quantity as cattle feed. The molasses is also used as an important medium for fermentation, particularly for the production of citric acid, a common food additive. Muns, Stone, and Foley (*3*) reported that 3 lb/a (3.4 kg/ha.) toxaphene applied as a soil treatment resulted in residues of less than 0.4 ppm toxaphene in mature sugarbeets. Johnson and Bischel (*2*) emphasized the potential public health problem of residues in sugarbeet byproducts and found that DDT residues in mature whole beets were less than 0.2 ppm. In studying the fate of aldrin, dieldrin, and endrin residues during partial laboratory processing of raw sugarbeets, Walker et al. (*6*) found that the dried pulp contained the major portion of these pesticide residues. However, published reports of pesticide residues in sugarbeet pulp and molasses from industrial processing plants are rare.

Because of their uses in animal feed additives, sugarbeet pulp and molasses can be significant pathways for pesticide residue transport. The objective of this study was to determine the pesticide residue levels in pulp, molasses, and other commercial products from industrial sugarbeet processing plants.

Processing Technology

Sugarbeets are usually washed and transported from storage areas to the processing plant by small canals filled with warm water. In the plant, the beets are rewashed, sliced, and dropped into a diffuser which countercurrently extracts the beet sugar with water at 79.4°C. The pulp portion is dried and sold as cattle feed. The resulting raw juice is purified with milk of lime, carbon dioxide, and filtration. Soybean oil, tallow, or other oils are added in this purification step to reduce foaming (*4*). Concentrated Steffens' filtrate comes from the process and is later stripped of its residual sugar contents by crystallization.

Materials and Sampling Methods

Sugarbeet processing plants were identified in 16 States: Arizona, California, Colorado, Idaho, Iowa, Kansas, Michigan, Minnesota, Montana, Nebraska, North Dakota, Ohio, Oregon, Utah, Washington, and Wyoming. All samples in this study were collected from the 57 processing plants in operation at the study's initiation.

Samples were collected in the fall of 1970. The primary products sampled were sugarbeet pulp, molasses, and related processing materials such as soybean oil, tallow, and Steffens' filtrate. The sampling methods of the U.S. Department of Agriculture were employed (*5*). The number and kinds of samples are listed by State in Table 1.

Chemical Analysis

All analyses reported in this paper were conducted at the Pesticide Monitoring Laboratory, Bay St. Louis, Miss. The extraction of samples of sugarbeet pulp, soy-

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TABLE 1. *Number and type of samples collected by State, 1971*

State	No. Plants	No. Samples				
		Pulp	Molasses	Soybean Oil	Tallow	C.S.F.[1]
Arizona	1	2	—	—	—	—
California	10	20	3	—	—	—
Colorado	10	20	14	—	—	—
Idaho	4	8	8	—	—	8
Iowa	1	2	2	2	—	—
Kansas	2	4	—	—	—	—
Michigan	5	10	—	—	—	—
Minnesota	4	8	8	—	—	—
Montana	3	6	3	—	—	3
Nebraska	4	8	7	—	—	4
North Dakota	1	2	2	2	—	—
Ohio	3	6	2	—	1	—
Oregon	1	2	2	—	—	—
Utah	3	6	6	—	—	—
Washington	2	4	4	—	—	—
Wyoming	3	6	4	—	—	—
TOTAL	57	114	65	4	1	15

NOTE: — = no sample collected
[1] Concentrated Steffens' filtrate.

bean oil, and tallow was similar to methods reported previously (*1*).

The molasses and filtrate were extracted by weighing a 20-g sample into a 100-ml beaker and then thinning with 20 ml distilled water so that less than 5 percent of the sample adhered to the beaker. This mixture was poured into a 500-ml separatory funnel and 150 ml redistilled hexane was added and mixed a few seconds by shaking. Fifty ml isopropanol was added, and the mixture was shaken again and allowed to settle. The mixture was then washed three times with 150 ml distilled water and the aqueous layers were discarded. The hexane layer was then filtered through a sodium sulfate filter tube into a 500-ml conical jointed flask. The excess solvent was evaporated through a Snyder column to about 5 ml and transferred to a graduated centrifuge tube or other container. The extract was diluted to 10 ml with hexane and stored at low temperature for gas chromatography. No cleanup was necessary.

Analyses were performed on gas chromatographs equipped with tritium foil electron affinity detectors for organochlorine compounds and flame phytometric detectors for organophosphorus compounds. Pesticides and related chemicals detectable by these methods are listed in Table 2. A multiple-column system employing polar and nonpolar stationary phases was used to identify the pesticides. Dual-column gas chromatography was employed for each sample: the main column and one of the two alternative supplementary columns. Instrument parameters were:

Columns
glass, 6 mm OD by 4 mm ID, 183 cm long packed with one of the following:
1.5 percent OV-17 1.95 percent QF-1 on 100 120 mesh diatoport (alternative and supplementary column)
3 percent DC-200 on 100/120 mesh gas-chrom Q (main column)
9 percent QF-1 on 100/120 mesh diatoport (alternative and supplementary column)

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

TABLE 2. *Chemical compounds detectable by the analytical method used in the present study*

Organochlorine Compounds	Organophosphorus Compounds
Aldrin	DEF
Benzene hexachloride isomers	Diazinon
Dieldrin	Ethion
o,p'-DDE	Ethyl parathion
p,p'-DDE	Malathion
o,p'-TDE	Methyl parathion
p,p'-TDE	Phorate
o,p'-DDT	Trithion
p,p'-DDT	
Endrin	
Heptachlor	
Heptachlor epoxide	
Polychlorinated biphenyls	
Technical chlordane	
Toxaphene	
Trifluralin	

Generally, the limit of minimum detection was 0.01 ppm. Mixed pesticides such as polychlorinated biphenyls, toxaphene, and chlordane are exceptions, and the limits for these pesticides range from 0.03 to 0.05 ppm.

RECOVERY

Recovery rates from sugarbeet pulp ranged from 89 to 105 percent except heptachlor epoxide which was 82 percent. Recovery rates from molasses and filtrate ranged from 83 to 88 percent with an average of 87 percent. Results presented here were corrected for recovery.

Results and Discussion

All residue results were reported on the sample as it had been received. Nearly 15 percent of the 114 pulp samples contained pesticide residues as shown in Table 3. Residues of *p,p'*-DDE, *o,p'*-DDT, *p,p'*-DDT, dieldrin, toxaphene, and *o,p'*-DDE were found but the arithmetic mean concentrations of all these residues were less than 0.01 ppm.

The mean dieldrin residue value for pulp was below 0.01 ppm and maximum value detected was 0.01 ppm. Walker et al. (*6*) reported the dieldrin residue of dried sugarbeet pulp for three different pesticide treatments

TABLE 3. *Arithmetic mean and range of pesticide residues in sugarbeet pulp and related materials from processing plants*

Material	No. Analyses	Positive Samples, %	*o,p'*-DDE		*p,p'*-DDE		*o,p'*-DDT		*p,p'*-DDT		Dieldrin		Toxaphene		Heptachlor Epoxide	
			Mean	Range	Mean	Range	Mean	Range	Mean	Range	Mean	Range	Mean	Range	Mean	Range
Pulp	114	14.7	<0.01	ND-0.01	<0.01	ND-0.16	<0.01	ND-0.01	<0.01	ND-0.05	<0.01	ND-0.01	<0.03	ND-0.34	ND	ND
Molasses	65	0	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
Soybean Oil	4	50.0	ND	ND	ND	ND	ND	ND	ND	ND	0.02	ND-0.05	ND	ND	<0.01	ND-0.01
Tallow	1	100.0	ND	ND	ND	ND	ND	ND	ND	ND	0.01	NA	ND	ND	ND	ND
C.S.F.[1]	15	0	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND

NOTE: ND = not detected.
NA = not applicable.
Limit of minimum detection is generally 0.01 ppm except for toxaphene, which ranges from 0.03 to 0.05 ppm.
All residues were reported on the sample as it had been received

[1] Concentrated Steffens' filtrate.

of soil in their pilot laboratory study; the mean of their three dieldrin residue values was 1.096 ppm and the range was 0.089-1.712 ppm. The difference between findings of these two studies may reflect differences in handling and processing practices between industrial processing plants and the pilot laboratory.

No pesticide residues were found in samples of molasses or concentrated Steffens' filtrate, a fact which may result from the manufacturing process. Pulp is extracted with water at 79.4°C. Since chlorinated hydrocarbons are quite insoluble in water, much of the pesticide residue may remain in the pulp. Even if residues were found in the juice, it is highly probable that the severe treatments with milk of lime, sulfur dioxide, and activated carbon would remove or destroy residues. Because the concentrated Steffens' filtrate and molasses are both derivatives of juice, it is not surprising that no pesticide residues could be detected.

The detection of dieldrin and heptachlor epoxide in soybean oil is consistent with the result of a previous study (*1*) which showed that soybeans contained mean levels of 0.12 ppm dieldrin and less than 0.01 ppm heptachlor epoxide.

All pesticide residues detected in the study of sugarbeet pulp, that is, DDT, dieldrin, and toxaphene, had been commonly applied to soil or mixed with dry seed prior to planting for control of various sugarbeet pests such as wireworms, root maggots, and cutworms. Therefore, the detected residues are indication of cause and effect of pesticide application.

Conclusion

Use of sugarbeet pulp as cattle feed presents a potential problem of pesticide entry into cattle and eventually into the human food chain. However, the small amount of residues present in the pulp may never build up enough in the human food chain to endanger health. Molasses from sugarbeet processing does not present such a problem.

LITERATURE CITED

(*1*) *Carey, A. E., G. B. Wiersma, H. Tai, and W. G. Mitchell. 1973.* Organochlorine pesticide residues in soils and crops of the corn belt region, United States—1970. Pestic. Monit. J. 6(4):369-376.

(*2*) *Johnson, J. R., and S. E. Bischel. 1962.* Insecticide residues in sugarbeet byproducts. J. Amer. Soc. Sugar Beet Technol. 12(3):255-258.

(*3*) *Muns, R. P., M. W. Stone, and F. Foley. 1960.* Residues in vegetable crops following soil applications of insecticides. J. Econ. Entomol. 53(5):832-835.

(*4*) *Shieves, R. N. 1967.* Chemical Process Industries. McGraw-Hill Book Co., pp. 631-633.

(*5*) *U.S. Department of Agriculture—Plant Protection Division. 1970.* Sugar Beet Pulp Sampling at Sugar Beet Processing Plants in the Conterminous United States. 4 pp.

(*6*) *Walker, K. C., J. C. Maitlen, J. A. Onsager, D. M. Powell, and L. I. Butler. 1965.* The Fate of Aldrin, Dieldrin, and Endrin Residues during the Processing of Raw Sugarbeets. U.S. Department of Agriculture, pp. 1-10.

Organochlorine Residues in Three Bat Species from Four Localities in Maryland and West Virginia, 1973 [1]

Donald R. Clark, Jr., and Richard M. Prouty

ABSTRACT

In 1973, 119 bats of three species were collected from four localities in Maryland and West Virginia. The collection included 43 big brown bats (Eptesicus fuscus), *43 little brown brown bats* (Myotis lucifugus), *and 33 eastern pipistrelles* (Pipistrellus subflavus). *The bats were collected from Round Top Mountain, Washington Co., Md.; Trout Cave, Pendleton Co., W. Va.; Montpelier Barn, Prince Georges Co., Md.; and North East Methodist Church in Cecil Co., Md. Residues of ΣDDT were highest in carcasses of bats from Round Top Mountain, which is surrounded by apple orchards. Bats from Trout Cave had the lowest residues, a circumstance which probably reflects the absence of agriculture and industry in the area. A polychlorinated biphenyl (PCB) and oxychlordane were highest at Montpelier Barn. Sources of the PCB are unknown, but chlordane is used against termites and in gardening at nearby housing developments. Residues in bats from North East Methodist Church were low except for dieldrin. Among species, little brown bats usually had the highest residue concentrations in their carcasses, whereas big brown bats had the lowest.*

When DDE in carcass fat of all species was above 60-90 ppm, it became measurable in brain tissue. Above 60-90 ppm, DDE levels in brains rose with increasing levels in carcass lipids. Residues of the PCB tended to respond similarly. Residue levels in brains were greatest in little brown bats; the maximum level of the PCB, 7.9 ppm, was more than twice that of DDE.

Introduction

Several [illegible] have postulated that organochlorine insecticides [illegible] caused declines in bat populations (*2,7,11,12,15,16,19*). [illegible]-living bats have been sampled for organochlorine residues in Britain (*13*), Arizona and Mexico (*17*), Australia (*1,10*), and Texas (*6*). Data also indicate that Aroclor 1260, a polychlorinated biphenyl (PCB), caused stillbirths in a Maryland colony of big brown bats (*Eptesicus fuscus*) (*4*). The extent of contamination of bat populations is only partly described by these few studies. Furthermore, proper interpretation of such residue data will not be possible until tissue levels of residues are experimentally correlated with toxicological effects.

At four ecologically diverse localities, authors sampled residues in three bat species (big brown bat; little brown bat, *Myotis lucifugus;* and eastern pipistrelle, *Pipistrellus subflavus*), which are common and wide-ranging in North America.

Materials and Methods

All three species were present at the two collection localities in the Allegheny Mountains. One locality, Round Top Mountain, has several abandoned mine tunnels adjacent to the Potomac River, 5.4 km southwest of Hancock, Washington Co., Md. Extensive apple orchards are located near this site. The second locality, Trout Cave, is adjacent to Highway 220, 5.6 km southwest of Franklin, Pendleton Co., W. Va. The surrounding area is mostly undisturbed forest. Additional information about these two sites is available elsewhere (*8,9*). Big brown and little brown bats were collected at a third locality, Montpelier Barn, at Montpelier State Historical Site, Laurel, Prince Georges Co., Md. This locality is in the urbanized corridor between Washington, D.C., and Baltimore, Md. It is surrounded by housing developments, shopping centers, and highways. Only little brown bats occur at the fourth site, the attic of the Methodist Church in North East. This is a town of 1,600 residents in Cecil Co., Md., at the northern end of the Chesapeake Bay.

Authors collected bats at or near the extremes of the animals' fat cycles in spring and fall 1973. Collection dates were: Round Top Mountain, April 3 and October 31; Trout Cave, April 12 and November 1; Montpelier Barn, April 26 and October 2; and North East Methodist Church, May 2 and October 3. Numbers of bats caught on these dates are given in Table 1. To obtain

[1] Fish and Wildlife [illegible] U.S. Department of Interior, Patuxent Wildlife Research [illegible] Laurel, Md. 20811

TABLE 1. *Summary of principal organochlorine residues in carcasses of 110 bats, Maryland and West Virginia—1973*

Sample	*n*	Residue levels, ppm wet weight											
		PCB		DDE		DDT		TDE		Dieldrin		Oxychlordane	
		Geom. Mean	Range	Geom. Mean	Range	Geom. Mean	Range	Geom. Mean	Range	Geom. Mean	Range	Geom. Mean	Range
Round Top Mountain													
Spring													
BBB ♂	6	1.27	0.50-2.4	11.16	4.6-67	0.86	0.41-2.1	0.22	0.11-0.50	0.55	0.34-1.1	0.20	0.15-0.31
♀	3	1.48	1.2-1.8	7.29	2.2-32	0.41	0.20-0.95	0.04	ND-0.14	0.56	0.28-0.81	0.10	ND-0.19
LBB ♂	2	7.75	6.0-10	10.78	8.3-14	1.08	0.83-1.4	0.62	0.55-0.71	0.73	0.38-1.4	0.43	0.38-0.48
EPB ♂	7	8.18	3.4-20	6.39	0.93-21	0.59	0.44-1.1	0.22	0.10-0.48	0.29	0.14-0.74	0.36	0.23-0.60
♀	3	6.01	2.3-11	3.32	2.6-4.4	0.52	0.34-0.68	0.18	0.15-0.22	0.30	0.22-0.56	0.36	0.28-0.46
Fall													
BBB ♂	3	0.77	0.55-0.91	6.35	2.9-17	0.41	0.22-1.3	ND	ND-ND	0.35	0.11-0.82	0.04	ND-0.13
LBB ♂	3	4.60	3.7-6.4	38.54	14-87	2.45	1.4-5.0	0.49	0.21-2.0	0.64	0.37-1.1	0.65	0.52-1.0
♀	1	2.3		23		2.0		0.77		1.3		0.38	
EPB ♂	5	3.76	0.60-9.1	9.72	4.0-34	0.74	0.33-1.4	0.27	ND-1.9	0.52	0.22-1.2	0.40	0.15-0.58
Trout Cave													
Spring													
BBB ♂	10	0.75	0.45-0.99	0.67	0.36-1.9	0.14	ND-0.25	ND	ND-ND	0.20	ND 0.28	0.02	ND-0.11
LBB ♂	7	4.21	1.2-26	2.83	0.69-18	0.55	0.17-3.2	0.55	ND-1.9	0.64	ND-2.2	0.45	0.07-1.9
EPB ♂	10	1.74	0.56-8.1	2.21	0.14-6.9	0.67	0.12-1.9	0.32	ND-0.96	0.14	ND-0.49	0.27	ND-0.63
♀	3	1.19	ND-2.6	2.56	1.0-12	0.83	0.12-3.2	0.49	ND-1.0	0.41	0.20-0.63	0.24	0.11-0.40
Fall													
BBB ♂	1	0.27		0.29		ND		ND		ND		ND	
♀	2	0.50	0.50-0.50	0.23	0.17-0.32	0.21	ND-0.47	ND	ND-ND	ND	ND-ND	ND	ND-ND
LBB ♂	1	10		2.9		0.96		0.14		0.18		0.29	
♀	4	4.69	1.3-12	1.90	0.85-4.9	1.60	ND-20	0.44	ND-2.2	0.22	0.13-0.31	0.35	0.18-0.61
EPB ♂	2	0.60	0.59-0.61	0.38	0.26-0.55	ND	ND-ND	ND	ND-ND	ND	ND-ND	0.19	0.10-0.28
♀	3	0.71	ND-2.9	1.38	0.35-4.2	0.15	ND-0.31	0.17	ND-0.36	0.09	ND-0.31	0.13	ND-0.21
Montpelier Barn													
Spring													
BBB ♂	4	4.99	4.1-5.7	5.32	4.5-5.9	0.70	0.63-0.86	0.23	0.18-0.35	0.50	0.43-0.62	0.81	0.66-0.93
♀	3	2.87	2.3-3.2	3.48	3.0-3.8	0.32	0.27-0.40	0.04	ND-0.11	0.51	0.44-0.58	0.40	0.31-0.58
LBB ♀	5	11.61	3.9-21	3.00	1.9-7.6	0.54	0.28-1.1	0.25	ND-0.52	1.04	0.71-1.5	1.52	1.1-2.7
Fall													
BBB ♂	2	2.50	2.4-2.6	2.05	2.0-2.1	0.42	0.39-0.45	ND	ND-ND	0.59	0.48-0.73	0.31	0.24-0.41
♀	3	0.48	0.14-1.5	0.59	0.19-2.0	0.05	ND-0.15	ND	ND-ND	0.26	0.12-0.47	0.11	ND-0.17
North East Church													
Spring													
LBB ♀	11	3.22	1.6-5.9	1.80	0.71-3.7	0.38	0.13-1.3	0.29	ND-0.87	1.01	0.45-3.2	0.52	ND-3.0
Fall													
LBB ♀	6	2.34	1.4-4.0	1.47	0.70-3.1	0.30	0.18-0.64	0.09	ND-0.18	0.70	0.24-3.2	0.63	0.31-1.2

NOTE: BBB = big brown bat.
LBB = little brown bat.
EPB = eastern pipistrelle bat.
n = number of bats sampled.

additional samples of stomach contents for chemical analysis, authors collected nine more bats in July 1973 after their evening feeding flights: on July 11 four big brown bats (3 males, 1 female) and one little brown bat (male) were collected at Montpelier Barn, and on July 25 two big brown bats (males) and two little brown bats (1 male, 1 female) were caught at Trout Cave. In sum, 119 bats were collected and analyzed.

Bats were frozen at capture and later thawed and weighed before dissection. Brains, carcasses, pooled samples of masticated insects from stomachs, and guano samples were analyzed. Wings, feet, and skin were removed and discarded, the head was severed at the base of the skull, and the brain was removed after clipping away the top of the cranium with iris scissors. Major masses of head masculature were placed with the carcass for analysis and the skull was dried and stored. The gastro-intestinal tract was removed from the remaining body portion, which was then analyzed as carcass. The occlusal tip width of the upper left canine (canine tip width, CTW) was measured using a 30X dissecting microscope and ocular micrometer. This measurement was used as an indicator of relative age (*3*). Samples were placed individually into cleaned and weighed glass jars, weighed, and refrozen until grinding.

All samples were analyzed at the Patuxent Wildlife Research Center. Personnel immunized against rabies prepared the tissue under a bacteriological hood in an isolated area of the laboratory because bat tissues can carry rabies. After extraction, no special precautions were required. The material was thawed and ground with anhydrous sodium sulfate to remove moisture. The resultant mixture was transferred to a paper extraction thimble and extracted with hexane on a Soxhlet apparatus for approximately 7 hours. The extract was cleaned

on a florisil column with 200 ml of 6 percent ethyl ether in hexane.

Pesticides and polychlorinated biphenyls (PCB's) were separated into three fractions on a Silicar column and analyzed with a Hewlett-Packard 5753 gas-liquid chromatograph equipped with a Ni^{63} detector, automatic sampler, digital integrator, and a 4 percent SE-30 6 percent QF-1 column at 190 C. The flow rate of 5 percent methane in argon was 60 ml/min for columns and 40 ml min for purge. DDE was quantitated by peak height to avoid errors from PCB interference; other pesticides were measured by digital integration of area, and the PCB was quantified by comparing total peak area with that of Aroclor 1260, the compound whose pattern matched it most closely.

Samples were analyzed for *p,p'*-DDE, *p,p'*-TDE, *p,p'*-DDT, dieldrin, heptachlor epoxide, mirex, oxychlordane, *cis*-chlordane and/or *trans*-nonachlor, *cis*-nonachlor, hexachlorobenzene (HCB), toxaphene, and PCB's. Average percent recoveries from spiked tissues of mallard duck (*Anas platyrhynchos*) were DDE, 96; TDE, 103; DDT, 112; dieldrin, 101; heptachlor epoxide, 104; oxychlordane, 98; *cis*-chlordane, 100; *cis*-nonachlor, 98; HCB, 69; and the PCB, 101 percent. Residue data were not adjusted for recovery. The lower limit of sensitivity was 0.1 ppm for pesticides and 0.5 ppm for PCB in carcass and guano samples. The small size of brain and stomach samples limited sensitivity to 0.5 ppm.

Residues in 12 percent of the samples were confirmed with a gas chromatograph – mass spectrometer equipped with a temperature-programmed 1 percent SE-30 column. Program rate was 2 C min; initial temperature, 135 C, rose to a maximum of 220 C. Operating conditions were: flow rate, 35 ml min helium; oven temperature, 200°C; flash heater, 220 C; separator, 240°C; and ion source, 290°C. The ionization potential was 70 eV, and the accelerating voltage was 3.5 kV. Results are given as ppm wet weight unless lipid weight is designated. Guano was weighed dry as it came from the roost and masticated insects were weighed as they came from stomachs.

Because the residue data were positively skewed, they were log transformed for all statistical testing. Geometric means are given for residue data. Differences between means were tested for significance using Student's *t*-test adjusted for sample size (*18*). Significance levels were: $0.05 < P < 0.01$; $0.01 < P < 0.001$; and $P < 0.001$. Residue levels reported as not detected (ND) entered computations as zeros.

Results and Discussion

RESIDUES ACCORDING TO AGE

When the 119 bats sampled were subdivided by species, locality, and sex, four groups remained which included ten or more bats each: female little brown bats at North East Methodist Church (n=17); male big brown bats at Trout Cave (n=13); male pipistrelles at Trout Cave (n=12); and male pipistrelles at Round Top (n=12). For each of these four groups, the regression between CTW and μg of residue in the carcass was calculated for the PCB, DDE, DDT, TDE, dieldrin, and oxychlordane. DDE declined significantly with increased CTW among male pipistrelles from Trout Cave (r=0.63*, slope=-1.42). Similarly, the PCB declined among female little brown bats at North East Methodist Church, but the correlation coefficient was not significant (r=-0.46, $0.1>P>0.05$, slope =-0.81).

These negative relationships resemble those found for the PCB in female big brown bats and their newborn young from both Montpelier Barn (*4*) and a house attic in Gaithersburg, Md. (*5*). They differ, however, from the relationship of DDE in female free-tailed bats (*Tadarida brasiliensis*), which dropped abruptly after the first year of life and then increased with age (*6*). For the data at hand, the overall effect of age on residue load is minor and was ignored in subsequent analysis.

RESIDUES ACCORDING TO SEX

After subdividing samples by species, locality, and season, authors were able to conduct eight tests between means for males and females for the PCB, DDE, DDT, dieldrin, and oxychlordane, and seven tests for TDE. Six of 47 tests based on total μg in carcasses showed significant differences: males had higher residues than females in all six samples. Five of the six tests were for the spring sample of big brown bats from Montpelier Barn and included the PCB (t=3.60*), DDE (t=2.63*), DDT (t=5.04**), TDE (t=3.67*), and oxychlordane (t=3.14*). The sixth was the spring sample of big brown bats from Round Top and the chemical was TDE (t=3.17*).

When residues were treated as ppm, six of six significant tests also showed males with greater residues than females. Five of the six significant tests were again from the spring sample of big brown bats from Montpelier Barn: the PCB, t=4.47**; DDE, t=4.73**; DDT, t=6.01**; TDE, t=3.84*; and oxychlordane, t=3.83*. The sixth was the fall sample of big brown bats from Montpelier Barn; the chemical was DDT (t=4.91*).

Because high residues of PCB's and DDE have been found in bat milk (*5,6*), authors believe that lactation played a role in producing these differences in residues between males and females.

None of the eight male – female tests for dieldrin showed a significant difference, but means for females, expressed as both μg and ppm, were greater than those for males in seven cases. The probability of this happening if the sexes were equally likely to show a greater ... in any single comparison is P=0.03*. Thus the

kinetics of dieldrin in males and females may be unique among these toxicants.

Even though significant differences involved only big brown bats, it seems clear that comparisons of samples with markedly different proportions of males and females must be made cautiously regardless of species.

RESIDUES ACCORDING TO SEASON

After subdividing samples by species, locality, and sex, authors were able to conduct 10 tests between means for spring and fall for the PCB, DDE, DDT, dieldrin, and oxychlordane, and 8 tests for TDE. When residues were expressed as total μg in carcasses, 10 of 58 tests showed significant differences, but 6 of these showed greater residues in the spring and 4 showed greater residues in the fall. All 10 tests involved males. Samples with significantly more residues in the spring were big brown bats at Montpelier Barn (DDE, t=3.22*; TDE, t=10.15***), big brown bats at Round Top (TDE, t=5.12**; oxychlordane, t=2.79*), big brown bats at Trout Cave (dieldrin, t=2.36*), pipistrelles at Trout Cave (DDE, t=3.24**). Samples with more residue in the fall were big brown bats at Montpelier (dieldrin, t=3.46*), little brown bats at Round Top (oxychlordane, t=3.40*), and pipistrelles at Round Top (DDT, t=2.35*; dieldrin, t=2.34*).

Both significant tests with TDE showed higher residue in the spring. The spring mean for TDE was greater than that for fall in seven of eight cases (P=0.03*). Corresponding decreases in DDT did not occur during hibernation; thus increased TDE through breakdown of DDT is not indicated.

In sum, no spring/fall pattern in μg residues appeared in the bats except, perhaps, for TDE.

Considering that μg residues did not change consistently with season, and that the bats store abundant fat before winter, it is predictable that residues expressed as ppm would be greater in spring. Twelve of 58 tests showed significant differences; spring amounts were greater in all 12 cases. Male samples were big brown bats at Montpelier Barn (the PCB, t=6.42**); DDE, t=10.08***; DDT, t=4.37*; TDE, t=4.68**; oxychlordane, t=4.69**), big brown bats at Trout Cave (the PCB, t=3.52**; TDE, t=3.18*), big brown bats at Round Top (oxychlordane, t=3.69**), and pipistrelles at Trout Cave (DDT, t=2.72*). Female samples were big brown bats at Montpelier Barn (DDT, t=4.20*; oxychlordane, t=3.10*) and little brown bats at North East Methodist Church (TDE, t=2.31*). Authors conclude that utilization of stored fat during winter caused residues to be more concentrated in bats in the spring.

RESIDUES ACCORDING TO LOCALITY

Data comparing quantities of residues in bats according to locality (Table 2) were restricted as much as possible and include only spring males for the big brown bat and pipistrelle. For the little brown bat, the Round Top and Trout Cave samples were also spring males, but spring females had to be used for Montpelier and North East Methodist Church. Comparisons among means for the little brown bat must be made with this difference in mind.

Authors drew several conclusions from Table 2. First, bats from Round Top consistently had the highest residues of ΣDDT, whereas bats from Trout Cave usually had the smallest amounts of all residues. Presumably the Round Top data reflect previous use of DDT in the apple orchards, and the Trout Cave data reflect the

TABLE 2. *Comparisons of quantities of residues in bats by locality, Maryland and West Virginia—1973*

	Mean residue in carcass, μg					
	PCB	DDE	DDT	TDE	Dieldrin	Oxychlordane
Big Brown Bat [1]						
Round Top	10.52[b]	87.75[a]	6.80[a]	1.72[a]	4.33[a]	1.58[b]
Montpelier	40.48[a]	43.23[a]	5.75[a]	1.89[a]	4.09[a]	6.63[a]
Trout Cave	5.82[c]	5.19[b]	1.01[b]	0.00[b]	1.46[b]	0.11[c]
Little Brown Bat [2]						
Round Top	25.83[ab]	35.67[a]	3.53[a]	2.04[a]	1.41[b]	1.40[b]
Montpelier	45.88[a]	11.85[ab]	2.18[a]	0.87[a]	4.10[ac]	6.04[a]
Trout Cave	13.44[ab]	9.02[ab]	1.79[a]	1.55[a]	1.77[bc]	1.40[b]
North East	14.02[b]	7.90[b]	1.63[a]	1.17[a]	4.46[a]	1.79[b]
Eastern Pipistrelle Bat [1]						
Round Top	23.87[a]	18.67[a]	1.72[a]	0.65[a]	0.84[a]	1.03[a]
Trout Cave	4.92[b]	6.18[a]	1.90[a]	0.85[a]	0.37[a]	0.73[a]

NOTE: Superscripts indicate statistical significance among means.
Shared superscripts indicate means that are not significantly different at a minimum of 95 percent confidence.

[1] Samples include only spring males. Sample sizes are given in Table 1.

[2] Samples are spring males from Round Top Mountain and Trout Cave; spring females are from Montpelier and North East. Sample sizes are given in Table 1.

absence of agriculture and industry from that area. Second, residues of PCB and oxychlordane were highest at Montpelier Barn for the two species that occur there. Sources of PCB's in such urban situations are diffuse and difficult to identify (*14*). Oxychlordane may come from household usage of chlordane on ornamental vegetation or it may come from efforts to control termites. Third, whereas most residues seem low at North East Methodist Church when considering only the little brown bat, residues of dieldrin were high, comparable to those at Montpelier Barn. Sources of the dieldrin are not known. Because results among the species are similar, authors believe that sex differences among samples of little brown bats had little effect on the means.

Authors repeated the comparisons of Table 2 but utilized data for all bats from each locality by disregarding differences in season and sex. Even though means were changed somewhat by this procedure, the conclusions were not.

Residues in guano correspond with those in the bat carcasses, but they occurred only infrequently in stomach contents (Table 3). This result could be anticipated because guano samples were large (16-20 g), relatively dry, and originated from perhaps 50-500 different bats

TABLE 3. *Residues in masticated insect samples from bat stomachs, and in guano, Maryland and West Virginia—1973*

	Residues, ppm wet weight					
	PCB	DDE	DDT	TDE	Dieldrin	Oxychlordane
Big Brown Bat: Stomach Contents						
Montpelier [1]	ND	ND	ND	ND	ND	ND
Trout Cave [2]	ND	ND	ND	ND	ND	ND
Little Brown Bat: Stomach Contents						
Trout Cave [2]	1.40	ND	ND	ND	ND	ND
North East [3]	ND	ND	ND	ND	0.06	ND
Little Brown Bat: Guano						
Montpelier [4]	0.96	0.32	ND	ND	0.18	0.10
North East [4]	0.51	0.28	0.10	ND	0.75	ND

NOTE: ND = not detected

[1] Two pooled samples, one was from four bats and the other was from five.

[2] One pooled sample from two bats.

[3] Two pooled samples; one was from 11 bats and the other was from 6.

[4] Single sample of 16-20 g.

TABLE 4. *Comparisons of residue concentrations among bat species from Maryland and West Virginia—1973*

	Mean residues in carcass, ppm wet weight					
	PCB	DDE	DDT	TDE	Dieldrin	Oxychlordane
Round Top Mountain [1]						
LBB	7.75[a]	10.78[a]	1.08[a]	0.62[a]	0.73[a]	0.43[a]
EPB	8.18[a]	6.39[a]	0.59[a]	0.22[b]	0.29[a]	0.36[a]
BBB	1.27[b]	11.16[a]	0.86[a]	0.22[ab]	0.55[a]	0.20[b]
Trout Cave [1]						
LBB	4.21[a]	2.83[a]	0.55[a]	0.55[a]	0.64[a]	0.45[a]
EPB	1.74[a]	2.21[a]	0.67[a]	0.32[a]	0.14[b]	0.27[a]
BBB	0.75[b]	0.67[b]	0.14[b]	0.00[b]	0.20[b]	0.02[b]
Montpelier Barn [2]						
LBB	11.61[a]	3.00[a]	0.54[a]	0.25[a]	1.04[a]	1.52[a]
BBB	2.87[b]	3.48[a]	0.32[a]	0.04[a]	0.51[b]	0.40[b]

NOTE: BBB = big brown bat
LBB = little brown bat
EPB = eastern pipistrelle bat
Superscripts indicate statistical significance among means

[1] Samples include only spring males. Sample sizes are given in Table 1

[2] Samples include only spring females. Sample sizes are given in Table 1

feeding at various times of the year. Samples of stomach contents were smaller (0.398, 4.401, and 8.595 g for big brown bats; 1.033, 1.261, and 1.610 g for little brown bats), contained more moisture, and represented fewer bats feeding at fewer times of the year. Analyses of guano may be useful for surveying bat colonies for harmful levels of organochlorine residues.

RESIDUES ACCORDING TO SPECIES

Residues (Table 4) must be expressed as concentrations rather than as total weight because individuals of the three species sampled differ in average weight. Within samples from each locality, data are restricted to a single sex and season. Several conclusions emerge. First, where all three species occur, little brown bats and pipistrelles frequently have significantly more residues than have big brown bats. Where little brown bats and pipistrelles differ significantly, little brown bats have more residues. Second, at Montpelier Barn none of the DDT-group compounds showed significant differences between species. When all data were compiled and comparisons among species were repeated, conclusions were similar except that means for little brown bats at Montpelier Barn were higher for all six residues and the differences were significant for all compounds except DDE.

The relatively low residue accumulation by big brown bats, whether the result of smaller dietary intake, more efficient excretion, or both, may be at least partly responsible for the occurrence of this species in highly urbanized localities.

The same data in Table 4 show relatively high residue accumulation by little brown bats. Knowledge of this propensity, if it is characteristic of other species in the genus, could be important in management of the endangered gray bat (*Myotis grisescens*) and Indiana bat (*Myotis sodalis*).

RESIDUES IN BRAINS

Residues of DDE in brains may be expected to vary in relation to the ratio of DDE to lipid in the entire animal. Indeed, when DDE in carcass fat was above certain concentrations, it became measurable in brains and increased with increasing levels in carcass lipids (Fig. 1, 2). It appears that DDE residues enter the brain sooner and increase more rapidly in the little brown bat than in the big brown bat (Fig. 1). Such comparisons of present data, however, may be misleading.

Even maximum brain levels of DDE are low (Fig. 1, 2). Brain levels of DDE ranging up to 8.2 ppm were found in Maryland big brown bats (5). The bat with the maximum level was young, feeding entirely on milk, and contained only 140 ppm DDE in its carcass lipids. Residue data for the young bat lead authors to suspect that a greater percentage of total DDE residue is found in the brain during the first weeks of life.

For comparison, previously reported residues in free-tailed bats (6) are included in Figure 2. Maximal brain levels for adult free-tails are similar to those in big and little brown bats. Higher levels were found in nursing young, especially those that had been deprived of food and had fallen to the cave floor.

The dependency of brain levels of the PCB on concentrations in carcass fat is not so clear as it is for DDE (Fig. 3). Authors do not know why the PCB should be less dependent.

Brain levels of the PCB reached 7.9 ppm among adult little brown bats; this is more than twice the maximum found among adults for DDE. Experimental data are needed before the significance of this concentration of the PCB can be judged. The highest brain level of Aroclor 1260 found previously (4.8 ppm) was in a nursing neonate big brown bat that contained only 90 ppm in its carcass fat (5). Again, the percentage of residue in the brain may be greater during the first weeks of life. The PCB was recovered from the brain of only one pipistrelle (0.66 ppm).

In sum, adult little brown bats accumulated the greatest brain residues of both DDE and the PCB; thus this species may be more susceptible to poisoning than are the other two.

OTHER RESIDUES

In addition to the six residues discussed thus far, there were six others found in carcasses infrequently and/or in small quantities. At Round Top, four big brown bats contained up to 0.25 ppm heptachlor epoxide, and three contained traces (<0.1 ppm) of *trans*-nonachlor. Three pipistrelles contained traces of *trans*-nonachlor, and one contained a trace of *cis*-chlordane.

At Trout Cave, one big brown bat contained a trace of heptachlor epoxide. Three little brown bats contained as much as 0.44 ppm *trans*-nonachlor, three had up to 0.61 ppm *cis*-chlordane, and one contained 4.5 ppm heptachlor epoxide. One pipistrelle had 0.12 ppm heptachlor epoxide and another contained 1.1 ppm mirex.

At Montpelier Barn, 13 big brown bats contained up to 0.52 ppm heptachlor epoxide, nine contained up to 0.88 ppm HCB, eight had up to 0.45 ppm *trans*-nonachlor, five had up to 0.27 ppm *cis*-chlordane, and five contained traces of *cis*-nonachlor. Six little brown bats had as much as 4.2 ppm *cis*-chlordane, five had up to 0.54 ppm heptachlor epoxide, four had up to 0.17 ppm HCB, three contained up to 0.42 ppm *cis*-nonachlor, and two had up to 0.85 ppm *trans*-nonachlor.

At North East Methodist Church, 13 little brown bats contained up to 4.4 ppm *cis*-chlordane (12 contained less than 0.5 ppm), six had up to 1.2 ppm *cis*-nonachlor, five had up to 0.17 ppm *trans*-nonachlor, and one had 0.18 ppm heptachlor epoxide.

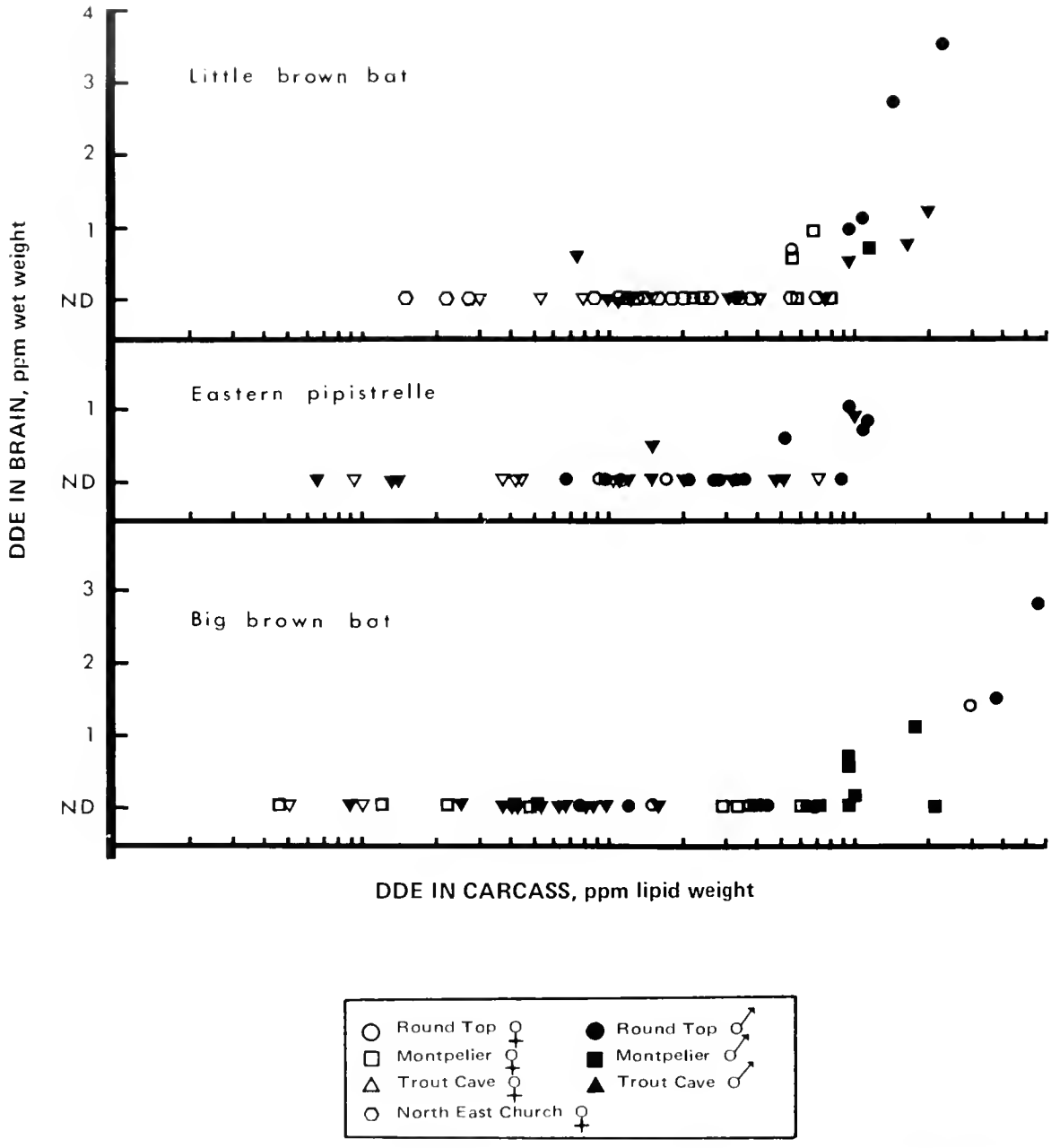

FIGURE 1. *Relationship of DDE residues in brain to those in carcass lipids of little brown bat, eastern pipistrelle, and big brown bat*

Among the lesser residues, the unique occurrence of HCB at Montpelier Barn is surprising. The source of the fungicide in this urban location is not known.

Only three bat brains that contained detectable organochlorine residues had materials other than a PCB and DDE; all three were collected in the spring. A male pipistrelle from Trout Cave had 0.46 ppm oxychlordane, and two female little brown bats from Montpelier Barn contained 0.50 ppm and 0.56 ppm oxychlordane. The latter bat also had 0.42 ppm dieldrin in its brain.

COMPARISONS WITH OTHER LOCALITIES AND SPECIES

Jefferies reported residues of DDE, DDT, and dieldrin in four pipistrelles (*Pipistrellus pipistrellus*) collected in Britain (*13*). Average carcass residues were 3.33 ppm

DDE, 1.99 ppm DDT, and 0.20 ppm dieldrin (authors' calculations). Carcass residues were given for three other bats belonging to three other species, but the highest concentrations were among the four pipistrelles. Numerous means for DDE and dieldrin from the present study (Table 1) are larger than those for the pipistrelles of Jefferies (*13*). However, for DDT, only the mean for fall-captured little brown bats at Round Top is larger than the corresponding value reported by Jefferies. The pipistrelle population sampled by Jefferies apparently experienced more direct exposure to DDT than did most populations sampled in Maryland and West Virginia. Jefferies also reported that PCB's were not found in the bats he analyzed (*13*); this differs from findings of the present study.

DDE residues in carcasses among cave populations of free-tailed bats in Arizona (*17*) and Texas (*6*) were generally lower than those in carcasses at Round Top, higher than those at both Trout Cave and North East Methodist Church, and similar to those at Montpelier Barn. PCB's were rare in free-tails, occurring in one from Arizona (1-2 ppm) and in four from Texas (0.48-1.2 ppm). Five free-tailed bats found dead on the University of Arizona campus in Tucson had apparently been exposed directly to DDT; amounts in carcasses averaged 61.4 ppm (range: 2.4-550 ppm) (*17*). Carcasses of five female big brown bats collected from a house in Tucson contained an average 117.0 ppm DDE (range: 65-160 ppm) (*17*). These values are the highest reported thus far for free-living bats.

Pooled samples from each of three bat species (*Eptesicus pumilis*, *Taphozous georgianus*, and *Pteropus alecto*) from the Northern Territory of Australia contained mostly trace residues (*1*). Levels reached as high as 1.82 ppm DDE, 0.25 ppm DDT, and 4.03 ppm dieldrin in the pooled whole animal samples of *E. pumilis*. PCB's were not accounted for in the analytical procedures of the Australian study (*1*). Dunsmore et al. (*10*) reported DDT and metabolites in carcasses of the Australian bat *Miniopterus schreibersii*, judging from the total μg quantities detected, average concentrations in seven samples must have ranged up to 1.4 ppm. PCB's were not reported.

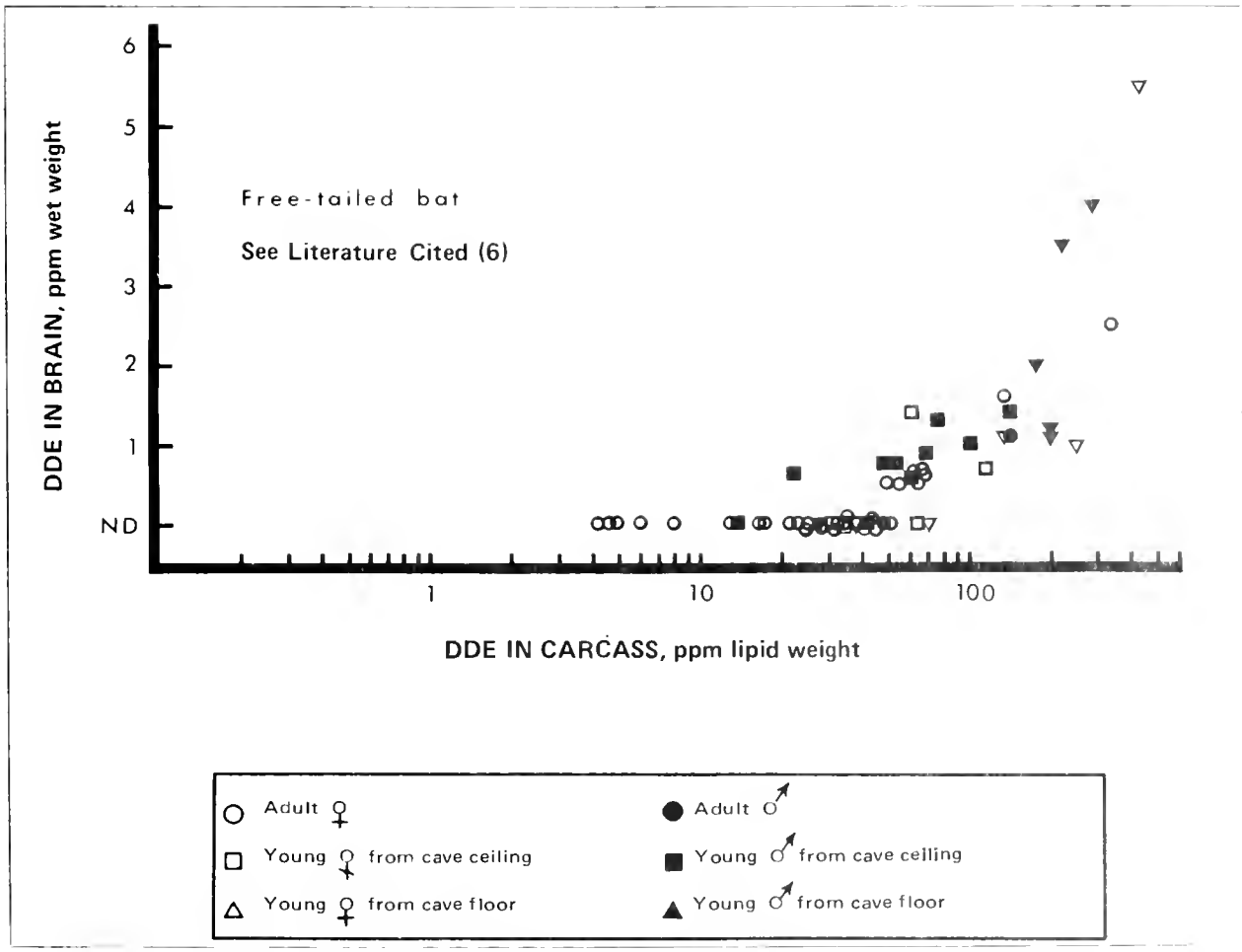

FIGURE 2. *Relationship of DDE residues in brain to those in carcass lipids of free-tailed bat*

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LITERATURE CITED

(1) *Best, S. M. 1973.* Some organochlorine pesticide residues in wildlife of the Northern Territory, Australia, 1970-71. Aust. J. Biol. Sci. 26(5):1161-1170.

(2) *Braaksma, S., and J. W. P. T. van der Drift. 1972.* Bats pesticide conflicts. TNO-Nieuws 27(10):579-583.

(3) *Christian, J. J. 1956.* The natural history of a summer aggregation of the big brown bat, *Eptesicus fuscus fuscus*. Am. Midl. Nat. 55(1):66-95.

(4) *Clark, D. R., Jr., and T. G. Lamont. 1976.* Organochlorine residues and reproduction in the big brown bat. J. Wildl. Manage. 4(2):249-254.

(5) *Clark, D. R., Jr., and T. G. Lamont. 1976.* Organochlorine residues in females and nursing young of the big brown bat (*Eptesicus fuscus*). Bull. Environ. Contam. Toxicol. 15(1):1-8.

(6) *Clark, D. R., Jr., C. O. Martin, and D. M. Swineford. 1975.* Organochlorine insecticide residues in the free-tailed bat (*Tadarida brasiliensis*) at Bracken Cave, Texas. J. Mammal. 56(2):429-443.

(7) *Cockrum, E. L. 1970.* Insecticides and guano bats. Ecology 51(5):761-762.

(8) *Davies, W. E. 1950.* The caves of Maryland. State of Md. Dept. Geol., Mines Water Resour. Bull. No. 7. 76 pp.

(9) *Davies, W. E. 1958.* Caverns of West Virginia. State of W. Va. Geol. Econ. Surv. XIX(A). 330 pp.

(10) *Dunsmore, J. D., I. S. Hall, and K. H. Kottek. 1974.* DDT in the bent-winged bat in Australia. Search 5(3):110-111.

(11) *Findley, J. S. 1973.* The status of southwestern bat populations. Pages 12-17 *in* Symposium on Rare and Endangered Wildlife of the Southwestern United States. N. Mex. Dept. Game Fish, Santa Fe, N. Mex.

(12) *Gould, E. 1970.* Bat conservation. Page 313 *in* About Bats. Edited by B. Slaughter and D. Walton. Southern Methodist Univ. Press, Dallas, Tex.

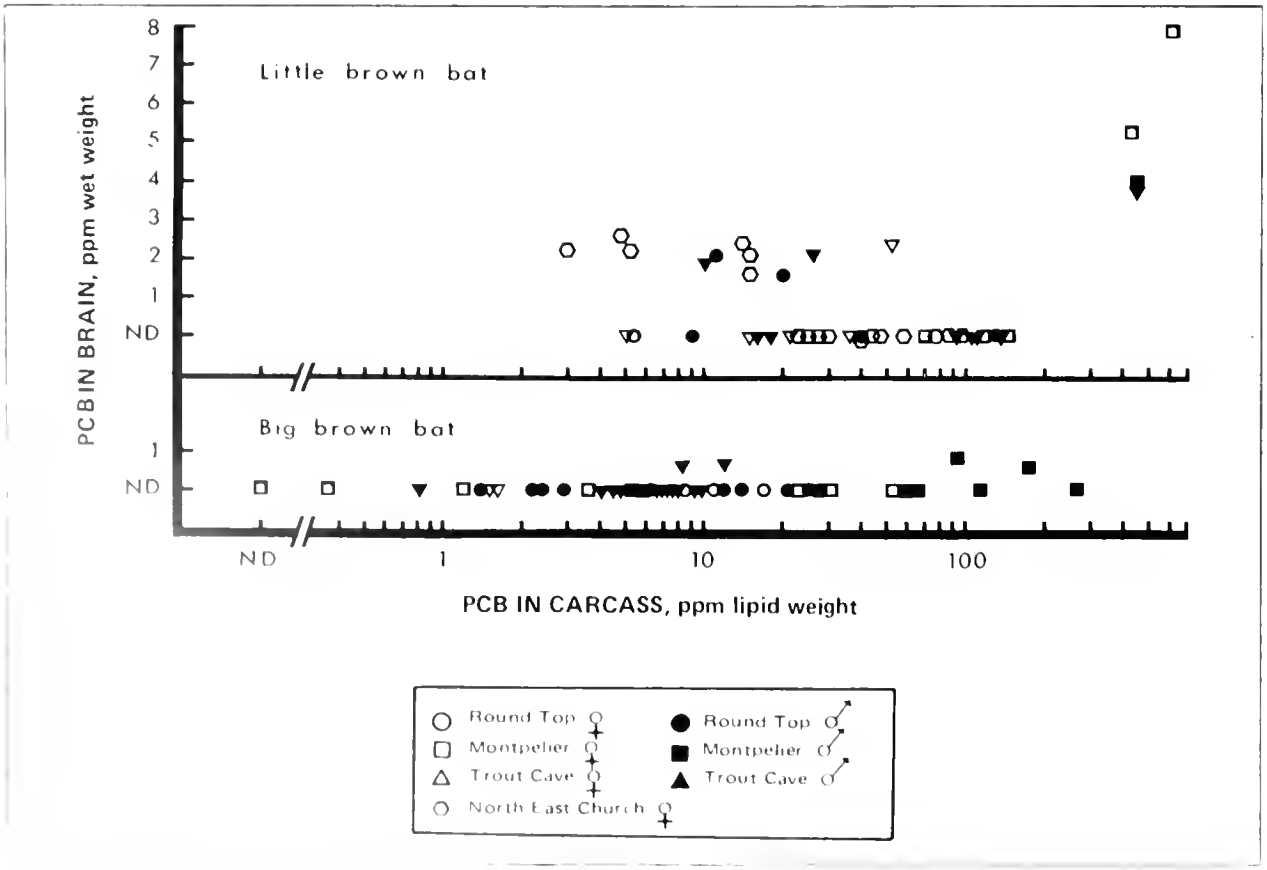

FIGURE 3. *Relationship of PCB (Aroclor 1260) residues in brain to those in carcass lipids for two bat species, Maryland and West Virginia—1973*

(13) *Jefferies, D. J. 1972.* Organochlorine insecticide residues in British bats and their significance. J. Zool. 166:245-263.

(14) *Martell, J. M., D. A. Rickert, and F. R. Siegel. 1975.* PCB's in suburban watershed, Reston, Va. Environ. Sci. Technol. 9(9):872-875.

(15) *Mohr, C. E. 1972.* The status of threatened species of cave-dwelling bats. Bull. Nat. Speleological Soc. 34(2): 33-47.

(16) *Punt, A. 1970.* Round table discussion on bat conservation: summary. Proc. 2nd Int. Bat Conf. Bijdragen tot de Dierkunde 40(1):3-4.

(17) *Reidinger, R. J., Jr. 1972.* Factors influencing Arizona bat population levels. Unpublished Ph.D. dissertation, Univ. Ariz., Tucson, Ariz. 172 pp.

(18) *Simpson, G. G., A. Roe, and R. C. Lewontin. 1960.* Quantitative Zoology. Harcourt, Brace and Co., New York. 440 pp.

(19) *Stebbings, R. E. 1970.* Bats in danger. Oryx 10(5): 311-312.

RESIDUES IN SOIL

Pesticide Residues in Urban Soils from 14 United States Cities, 1970

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ABSTRACT

Soil in 14 cities was sampled and analyzed for arsenic and chlorinated hydrocarbon pesticide residues. Heavy loads of chlorinated hydrocarbon residues were detected in the soil. In addition to DDT and its metabolites, chlordane, dieldrin, endrin, heptachlor, heptachlor epoxide, and toxaphene were detected. Distinct variation appeared in some residue levels among cities. Pesticide residue levels in urban soils were generally higher than the residue levels detected in cropland soils of the same States.

Introduction

The deterioration of urban environmental quality has been the object of an increasing number of scientific investigations. Most of these have been concerned with air and water pollution. Very few investigations have focused on contamination of urban soil and fewer still on contamination with pesticides, a problem associated primarily with agricultural soils.

It has been estimated that only about half the 470 million kg active ingredients (a.i.) in pesticides and formulated products produced in the United States in 1970 were used in domestic agriculture. Most of the remaining portion is assumed to have been used by industries, public agencies, and householders (*3*). Although total pesticide use in urban and suburban areas hardly equals agricultural use, these compounds are applied to a much smaller land area. In a study of pesticide use conducted for the U.S. Environmental Protection Agency (EPA), the average amount of pesticides applied to lawns and gardens in the three cities surveyed was estimated to be between 5.9 and 11.9 kg/ha. a.i. (*3*).

Little information has been published on pesticide residue levels in urban soil. Fahey, Butcher, and Murphy (*1*) found that 86.5 percent of the soil samples collected from Battle Creek, Mich., contained chlorinated hydrocarbon pesticide residues. In another study, Purves (*2*) found the levels of certain trace elements to be higher in urban garden plots than in rural plots.

In 1969, Wiersma, Tai, and Sand (*4*) sampled eight U. S. cities and found that the occurrence of DDT and its metabolites (DDTR) among urban sampling sites ranged from 40 percent in Houston, Tex., to 100 percent in Miami, Fla. Average DDTR residues in lawns and gardens were significantly higher than those in unkept areas within the cities. Reported here are the results for the second year of urban soil monitoring.

Sampling Procedures

Fourteen U. S. cities were selected for sampling during the summer and fall of 1970. The cities were stratified by population: there was one city with a population greater than 1,000,000; six cities between 100,000 and 1,000,000; and five cities between 25,000 and 100,000; and two cities of less than 25,000. Randomly allocated sample sites were selected within the political boundaries of each city. Sites were 231 m^2, usually 15.2-by-15.2-m plots. Sixteen soil cores, each 5.1 cm in diameter by 7.6 cm deep, were taken on an evenly spaced 4-by-4 grid. The cores were then composited, sieved through a 6.3-mm mesh, and sent for analyses to the EPA Pesticide Monitoring Laboratory in Gulfport, Miss. (now located at the NASA Mississippi Test Facility, Bay St. Louis).

Analytical Procedures

PREPARATION OF SAMPLES

A 300-g soil sample was moistened with 80 ml water and extracted with 600 ml 3:1 hexane:isopropanol by concentric rotation for 4 hours. The liquid was decanted, the alcohol was removed by three water washes,

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and the hexane extract was dried through anhydrous sodium sulfate. The sample extract was then stored at low temperature for subsequent gas-chromatographic (GC) analysis.

GAS CHROMATOGRAPHY

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

Columns

Glass, 6 mm OD by 4 mm ID, 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 (minimum detectable levels) of organochlorine compounds ranged from 0.002 to 0.03 ppm except for mixtures of polychlorinated biphenyls (PCB's), chlordane, toxaphene, etc., whose minimum detectable levels were 0.05 to 0.1 ppm. Minimum detectable levels for organophosphorus compounds were approximately 0.01 to 0.03 ppm. When necessary, residues were confirmed by thin-layer chromatography or *p*-values. The compounds detectable by this method are listed in Table 1.

Atomic absorption spectrophotometry was used to determine arsenic content. The soil sample was first extracted with 9.6N hydrochloric acid (HCl) and reduced to trivalent arsenic with stannous chloride. The trivalent arsenic was partitioned from HCl solution to benzene, then further partitioned into water for the absorption measurement. A Perkin-Elmer Model 303 instrument was used and absorbance was measured with an arsenic lamp at 1972 Å with argon as an aspirant to an air-hydrogen flame. The minimum detection limit was 0.1 ppm.

TABLE 1. *Organochlorine compounds detectable by chemical methodology of the present study*

Alachlor	Heptachlor
Aldrin	Heptachlor epoxide
Chlordane	Lindane (γ-BHC)
DDTR (*o,p'*-DDT; *p,p'*-DDT; *o,p'*-DDE; *p,p'*-DDE; *o,p'*-TDE; *p,p'*-TDE)	Methoxychlor
Dieldrin	PCB's
Endrin	PCN's
	Toxaphene
	Trifluralin

RECOVERY STUDIES

For organochlorine pesticides, the average recovery rate in soil was 90 to 110 percent. Recovery values for arsenic ranged from 70 to 80 percent. All residue levels are expressed on a dry-weight basis and are corrected for percent recovery.

Results

Results of the chemical analyses are presented in Table 2. For each city, the total number of sites is given as well as the arithmetic and geometric mean values for each residue, the range of residue values detected, and the number and percentage of sites with detectable residues.

The geometric mean estimate was used as an alternative to the arithmetic mean as a measure of central tendency for the data evaluation. Pesticide residue data frequently contain a large number of zero values, resulting either from the absence of pesticides or their presence at levels below analytical sensitivity. The data are seldom distributed normally, as shown by tests for skewness and kurtosis, but can be described by a log-normal distribution. After repeated tests for significant kurtosis and/or skewness, the ln $(X + 0.01)$ transformation was used in determining the logarithmic means. The antilogs of these figures minus 0.01 were taken to get estimates of the geometric means and 95 percent confidence intervals in the untransformed dimension (Table 2). The geometric mean estimate was calculated only for those compounds with more than one positive detection.

Of the 356 urban sites sampled, 204 or 57 percent of the sites had detectable levels of pesticide residues excluding arsenic. Residues of DDTR (the sum of all DDT isomers and metabolites) and chlordane were detected in all 14 cities. However, the frequency of occurrence within each city varied considerably. DDTR was detected in 51 percent of all samples analyzed but the frequency of detection ranged from 7 percent in Augusta, Maine, to 89 percent in Greenville, Miss. Similarly, chlordane was found in 19 percent of all samples but individual city frequencies ranged from 5 percent in Cheyenne, Wyo., to 44 percent in Grand Rapids, Mich.

Residues of heptachlor and heptachlor epoxide were detected in three and ten of the fourteen cities, respec-

TABLE 2. *Pesticide residues in soil from 14 United States cities, 1970*

Pesticide	No. Positive Sites	Percent Positive Sites	Range of Residues, ppm	Arith. Mean	Geom. Mean	95 % CI Upper	95 % CI Lower
			Augusta, Maine: 27 Sites				
Arsenic	27	100.00	0.40-15.30	5.39	4.0312	5.6517	2.8746
Chlordane	3	11.1	0.21- 0.27	0.03	0.0043	0.0115	0.0000
Dieldrin	ND						
Endrin	ND						
Heptachlor	ND						
Heptachlor Epoxide	ND						
Toxaphene	ND						
o,p'-DDE	ND						
p,p'-DDE	2	7.4	0.14- 0.42	0.02	0.0027	0.0080	0.0000
o,p'-DDT	1	3.7	0.20	0.01	*	—	—
p,p'-DDT	2	7.4	0.25- 0.61	0.03	0.0031	0.0095	0.0000
o,p'-TDE	ND						
p,p'-TDE	2	7.4	0.14- 0.46	0.02	0.0027	0.0081	0.0000
DDTR	2	7.4	0.53- 1.69	0.08	0.0040	0.0128	0.0000
			Charleston, S.C.: 27 Sites				
Arsenic	27	100.00	0.40-10.10	3.35	2.1325	3.1817	1.4282
Chlordane	7	25.9	1.01- 1.35	0.12	0.0094	0.0245	0.0009
Dieldrin	ND						
Endrin	ND						
Heptachlor	ND						
Heptachlor Epoxide	1	3.7	0.07	<0.01	*	—	—
Toxaphene	ND						
o,p'-DDE	1	3.7	0.03	<0.01	*	—	—
p,p'-DDE	19	70.4	0.01- 2.21	0.16	0.0417	0.0810	0.0194
o,p'-DDT	8	29.6	0.07- 8.47	0.36	0.0163	0.0417	0.0034
p,p'-DDT	17	70.0	0.06-33.80	1.54	0.0858	0.2143	0.0309
o,p'-TDE	1	3.7	0.05	<0.01	*	—	—
p,p'-TDE	15	55.6	0.03- 0.29	0.06	0.0250	0.0474	0.0113
DDTR	20	74.1	0.06-44.48	2.12	0.1589	0.3863	0.0620
			Cheyenne, Wyo.: 19 Sites				
Arsenic	17	89.5	0.20- 5.50	1.23	0.5658	1.2893	0.2451
Chlordane	1	5.3	8.99	0.47	*	—	—
Dieldrin	ND						
Endrin	ND						
Heptachlor	ND						
Heptachlor Epoxide	1	5.3	0.32	0.02	*	—	—
Toxaphene	ND						
o,p'-DDE	ND						
p,p'-DDE	3	15.8	0.03- 0.09	0.01	0.0031	0.0079	0.0000
o,p'-DDT	ND						
p,p'-DDT	ND						
o,p'-TDE	ND						
p,p'-TDE	ND						
DDTR	3	15.8	0.03- 0.09	0.01	0.0031	0.0079	0.0000
			Grand Rapids, Mich.: 23 Sites				
Arsenic	22	95.6	1.70-112.0	9.11	3.7194	7.2176	1.9144
Chlordane	10	43.5	0.15- 6.58	0.71	0.0556	0.1713	0.0137
Dieldrin	ND						
Endrin	ND						
Heptachlor	1	4.3	0.13	0.01	*	—	—
Heptachlor Epoxide	5	21.7	0.03- 0.23	0.02	0.0066	0.0159	0.0006
Toxaphene	ND						
o,p'-DDE	ND						
p,p'-DDE	19	82.6	0.02- 2.67	0.20	0.0564	0.1103	0.0266
o,p'-DDT	5	21.7	0.04- 0.71	0.09	0.0108	0.0295	0.0009
p,p'-DDT	19	82.6	0.05- 2.67	0.33	0.1154	0.2342	0.0544
o,p'-TDE	1	4.3	0.01	<0.01	*	—	—
p,p'-TDE	3	13.0	0.12- 0.60	0.04	0.0051	0.0144	0.0000
DDTR			0.02- 6.66	0.66	0.1833	0.3897	0.0834
			Greenville, Miss.: 28 Sites				
Arsenic	27	96.4	2.60-48.90	8.10	5.4608	9.1897	3.2434
Chlordane	2	7.1	0.37- 1.40	0.06	0.0036	0.0111	0.0000
Dieldrin	1	3.6	0.48	0.02	*	—	—
Endrin	ND						
Heptachlor	ND						
Heptachlor Epoxide	ND						
Toxaphene	3	10.7	7.73-33.40	1.94	0.0119	0.0437	0.0000
o,p'-DDE	1	3.6	0.15	0.01	*	—	—
p,p'-DDE	24	85.7	0.01- 1.79	0.18	0.0641	0.1134	0.0345
o,p'-DDT	8	28.6	0.05- 0.88	0.10	0.0141	0.0335	0.0033
p,p'-DDT	25	89.3	0.02- 3.03	0.44	0.1666	0.2997	0.0907
o,p'-TDE	1	3.6	0.12	<0.01	*	—	—
p,p'-TDE	10	35.7	0.02- 0.74	0.08	0.0148	0.0330	0.0043
DDTR	25	89.3	0.05- 5.87	0.80	0.2471	0.4724	0.1270

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TABLE 2 (cont.). *Pesticide residues in soil from 14 United States cities, 1970*

Pesticide	No. Positive Sites	Percent Positive Sites	Range of Residues, ppm	Arith Mean	Geom. Mean	95 % CI Upper	95 % CI Lower
Honolulu, Hawaii: 21 Sites							
Arsenic	21	100.00	0.50-17.40	3.34	2.1024	3.1464	1.4037
Chlordane	6	28.6	1.00-13.90	1.27	0.0406	0.1609	0.0050
Dieldrin	ND						
Endrin	ND						
Heptachlor	ND						
Heptachlor Epoxide	1	4.8	0.06	<0.01	*	—	—
Toxaphene	ND						
o,p'-DDE	1	4.8	0.12	0.01	*	—	—
p,p'-DDE	4	19.0	0.14- 0.65	0.07	0.0009	0.0257	0.0001
o,p'-DDT	1	4.8	0.11	0.01	*	—	—
p,p'-DDT	4	19.0	0.26- 0.47	0.06	0.0096	0.0274	0.0002
o,p'-TDE	1	4.8	0.33	0.02	*	—	—
p,p'-TDE	4	19.0	0.15- 0.52	0.05	0.0087	0.0242	0.0002
DDTR	4	19.0	0.57- 1.83	0.21	0.0140	0.0461	0.0003
Memphis, Tenn.: 28 Sites							
Arsenic	28	100.0	1.90-20.10	6.63	5.7837	7.1097	4.7036
Chlordane	6	21.4	0.11- 8.02	0.36	0.0138	0.0379	0.0018
Dieldrin	16	57.1	0.02-12.80	1.07	0.0525	0.1399	0.0161
Endrin	1	3.6	0.07	<0.01	*	—	—
Heptachlor	1	3.6	0.23	0.01	*	—	—
Heptachlor Epoxide	3	10.7	0.02- 0.70	0.03	0.0034	0.0095	0.0000
Toxaphene	ND						
o,p'-DDE	ND						
p,p'-DDE	12	42.9	0.01- 1.62	0.10	0.0162	0.0353	0.0052
o,p'-DDT	7	25.0	0.04- 0.24	0.03	0.0086	0.0188	0.0020
p,p'-DDT	12	42.9	0.02- 0.91	0.17	0.0319	0.0741	0.0109
o,p'-TDE	ND						
p,p'-TDE	13	46.4	0.02- 0.22	0.04	0.0159	0.0308	0.0064
DDTR	18	64.3	0.01- 2.92	0.34	0.0702	0.1582	0.0283
Mobile, Ala.: 29 Sites							
Arsenic	29	100.0	0.30- 5.20	1.12	0.8168	1.0731	0.6212
Chlordane	7	24.1	0.10- 2.50	0.18	0.0157	0.0403	0.0032
Dieldrin	3	10.3	0.04- 0.36	0.02	0.0035	0.0092	0.0000
Endrin	ND						
Heptachlor	1	3.4	0.01	<0.01	*	—	—
Heptachlor Epoxide	6	20.7	0.01- 0.09	0.01	0.0036	0.0074	0.0006
Toxaphene	ND						
o,p'-DDE	ND						
p,p'-DDE	9	31.0	0.02- 0.50	0.05	0.0109	0.0237	0.0030
o,p'-DDT	5	17.2	0.02- 0.22	0.02	0.0044	0.0100	0.0003
p,p'-DDT	9	31.0	0.02- 1.06	0.09	0.0140	0.0321	0.0037
o,p'-TDE	ND						
p,p'-TDE	9	31.0	0.02- 0.19	0.03	0.0088	0.0181	0.0027
DDTR	11	37.9	0.02- 1.37	0.19	0.0240	0.0575	0.0071
Philadelphia, Pa.: 26 Sites							
Arsenic	26	100.0	2.20-30.90	10.48	8.5081	11.1912	6.4677
Chlordane	11	42.3	0.18- 4.59	0.76	0.0705	0.2185	0.0191
Dieldrin	ND						
Endrin	ND						
Heptachlor	ND						
Heptachlor Epoxide	2	7.7	0.08- 0.11	0.01	0.0020	0.0055	0.0000
Toxaphene	ND						
o,p'-DDE	ND						
p,p'-DDE	17	65.4	0.03- 1.42	0.15	0.0431	0.0876	0.0188
o,p'-DDT	10	38.5	0.04- 1.06	0.17	0.0275	0.0681	0.0080
p,p'-DDT	19	73.1	0.04- 3.53	0.56	0.1456	0.3310	0.0610
o,p'-TDE	2	7.7	0.20- 0.45	0.03	0.0030	0.0090	0.0000
p,p'-TDE	10	38.5	0.03- 1.17	0.09	0.0181	0.0408	0.0055
DDTR	20	76.9	0.07- 6.98	1.00	0.2315	0.5492	0.0943
Portland, Oreg.: 25 Sites							
Arsenic	25	100.0	0.80-26.00	6.63	4.5113	6.5622	3.1004
Chlordane	3	12.0	0.40- 0.59	0.06	0.0059	0.0169	0.0000
Dieldrin	2	8.0	0.08- 1.19	0.05	0.0032	0.0103	0.0000
Endrin	ND						
Heptachlor	ND						
Heptachlor Epoxide	ND						
Toxaphene	ND						
o,p'-DDE	ND						
p,p'-DDE	16	64.0	0.03- 1.46	0.15	0.0413	0.0852	0.0176
o,p'-DDT	2	8.0	0.09- 0.29	0.02	0.0025	0.0075	0.0000
p,p'-DDT	11	44.0	0.07- 2.63	0.24	0.0328	0.0812	0.0101
o,p'-TDE	3	12.0	0.07-1.288	0.06	0.0045	0.0131	0.0000
p,p'-TDE	10	40.0	0.04- 3.46	0.22	0.0235	0.0582	0.0064
DDTR	17	68.0	0.03- 7.64	0.67	0.0923	0.2262	0.0343

(Continued next page)

TABLE 2 (cont.). *Pesticide residues in soil from 14 United States cities, 1970*

Pesticide	No. Positive Sites	Percent Positive Sites	Range of Residues, ppm	Arith. Mean	Geom. Mean	95 % CI Upper	95 % CI Lower
			Richmond, Va.: 27 Sites				
Arsenic	26	96.3	0.10-14.80	2.39	1.2014	2.1517	0.6689
Chlordane	5	18.5	0.18- 6.42	0.51	0.0154	0.0474	0.0012
Dieldrin	4	14.8	0.07- 2.99	0.14	0.0075	0.0210	0.0000
Endrin	ND						
Heptachlor	ND						
Heptachlor Epoxide	5	18.5	0.01- 0.10	0.01	0.0034	0.0076	0.0002
Toxaphene	ND						
o,p'-DDE	2	7.4	0.09- 0.15	0.01	0.0021	0.0058	0.0000
p,p'-DDE	17	63.0	0.01- 4.24	0.35	0.0544	0.1257	0.0206
o,p'-DDT	4	14.8	0.18- 3.25	0.16	0.0081	0.0229	0.0000
p,p'-DDT	7	25.9	0.22-15.10	0.79	0.0234	0.0696	0.0040
o,p'-TDE	2	7.4	0.04- 0.46	0.02	0.0022	0.0067	0.0000
p,p'-TDE	17	63.0	0.03- 5.65	0.40	0.0509	0.1163	0.0194
DDTR	18	66.7	0.03-28.33	1.73	0.0034	0.0076	0.0002
			Sikeston, Mo.: 27 Sites				
Arsenic	26	96.3	1.00- 7.20	3.00	2.2217	3.5780	1.3781
Chlordane	2	7.4	0.30- 1.19	0.06	0.0036	0.0111	0.0000
Dieldrin	1	3.7	0.33	0.01	*	—	—
Endrin	ND						
Heptachlor	ND						
Heptachlor Epoxide	ND						
Toxaphene	1	3.7	16.10	0.60	*	—	—
o,p'-DDE	ND						
p,p'-DDE	7	25.9	0.02- 0.23	0.03	0.0084	0.0187	0.0018
o,p'-DDT	2	7.4	0.12- 0.14	0.01	0.0022	0.0061	0.0000
p,p'-DDT	6	22.2	0.10- 0.49	0.06	0.0101	0.0245	0.0017
o,p'-TDE	ND						
p,p'-TDE	5	18.5	0.06- 0.21	0.02	0.0053	0.0121	0.0006
DDTR	7	25.9	0.03- 0.89	0.12	0.0147	0.0374	0.0029
			Sioux City, Iowa: 22 Sites				
Arsenic	21	95.5	4.20-24.70	10.25	7.0473	13.9439	3.5593
Chlordane	4	18.2	0.30- 3.00	0.24	0.0127	0.0408	0.0001
Dieldrin	ND						
Endrin	ND						
Heptachlor	ND						
Heptachlor Epoxide	1	4.5	0.06	<0.01	*	—	—
Toxaphene	ND						
o,p'-DDE	ND						
p,p'-DDE	5	22.7	0.01- 0.43	0.03	0.0062	0.0156	0.0002
o,p'-DDT	ND						
p,p'-DDT	4	18.2	0.05- 0.19	0.02	0.0055	0.0139	0.0001
o,p'-TDE	ND						
p,p'-TDE	2	9.1	0.04- 0.07	0.01	0.0018	0.0051	0.0000
DDTR	5	22.7	0.06- 0.69	0.06	0.0094	0.0245	0.0009
			Wilmington, Del.: 27 Sites				
Arsenic	24	88.9	0.60-32.00	9.10	3.5252	8.6773	1.4286
Chlordane	2	7.4	0.04- 0.07	<0.01	0.0015	0.0040	0.0000
Dieldrin	ND						
Endrin	ND						
Heptachlor	ND						
Heptachlor Epoxide	1	3.7	0.02	<0.01	*	—	—
Toxaphene	ND						
o,p'-DDE	1	3.7	0.09	<0.01	*	—	—
p,p'-DDE	11	40.7	0.01- 0.30	0.05	0.0155	0.0322	0.0055
o,p'-DDT	7	25.9	0.02- 0.26	0.03	0.0074	0.0161	0.0015
p,p'-DDT	11	40.7	0.07- 0.83	0.11	0.0246	0.0551	0.0084
o,p'-TDE	1	3.7	0.12	<0.01	*	—	—
p,p'-TDE	9	33.3	0.01- 0.60	0.06	0.0139	0.0312	0.0038
DDTR	11	40.7	0.08- 2.20	0.25	0.0362	0.0911	0.0111

NOTE: Compounds not listed were not detected in residue analyses.
ND = not detected.
Asterisk = geometric mean estimate not calculated with only one positive detection.

tively, dieldrin was detected in six and endrin in only one.

Arsenic is a naturally occurring element in soil, which accounts for its detection in 97 percent of the samples analyzed. As a result, it is difficult to determine whether the arsenic residues present reflect human associated activity in addition to natural background levels. In the present study, geometric mean values for arsenic ranged from 0.5658 ppm in Cheyenne to 8.5081 ppm in Philadelphia, Pa.

Sampling sites in all cities except Mobile, Ala., were categorized as either lawn or waste according to the criteria established by Wiersma, et al. (*4*).

Lawn was defined thus:

1. Mowed grass close to a house, factory, or other structure.
2. Mowed grass in municipal parks or other city-owned or city-maintained land.
3. Garden or cultivated areas.
4. A yard that was in obvious proximity to a home.

Waste included:

1. Vacant lots where grass was apparently unkept.
2. Small wooded lots, brush or overgrown fields.
3. Areas such as power lines and gas lines.
4. Exposed soil around construction sites, eroded areas, and the like.

A *t*-test based on the transformed variate ln (X + 0.01) was used to compare residue levels of selected compounds in lawn and waste areas (Table 3). Residue

TABLE 3. *Statistical significance of differences between residue levels of specific chemicals in lawn and waste areas of 13 United States cities, 1970* [1]

City [2]	DDTR	Arsenic	Chlordane
Augusta, Maine	**	*	NS
Charleston, S.C.	NS	**	NS
Cheyenne, Wyo.	NS	NS	NS
Grand Rapids, Mich.	*	NS	NS
Greenville, Miss.	NS	NS	NS
Honolulu, Hawaii	*	NS	NS
Memphis, Tenn.	**	NS	NS
Philadelphia, Pa.	*	NS	*
Portland, Oreg.	**	NS	NS
Richmond, Va.	*	NS	NS
Sikeston, Mo.	NS	*	NS
Sioux City, Iowa	NS	NS	NS
Wilmington, Del.	NS	NS	NS

NOTE: NS = not significant.
* = significant ($P<0.05$).
** = highly significant ($P<0.01$).

[1] Based on *t*-tests of the transformed variate ln (X + 0.01), U.S Environmental Protection Agency.

[2] Mobile, Ala., omitted because lawn and waste sites had not been differentiated.

levels of DDTR were significantly higher ($p<0.05$) in lawn areas than in waste areas in seven of the thirteen cities tested. Differences may reflect multiple sources of pesticide applications (e.g., householders, municipalities) within the cities. No significant difference occurred between DDTR levels in lawn and those in waste areas of southern cities; perhaps this is a subtle reflection of the extensive use of DDT in the regional agriculture before the compound was banned.

The *t*-test based on ln (X + 0.01) was also used to compare residue levels of chlordane in lawn sites with those in waste sites among all cities except Mobile. Only in Philadelphia were the chlordane levels in lawns significantly higher than in waste areas. In three of the thirteen cities arsenic levels in lawns were significantly greater ($p<0.05$) than in waste areas. Perhaps human-associated activity is responsible for this difference:

TABLE 4. *Comparison of selected compounds in urban and cropland soils of 12 States, 1970* [1,2]

	Mean Residues, ppm dry wt		
	Arsenic	DDTR	Chlordane
Maine			
Augusta	4.0312	0.0040	0.0043
	*	NS	NS
Cropland [3]	7.7028	0.0220	0.0016
South Carolina			
Charleston	2.1325	0.1589	0.0094
	NS	NS	NS
Cropland	1.3588	0.3110	0.0031
Wyoming			
Cheyenne	0.5658	0.0031	0.0043
	NS	NS	NS
Cropland [4]	0.3003	ND	0.0095
Michigan			
Grand Rapids	3.7194	0.1833	0.0556
	NS	**	**
Cropland	3.4326	0.0064	0.0018
Mississippi			
Greenville	5.4608	0.2471	0.0036
	NS	NS	NS
Cropland	5.0177	0.6326	0.0008
Tennessee			
Memphis	5.7837	0.0702	0.0138
	NS	**	NS
Cropland	6.9335	0.0102	0.0050
Alabama			
Mobile	0.8168	0.0240	0.0157
	NS	**	NS
Cropland	0.2747	0.2247	0.0016
Pennsylvania			
Philadelphia	8.5081	0.2315	0.0705
	NS	**	**
Cropland	7.1960	0.0125	0.0131
Virginia			
Richmond	1.2014	0.0034	0.0154
	NS	NS	**
Cropland [5]	1.2054	0.0038	0.0038
Missouri			
Sikeston	2.2217	0.0147	0.0036
	*	**	NS
Cropland	4.0719	0.0021	0.0063
Iowa			
Sioux City	7.0473	0.0094	0.0127
	**	*	NS
Cropland	2.4065	0.0025	0.0092
Delaware			
Wilmington	3.5252	0.0362	0.0015
	NS	NS	NS
Cropland [6]	4.2810	0.0091	0.0123

NOTE: ND = compound not detected
NS = urban/cropland difference not significant.
* = urban/cropland difference significant ($p<0.05$).
** = urban/cropland difference highly significant ($p<0.01$).

[1] Cropland data from National Soils Monitoring Program, FY-70, unless otherwise indicated.

[2] Comparisons for Honolulu, Hawaii, and Portland, Oreg., omitted because no cropland data are available.

[3] New England States' data: Connecticut, Maine, Massachusetts, New Hampshire, Rhode Island, and Vermont.

[4] Cropland data from National Soils Monitoring Program, FY-69.

[5] Virginia/West Virginia data.

[6] Mid-Atlantic States' data: Delaware, Maryland, and New Jersey.

however, the question cannot accurately be resolved here. Natural arsenic levels in soil are dependent on parent material and most urban soil profiles are disturbed by such actions as construction, removal of topsoil, or use of fill from other areas.

Table 4 compares geometric means of three selected residues in urban soils and cropland soils in the same State or agricultural region. Generally, DDTR and chlordane residues detected in urban soils were higher than residues in corresponding cropland soils from those States or groups of States. However, there were statistically significant differences ($p < 0.05$) between the geometric means of DDTR for corresponding urban and cropland soils in only six of thirteen locations and significant differences for chlordane in only three of thirteen locations.

Conclusions

The cities sampled in 1970 generally had heavy loads of chlorinated hydrocarbon pesticides in soil. This coincides with results of the previous year's urban sampling published by Wiersma et al. (*4*). In over half the thirteen cities tested in 1970, DDTR residues in lawn areas were significantly higher than in waste and unkept areas. There appeared to be some distinct variation in pesticide residue levels among cities. Finally, pesticide residue levels were generally higher in urban soils than in cropland soils of the same States.

LITERATURE CITED

(*1*) *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(3):1026-1027.

(*2*) *Purves, D. 1968.* Trace element contamination of soils in urban areas. Int. Soc. Soil Sci., Trans. 9th Cong. 2:351-355.

(*3*) *U.S. Environmental Protection Agency. 1972.* Office of Water Programs. The use of pesticides in suburban homes and gardens and their impact on the aquatic environment. 487 pp.

(*4*) *Wiersma, G. B., H. Tai, and P. F. Sand. 1972.* Pesticide residues in soil from eight cities—1969. Pestic. Monit. J. 6(2):126-129.

Distribution of Pesticides and Polychlorinated Biphenyls in Water, Sediments, and Seston of the Upper Great Lakes—1974

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ABSTRACT

Samples of water, seston, and sediment from the upper Great Lakes were collected during the summer of 1974 for analyses of polychlorinated biphenyls (PCB's), 15 organochlorine pesticides, and 17 organophosphorus pesticides. Samples were taken from 9 sites in Lake Huron, 2 in the North Channel, 5 in Georgian Bay, and 17 in Lake Superior. In the water samples all compounds analyzed were below quantification limits and traces of lindane were found in each sample. In seston samples, PCB's were above quantification limits at nearly every station and some traces of dieldrin and DDE were measured. Sediments contained PCB compounds at all stations. Dieldrin was occasionally observed, and DDT and/or its derivatives DDE and TDE were found in over one-third of all samples. No clear correlation was found between quantities of these compounds in sediments and either the percentage of clay or organic matter in the samples. Nor were any definite geographic trends present in terms of distributions observed, although concentrations were higher in areas of higher sedimentary deposition such as deeper basins. No organophosphorus compounds were detected in any sample. The highest level of DDT residues detected, 20 ppb, was lower than levels found in other studies in the lower Great Lakes and some tributary river sediments of Georgian Bay. In general, DDT residues were higher in Lake Huron and Georgian Bay sediments than in Lake Superior although PCB's were higher in some Lake Superior sediments.

Introduction

Except for limited literature on tributaries (*3,14*) no information is available in the literature regarding levels of organochlorine and organophosphorus pesticides and polychlorinated biphenyls (PCB's) in water and sediments of Lakes Superior and Huron including Georgian Bay. In order to investigate the occurrence of these compounds, a survey cruise was conducted on the upper Great Lakes in late July and early August 1974, and samples of water, sediments, and seston (suspended particulate material consisting of plankton and both inorganic and organic detrital materials) were collected. Sampling was confined to open lake waters.

This study is part of the Upper Lakes Reference Group research program on Lakes Superior and Huron, a program under the auspices of the International Joint Commission (IJC).

Sampling

Figure 1 indicates the approximate locations of sampling stations which were chosen on the basis of proximity to major rivers, industrial plants, or municipal areas. Because a fairly large vessel was employed, no station was nearer to shore than 1 km except channel stations 18 and 30. Hence samples do not reflect immediate influence from these source areas. Several background central lake sites were also chosen. The collection and analysis procedures for the three sample types are given below.

WATER

Samples were collected using a 6-liter Van Dorn bottle triggered at a depth of 1 m. Two liters of this sample were filtered through a 47-mm-diameter Whatman GF/C filter and refrigerated in acid-washed glass bottles. After approximately 30 days in storage at 4°C in the dark, samples were extracted by procedure B described in the *Analytical Methods Manual* under "Procedure for the Analysis of Organochlorinated Pesticides and PCB's in Water" (*9*). Florisil cleanup was not used because backgrounds were free of interfering substances. Filters were not analyzed. After electron-capture gas-chromatographic (GC) analysis for organochlorine pesticides and PCB's, residues of the extracts were further examined for organophosphorus pesticides by gas chromatography using flame photometric detection in both phosphorus and sulfur modes. Gas-chromatographic procedures for the organophosphates are outlined in other publications (*18,19*) but the

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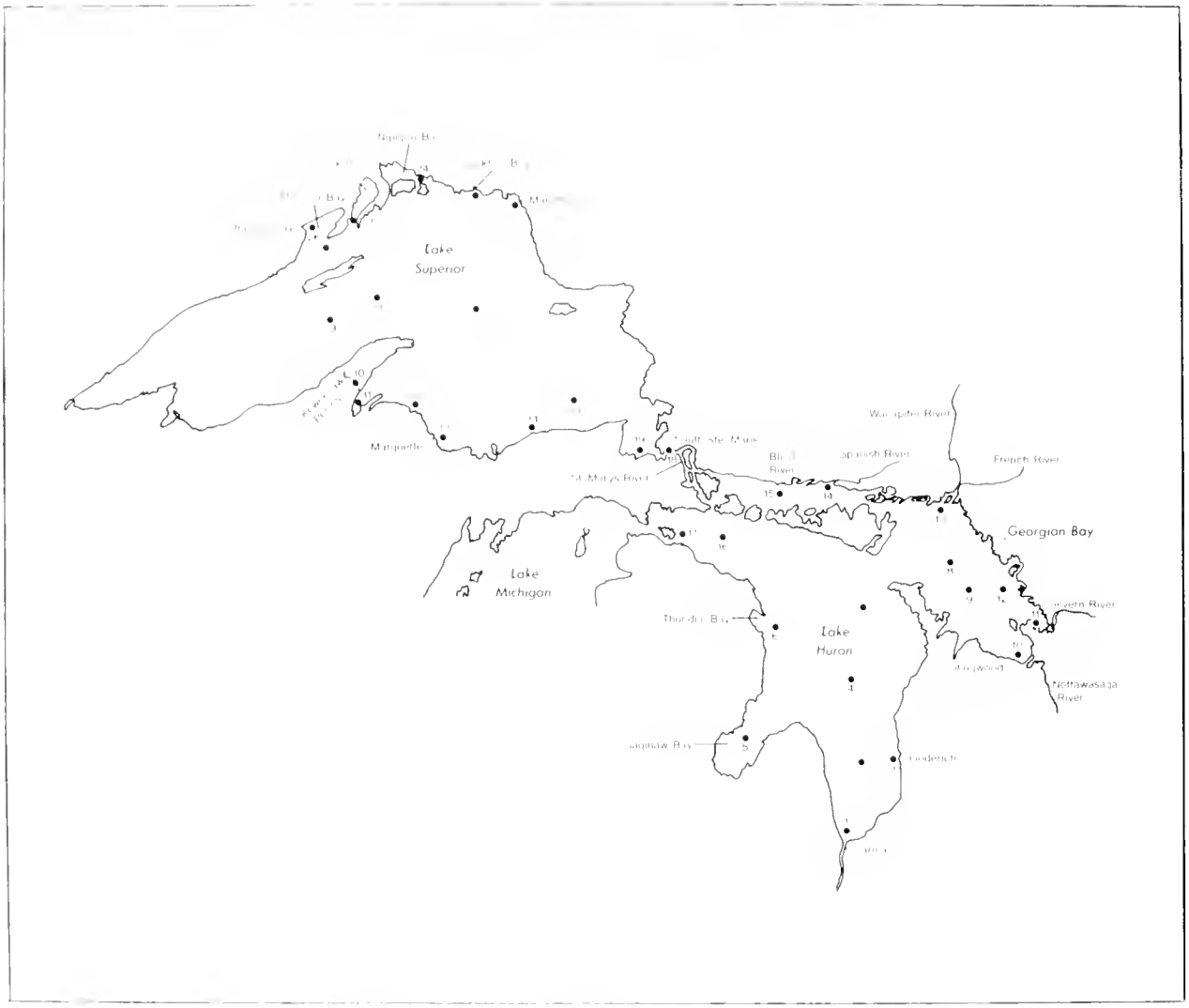

FIGURE 1. *Upper Great Lakes sampling stations*

preparation and extraction of organophosphorus samples under the same conditions as the organochlorines is an untested procedure.

SESTON

Sampling occurred whenever the vessel reached the stations and, as a consequence, seston masses and hence the concentrations therein may not be strictly comparable from station to station. Samples were collected with a plankton net which swept a cross-section of 0.126 m (40 cm [illegible]). It was dragged 2 m from the bottom or [illegible] m deep, whichever was more shallow. Collected [illegible] passed through GF/C filters and stored [illegible] in glass jars. They were subsequently [illegible] in acetonitrile and the homogenate plus [illegible] treated according to methods outlined in the [illegible] *Methods Manual* under "Procedure for the Analysis of Organochlorinated Pesticide and PCBs in Lipids and Sediments" (9). The extracts were further examined for organophosphates using the GC flame photometric detector system indicated for water samples. Since very little material was available on the filters and the filters were not preweighed, the seston yield could not be determined directly. Instead, a mean of a second box of filters (72.9 ± 1.1 mg) was obtained and subtracted from the weight of the dried seston plus filters.

SEDIMENTS

Shipek surface samples were obtained at each station and stored frozen in polyethylene bags until analyzed. In previous studies at the Canadian Centre for Inland Waters, the bags have not contaminated samples except with phthalates, which do not interfere with the analyses discussed here. The Eh of the sediments was measured at the time of sampling and examination for sediment type performed later at the laboratory. Separate 10-g subsamples were employed for detecting moisture and toxic organics. Moisture content was determined by weighing the subsample before and after 48 hours dry-

ing at 135°C. Toxic organics were analyzed as recommended in the *Analytical Methods Manual* under "Procedure for the Analysis of Organochlorinated Pesticide and PCB's in Fish and Sediments" (*9*). The extraction step was carried out by ultrasonic dispersion in a 1:4 water:acetonitrile solution rather than by homogenization and, as in the water samples, organophosphorus pesticides were examined in the extract residues.

Analysis

The PCB's and 15 organochlorines have been tested for stability in tap water at 4°C in the dark (A.S.Y. Chau, Water Quality Branch, Inland Waters Directorate, 1971: unpublished results). Except for heptachlor, quantitative recoveries of 80-100 percent were obtained in all cases after 6 weeks in storage. Additional details are available in other publications (*9* and citations therein). Stability of deep-frozen seston and sediment has not been determined.

Liquid-liquid partitioning and florisil cleanups were used for the seston and sediment samples. These, coupled with quantitative identification on three or more GC columns of varying polarity, were considered adequate confirmation of compound identity. Columns employed were:

3 percent OV-101 on 80/100 mesh Chromosorb W-HP

1.5 percent OV-17/1.95 percent OV-210 on 80/100 mesh Gas-Chrom Q

4 percent OV-101/6 percent OV-210 on 80/100 mesh Gas-Chrom Q

5 percent OV-210 on 100/120 mesh Gas-Chrom Q

3 percent OV-225 on 80/100 mesh Gas-Chrom Q

All chromatograms were run isothermally at 200°C (injector 250°C) with a pulsed, linearized ^{63}Ni detector at 300°C. The carrier gas was 5 percent methane in argon at 60-75 ml/min, purged at 15 ml/min. Compounds were identified and quantified using an Autolab computing integrator with a 2 percent retention window.

PCB's were quantitated using a modified version of the method of Webb and McCall (*25*) in which all GC peaks present in Aroclor 1242, 1254, and 1260 were examined and the amount of PCB was calculated by summing the contribution of each peak. PCB's and *p,p'*-DDE could be readily resolved on column 3 and *p,p'*-DDT was further confirmed by dehydrochlorination of the concentrate using a solid matrix derivatization technique (*2*).

Analytical limits of each compound for the sample types examined are given in Tables 1 and 2. These figures are the quantification levels, the lowest level to which an analytical laboratory will attach a quantity. In general, the detection limit is a level at which the compound is observable but not quantifiable. For such, the designation TR for trace is employed and it is generally about 10 percent of the quantification limit.

TABLE 1. *Quantification limits for organochlorine pesticides and polychlorinated biphenyls*

Compound	Quantification Limit		
	Water, ppb	Seston,[1] ng	Sediment, ppm
Lindane	0.005	1	0.001
Heptachlor	0.005	1	0.001
Heptachlor epoxide	0.005	1	0.001
Aldrin	0.005	1	0.001
Dieldrin	0.005	1	0.001
Endrin	0.01	10	0.001
p,p'-DDE	0.005	1	0.001
p,p'-TDE	0.005	1	0.001
p,p'-DDT	0.005	1	0.001
o,p'-DDT	0.005	1	0.001
α-Chlordane	0.01	5	0.005
β-Chlordane	0.01	5	0.005
α-Endosulfan	0.01	10	0.01
β-Endosulfan	0.01	10	0.01
p,p'-Methoxychlor	0.01	50	0.05
PCB's	0.1	10	0.01[2]

[1] Because seston weights were variable, estimated limits are given as absolute quantities rather than as a concentration. These should be compared with the absolute amounts in Table 3.

[2] The limit of quantitation for PCB's in this survey is 1/10 that of the referenced procedure as a result of evaporating the extraction solvent to 1 ml rather than 10 ml.

TABLE 2. *Quantification limits for organophosphorus pesticides*

Compound	Quantification Limit		
	Water,[1] ppb	Seston, pg	Sediment, ppm
Phorate	0.003	50	0.01
Diazinon	0.005	100	0.02
Disulfoton	0.003	50	0.01
Ronnel	0.005	100	0.02
Methyl Parathion	0.005	100	0.02
Malathion	0.005	100	0.02
Parathion	0.005	100	0.02
Crufomate	0.025	500	0.1
Methyl Trithion	0.01	200	0.04
Ethion	0.005	100	0.02
Carbophenothion	0.01	200	0.04
Imidan	0.05	1000	0.2
Azinphosmethyl	0.05	1000	0.2
Azinphosethyl	0.05	1000	0.2
Phosphamidon	0.03	500	0.1
Dimethoate	0.005	100	0.02
Fenitrothion	0.005	100	0.02

[1] Limits are half of those noted in the referenced procedures because 2-liter samples were employed. The absolute quantity that this represents, which is indicated under seston and under sediments, is calculated for sample size. In all cases, organophosphates have not been processed by the same method used to derive the original limits.

Results and Discussion

WATER

No organochlorine pesticides or PCB's were detected in the filtered water samples at levels above the quantification limits given in Table 1. There were detectable amounts of lindane in each of the water samples ex-

amined. In addition, station 4 in the middle of Lake Huron indicated trace amounts of both heptachlor and dieldrin, and station 3 off Goderich, Ontario, showed traces of *p,p'*-DDE. A study conducted in 1964-68 on 11 sites in the Great Lakes found dieldrin to be the main pesticide detected in the region, especially in the Detroit River and St. Mary's River at Sault Ste. Marie. The other two pesticides detected were BHC in the Saginaw and Detroit Rivers and lindane which was detected at a concentration of 0.003 ppb in St. Mary's River (*12*). Levels detected in the present study were similar to those reported for the Illinois waters of Lake Michigan (*21*) where such pesticides as DDT, heptachlor epoxide, and dieldrin were all below 0.001 ppb. The inability to detect PCB's in water contrasted with studies in Lakes Erie and Ontario where PCB's in surface waters average 0.027 ppb and 0.030 ppb, respectively (Canada Centre for Inland Waters, 1972: unpublished data). However, these levels are slightly below the Centre's current quantification limits in water.

SESTON

Data for the organochlorines and PCB's in the seston are given in Table 3. Quantification of seston in the water column and hence the concentration therein were calculated from the dry weight of seston plus filter minus the mean filter weight of 72.9 ± 1.1 mg.

TABLE 3. *Residues of dieldrin,* p,p'*-DDE, and PCB's in seston, upper Great Lakes—1974*

Station No.	Compound			
	Dieldrin	*p,p'*-DDE	PCB's [1]	
			Absolute Quantity, 10^{-9} g	Concentration, ppm
1	TR	ND	180	6.0
2	TR	TR	230	8.1
3	TR	ND	240	4.9
4	TR	TR	ND	
5	TR	ND	50	1.0
6	TR	TR	180	1.5
7	TR	TR	220	1.2
8	—	TR	150	2.1
10	TR	TR	170	6.7
11	TR	ND	74	1.3
12	TR	ND	140	5.9
13	ND	TR	33	0.7
14	TR	ND	26	1.0
16	TR	TR	85	0.8
17	TR	TR	32	0.5
19	TR	ND	37	0.9
20	ND	ND	TR	
22	TR	ND	30	1.1
23	TR	TR	24	1.0
24	TR	TR	TR	
25	TR	ND	95	1.3
26	TR	ND	ND	
27	TR	ND	47	0.8
28	TR	ND	49	1.3
29	TR	ND	TR	
30		TR	15	0.5
31	ND	ND	TR	
32	TR	ND	ND	
33	ND	ND	ND	
34	TR	ND	TR	

NOTE: TR = trace
ND = not detected

[1] Concentrations are based upon the difference between filter plus seston weight and the mean filter weight of 72.9 mg (± 1.1 mg). The mean seston weight used in this study was 47.0 mg with a minimum value of 23.7 mg.

Only PCB's were observed at quantifiable levels and these occurred at nearly every station. This agrees with observations of other workers who have examined the Great Lakes for the presence of these ubiquitous compounds (*10,21*). PCB concentrations in seston ranged from nondetectable or trace levels at stations 4, 20, 24, 26, 29, and 31-34 to a maximum of 8.1 ppm in station 2 in the middle of Lake Huron. Two of the highest levels, 6.7 ppm at station 10 and 5.9 ppm at station 12, were found in Georgian Bay, indicating possible local sources of this compound. It is significant that these levels are only slightly higher than PCB concentrations in oceanic zooplankton, which is probably best called seston due to the mode of collection (*5,8,20*). Although generally Lake Superior samples have lower PCB concentrations than have those of Georgian Bay and Lake Huron, there are some stations which have levels of the same magnitude: the outlet to St. Mary's River and the mouths of Black and Thunder Bays near Marathon, Ontario.

Dieldrin and *p,p'*-DDE were also observed but only in trace amounts. The former appeared almost throughout the sampling region; the latter appeared frequently in Lake Huron and Georgian Bay but only seldom in Lake Superior.

It is significant that, even in the open lake water and especially in Lake Superior, dieldrin and PCB's are present, the latter in quantifiable amounts.

SEDIMENTS

The survey placed major emphasis on sediments, which are the ultimate sink of many organic and inorganic particulate materials in the upper Great Lakes. Results of sediment analyses are given in Table 4. PCB's occurred in higher concentrations than any other substance. The two highest values, 1.3 ppm and 90 ppb, were found in Lake Superior off Marathon, Ontario (station 22), and in the middle of the lake (station 21), respectively. Lowest values were found in Lake Huron; residues in Georgian Bay were slightly higher.

DDT and its degradation products (ΣDDT) were generally higher in Lake Huron and Georgian Bay than in Lake Superior. The highest ΣDDT value was 22 ppb at station 4 which lies in the depositional Goderich Basin of Lake Huron (*24*). Half of this was analyzed as *p,p'*-DDT and half was *p,p'*-DDE, indicating lack of total degradation. Other maximum values, 20 ppb (station 10), 12 ppb (station 12), and 11 ppb (station 11), occurred in Georgian Bay. This is significant in the wake of other studies which have shown high concentrations of ΣDDT in tributaries to Georgian Bay, mainly from past insect control in recreational areas (*3,14*). At these three stations, DDE and TDE made up most of the ΣDDT analyzed, indicating active degradation of

TABLE 4. *Distribution of organochlorines in sediment, upper Great Lakes—1974*

Station No.	Sediment Type	Redox Potential, +mv	Organic Carbon, %	Concentrations, μg/g dry weight						
				PCB's	Dieldrin	*p,p'*-DDE	*p,p'*-TDE	*p,p'*-DDT	*o,p'*-DDT	DDT
1	Sand	130	0.11	TR	TR	ND	ND	ND	ND	ND
2	Sand	480	0.50	0.01	ND[1]	0.002	ND	ND	ND	0.002
3	Sand	240	—	TR	ND	ND	ND	ND	ND	ND
4	Clayey silt	460	2.70	0.01	ND	0.01	ND	0.012	ND	0.022
5	Sand	90	0.15	TR	ND	ND	ND	ND	ND	ND
6	Sand	455	0.31	TR	ND	ND	ND	ND	ND	ND
7	Clay	440	0.31	TR	TR	ND	ND	ND	ND	ND
8	Clayey sand	500	2.1	0.01	TR	0.005	ND	0.007	ND	0.012
10	Clay	300	0.94	0.02	TR	0.004	0.009	0.006	0.001	0.020
11	Sandy silt	95	3.6	0.02	ND	0.005	0.006	ND	ND	0.011
12	Silty clay	450	0.23	0.02	ND	0.003	ND	ND	ND	0.003
13	Sand	475	0.25	TR	ND	ND	ND	ND	ND	ND
14	Sandy clay	430	0.16	TR	ND	ND	ND	ND	ND	ND
15	Sand	407	0.09	0.01	ND	ND	ND	ND	ND	ND
16	Sandy clay	470	0.51	TR	ND	0.002	ND	ND	ND	0.002
17	Sand	375	0.03	TR	ND	0.005	ND	ND	ND	0.005
18	Sand	488	0.20	0.02	ND	0.005	ND	ND	ND	0.005
19	Sand	198	0.68	TR	ND	ND	ND	ND	ND	ND
20	Clayey sand	450	1.2	TR	ND	ND	ND	0.007	ND	0.007
21	Clay	493	2.4	0.09	ND	0.002	ND	0.003	ND	0.005
22	Sandy silt	165	3.1	1.3[1]	TR	ND	ND	ND	ND	ND
23	Clayey silt	475	1.3	0.01	ND	ND	ND	ND	ND	ND
24	Silty clay	120	1.4	0.02	ND	0.006	ND	ND	ND	0.006
25	Clayey silt	147	0.77	TR	ND	ND	ND	ND	ND	ND
26	Sand	138	0.12	TR	ND	ND	ND	ND	ND	ND
27	Sand	475	0.21	0.01	ND	ND	ND	ND	ND	ND
28	Clay	490	1.2	TR	ND	ND	ND	ND	ND	ND
29	Sandy clay	470	0.22	0.01	ND	ND	ND	ND	ND	ND
30	Silty clay	100	1.7	0.02	ND	0.007	0.005	ND	ND	0.012
31	Sandy silt	490	0.17	0.02	ND	ND	ND	ND	ND	ND
32	Clayey sand	500	0.26	0.02	ND	ND	ND	ND	ND	ND
33	Sand	465	—	0.01	ND	ND	ND	ND	ND	ND
34	Sand	505	0.23	0.02	ND	ND	ND	ND	ND	ND

NOTE: TR = trace.
ND = not detected.
— = not determined.

[1] Aroclor 1260

the original compound. Another high value for ΣDDT, 12 ppb, was found in Torch Lake (station 30) in the Keweenaw waterway, which is also a recreational area.

Highest values of ΣDDT were lower often by an order of magnitude than levels of ΣDDT analyzed previously in sediments of creeks draining southern Ontario tobacco-growing areas (*3,4,7,13*) and mixed agricultural areas just south of the Canadian Shield, the Bay of Quinte watershed in Lake Ontario, and the Muskoka Lake System which drains into Georgian Bay near station 12 (*14*). One study (*14*) showed mainly DDE and TDE in such sediments, but no *o,p'*-DDT or dieldrin. Results of the present survey confirm this pattern.

Areas which revealed *p,p'*-DDT (stations 4, 8, 10, 20, 21) and *o,p'*-DDT (station 10) were located in basins of high-sediment deposition (R. L. Thomas, Canada Centre for Inland Waters, 1975: personal communication), which may explain why DDT is accumulating there. The single exception was station 10 in Georgian Bay off Collingwood, Ontario. Sediments of these sites are characterized generally by the presence of either clay, clayey silt, or clayey sand and higher organic carbon content than sediments from other stations. All also have redox potentials of at least +300 mv, indicating oxidizing environments. ΣDDT, especially TDE, generally appears to be degraded at faster rates in anaerobic environments (*11,22*). The three lowest redox potentials found were at stations 5 (+90 mv), 11 (+95 mv), and 30 (+100 mv). Station 5 in Saginaw Bay is characterized by sandy sediments in an area of active sediment transport which may explain the levels of DDT and PCB's below detection limit as there are potential inputs of these compounds in the area. However, station 11 off Penetanguishene, Ontario, and station 30 in Torch Lake, Keweenaw Peninsula, Michigan, appear to be zones of deposition in terms of sediment type; both are high in TDE and DDE, indicating degradation.

Of interest are the higher levels of DDE found in the sediments of stations 16 and 17 near the Straits of Mackinac. Station 16 lies in the depositional Mackinac Basin; station 17 is in an area of undifferentiated tills and bedrock (*24*). These higher levels may represent inputs from Lake Michigan or local insect control in the recreational or urban areas of adjacent Michigan. The former hypothesis may be supported by the fact that of all the Great Lakes, Lake Michigan appears to be highest in pesticide residues evidenced by comparative fish analyses. Lake Superior fish had the lowest concentrations: one-fourth to one-seventh the level of those in Lake Michigan fish (*15-17*). Lake Huron fish occupied the middle range of all the lakes, below Ontario fish but higher than Erie fish.

The PCB data demonstrate no clear correlation between sediment concentration and either sediment texture, organic carbon content, or redox potential. ΣDDT data, however, indicate that the highest sediment concentrations of the parent compound were found in geologic basins where accumulation of sediments also tended to be higher in clay content and organic carbon, and had higher redox potential. Dieldrin was found only in trace amounts at stations 1, 7, 8, 10, and 22; there appear to be no similarities in the nature of sediment environments at these stations and the significance of these trace amounts is uncertain.

Other organochlorine compounds were below detection limits at all stations. This may be explained by use patterns. In Ontario, the major use of organochlorines is in Lake Huron watersheds for such field crops as corn, soybeans, and small grains. Previous studies indicate that the main soil residues in these areas were aldrin, dieldrin, endrin, and ΣDDT (*1,6*). Since the late 1960's, however, use of many organochlorine compounds has diminished. Aldrin and dieldrin were banned for agricultural purposes in Ontario in 1970, and DDT was banned except for two uses in 1970. One would also have expected highest residues of DDT and dieldrin from orchards and vegetable and tobacco soils. Apparently no data have been published on the limited acreages of orchards in the Georgian Bay watershed and no studies are available to determine what inputs might come from these limited areas compared to recreational or municipal inputs from the same region. Michigan corn-belt soils analyzed for residues contained only dieldrin and DDT-related compounds; however, the sampling area could influence only the southern portion of Lake Huron (*1*).

The absence of correlation between possible sources of pesticides and sediment concentration could result from causes other than the nature and transport of sediments: atmospheric input, for example. W. M. J. Strachan (Canada Centre for Inland Waters, 1975: unpublished data) found PCB levels in atmospheric precipitation at Burlington, Ontario, to range from 0.02 to 0.05 ppb on a limited number of samples; at Parry Sound on Georgian Bay levels were less than 0.02 ppb. Also detected were nine organochlorine pesticides at levels between 0.001 and 0.026 ppb; *p,p'*-DDT and α-endosulfan occurred at the highest levels. Another study of air samples at Buffalo, N.Y., on Lake Erie detected *p,p'*-DDT and *o,p'*-DDT at levels of 11.0 and 2.9 ng m^3, respectively (*2*). Authors presume that levels of such pesticides are similar in the atmosphere over the upper Great Lakes. Unfortunately, no data exist on the magnitude of atmospheric pesticide contributions to the Great Lakes.

Conclusions

This survey indicates low concentrations of PCB's, DDT and or its degradation products TDE and DDE, and traces of dieldrin in sediments and seston of Lakes Superior and Huron and Georgian Bay. These compounds were below detection limits in water samples. No other organochlorine compounds were detected nor were any organophosphorus compounds found in any of the samples analyzed.

The source of these compounds is not known. In the Lake Superior watershed, agriculture is very limited; hence pesticides probably are not used in great volume. Unfortunately, use patterns of pesticides in the upper Great Lakes have not been published so inputs cannot be estimated nor are data available on use patterns of pesticides in recreational or urban areas around the upper Great Lakes. Atmospheric inputs also require further study.

Consequently, it cannot be ascertained whether the low concentrations of pesticides found in the upper lakes are due to use patterns, environmental degradation of such compounds, or both. Continuing surveillance is necessary to determine whether the organochlorine compounds detected are degrading in these lakes now that uses of some compounds such as DDT and dieldrin have been banned in the area. Such a program also would indicate whether compounds such as endosulfan and chlordane, whose usage is increasing, are accumulating in the upper Great Lakes environment.

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LITERATURE CITED

(*1*) *Carey, A. E., G. B. Wiersma, H. Tai, and W. G. Mitchell. 1973.* Organochlorine pesticide residues in soils and crops of the Corn Belt region, United States —1970. Pestic. Monit. J. 6(4):369-376.

(*2*) *Chau, A. S. Y., and M. Lanouette. 1972.* Confirmation of pesticide residue identity-II. Derivative formation in solid matrix for the confirmation of DDT, DDD, methoxychlor, perthane, cis- and trans-chlordane, heptachlor and heptachlor epoxide residues by gas chromatography. J. Ass. Offic. Anal. Chem. 55(5):1058-1066.

(*3*) *Frank, R., A. E. Armstrong, R. G. Bollens, H. E. Braun, and C. W. Douglas. 1974.* Organochlorine insecticide residues in sediment and fish tissues, Ontario, Canada. Pestic. Monit. J. 7(3 4):165-180.

(*4*) *Frank, R., K. Montgomery, H. E. Braun, A. H. Berst, and K. Loftus. 1974.* DDT and dieldrin in watersheds draining the tobacco belt of southern Ontario. Pestic. Monit. J. 8(3):184-201.

(5) *Giam, C. S., M. K. Wong, A. R. Hanks, W. M. Sackett, and R. L. Richardson. 1973.* Chlorinated hydrocarbons in plankton from the Gulf of Mexico and northern Caribbean. Bull. Environ. Contam. Toxicol. 9(6):376-382.

(6) *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.

(7) *Harris, C. R., W. W. Sans, and J. R. W. Miles. 1966* Exploratory studies on the occurrence of organochlorine insecticide residues in agricultural soils in southwestern Ontario. J. Agr. Food Chem. 14(4):398-403.

(8) *Harvey, G. R., H. P. Miklas, V. T. Bowen, and W. G. Steinhauer. 1974.* Observations on the distribution of chlorinated hydrocarbons in Atlantic Ocean organisms. J. Mar. Res. 32(2):103-118.

(9) *Inland Waters Directorate. 1974.* Analytical Methods Manual. Water Quality Branch. Ottawa, Canada. 188 pp.

(10) *International Joint Commission. 1972.* Great Lakes Water Quality Board Third Annual Report, Appendix B. Surveillance Subcommittee Report, Windsor, Ontario. 212 pp.

(11) *Kearney, P. C., and D. D. Kaufman. 1972.* Microbial degradation of some chlorinated pesticides. *In* National Academy of Sciences, Degradation of Synthetic Organic Molecules in the Biosphere. Washington, D.C., pp. 166-189.

(12) *Lichtenberg, J. J., J. W. Eichelberger, R. C. Dressman, and J. E. Longbottom. 1970.* Pesticides in surface waters of the United States—a 5-year summary. 1964-68. Pestic. Monit. J. 4(2):71-86.

(13) *Miles, J. R. W., and C. R. Harris. 1971.* Insecticide residues in a stream and controlled drainage system in agricultural areas of southwestern Ontario. Pestic. Monit. J. 5(3):289-294.

(14) *Miles, J. R. W., and C. R. Harris. 1973* Organochlorine insecticide residues in streams draining agricultural, urban-agricultural, and resort areas of Ontario, Canada—1971. Pestic. Monit. J. 6(4):363-368.

(15) *Reinert, R. E. 1970.* Pesticide concentrations in Great Lakes fish. Pestic. Monit. J. 3(4):233-240.

(16) *Reinert, R., and H. C. Bergman. 1974.* Residues of DDT in Lake Trout (*Salvelinus namaycosh*) and Coho Salmon (*Oncorhynchus kisutch*) from the Great Lakes. J. Fish. Res. Board Can. 31(2):191-199.

(17) *Reinke, J., J. F. Uthe, and D. Jamieson. 1972.* Organochlorine pesticide residues in commercially caught fish in Canada—1970. Pestic. Monit. J. 6(1):43-49.

(18) *Ripley, B. D., J. A. Hall, and A. S. Y. Chau. 1974.* Determination of fenitrothion, phosphamidan, and dimethoate in natural waters. Environ. Lett. 7(2): 97-118.

(19) *Ripley, B. D., J. Wilkinson, and A. S. Y. Chau. 1974.* Multi-residue analysis of fourteen organophosphorous pesticides in natural waters. J. Ass. Offic. Anal. Chem. 57(5):1033-1042.

(20) *Rischorough, R. W., V. Vreeland, G. R. Harvey, H. P. Miklas, and G. M. Carmignani. 1972.* PCB residues in Atlantic Zooplankton. Bull. Environ. Contam. Toxicol. 8(6):345-355.

(21) *Schacht, R. A. 1974.* Pesticides in Illinois Waters of Lake Michigan. U.S. Environ. Prot. Agency Rep. EPA 660 3-74-002. 55 pp.

(22) *Sethunathan, N. 1973.* Microbial degradation of insecticide in flooded soil and in anaerobic cultures. Residue Rev. 47:143-165.

(23) *Stanley, C. W., J. E. Barney, M. R. Helton, and A. R. Yobs. 1971.* Measurement of atmospheric level of pesticides. Environ. Sci. Technol. 5(5):430-435.

(24) *Thomas, R. L., A. L. W. Kemp, and C. F. M. Lewis. 1973.* The surficial sediments of Lake Huron. Can. J. Earth Sci. 10(2):226-271.

(25) *Webb, R. G., and A. C. McCall. 1973.* Quantitative PCB standards for electron capture gas chromatography. J. Chromatogr. Sci. 11(7):366-373.

GENERAL

Residues of Quintozene, Its Contaminants and Metabolites in Soil, Lettuce, and Witloof-Chicory, Belgium—1969-74 [1]

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ABSTRACT

Authors studied contamination of soils used to raise lettuce in greenhouses and witloof-chicory (French endive) in forcing beds. The crops had been treated with the fungicide quintozene; residues detected included quintozene, its technical impurities and metabolites hexachlorobenzene, pentachlorobenzene, pentachloroaniline, and pentachlorothioanisole. Analyses of 72 soil samples indicated that soils remain contaminated with these chemicals one or more years after application. This is attributed to the high persistence of quintozene, its impurities and metabolites, and the almost annual application of the fungicide. Analyses of the crops show that quintozene, hexachlorobenzene, and pentachloroaniline are taken up from contaminated soils, especially by lettuce. Pentachlorothioanisole, although present in the soils, was not detected in the crops.

Introduction

The fungicide quintozene [pentachloronitrobenzene (PCNB)] is used on lettuce and witloof-chicory (French endive) to control *Rhizoctonia* bottom rot and *Botrytis* gray mold rot. This practice generally produces residues of quintozene and related compounds in the marketable product (*3,4*). When applied to lettuce in a greenhouse and to witloof-chicory in a forcing bed, the fungicide is taken up by the plants from the soil. Due to the stability of the compound a large fraction of the applied dose remains in the soil after the crop has been harvested (*1,4,6*).

Successive yearly applications of quintozene to lettuce foliage or soil and to witloof-chicory soil may increase quintozene content of the soil. Residues may then be found in crops grown on soils which have not been treated during the current growing season. This explains why certain experiments have shown no correlation between the residue content in lettuce and witloof-chicory and the dose applied during that particular growing season.

In order for authors of the present study to obtain some reliable data on the degree of contamination following yearly quintozene treatments, soil samples from lettuce greenhouses and from witloof-chicory forcing beds were analyzed.

Apart from quintozene, amounts were also determined for hexachlorobenzene (HCB), pentachlorobenzene (QCB), pentachloroaniline (PCA), and pentachlorothioanisole (PCTA); these chemicals were present as a result of the quintozene treatments (Fig. 1; *8*). For a number of soils where no quintozene was applied after sampling, residues were analyzed in the lettuce

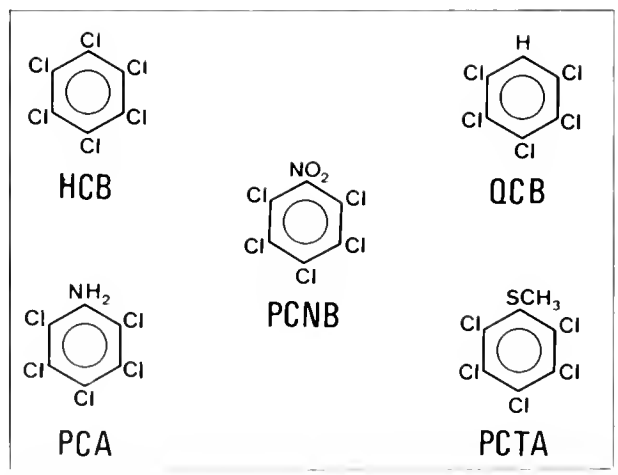

FIGURE 1. *Breakdown of PCNB: HCB and QCB are present as contaminants of the technical grade quintozene; PCA and PCTA are quintozene metabolites.*

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and witloof-chicory crops grown in these soils to determine the uptake of the compounds from the soil.

Sampling

Random soil samples were taken by inspectors of the Belgian Ministry of Agriculture. In total 72 plots were sampled: 24 from lettuce greenhouses and 48 from witloof-chicory forcing beds. Every soil composite consisted of five samples, each containing five cores of approximately 2.5 cm taken at random to a depth of 30 cm. After mixing, a subsample was taken for analysis.

The soil samples were accompanied by a statement about the quintozene treatments on the sampled area during the five previous years; information provided by the grower was sometimes vague. Samples were not air-dried nor sieved before analysis.

In order to obtain an accurate picture of the uptake of quintozene and its technical contaminants and metabolites from the soil, lettuce and witloof-chicory were sampled from plots that were not treated with quintozene during the growing season.

The 21 lettuce samples consisted of five heads taken at random in 21 greenhouses. The yellowing outer leaves were removed prior to analysis. After cutting up the leaves a subsample was taken for analysis. The 21 witloof-chicory samples which weighed about 2 kg each were taken randomly from 21 forcing beds. The crop was cleaned as customary before marketing, and cut into small pieces; a subsample was taken for analysis.

Materials and Methods

Reagents and apparatus used were:

Petroleum-ether: freshly distilled
Acetone: freshly distilled
Sodium sulfate: anhydrous, technical grade
Sodium chloride: technical grade
Ultra turax mixer: type 645 N Janke-Kunkel KG
Gas chromatographs: Varian, models 1400 and 2400, fitted with electron-capture detectors and glass columns filled with 2 percent OV-225 or 3 percent of a 3:22 OV-17:OV-210 mixture on Gas-Chrom Q.

EXTRACTION AND ANALYSIS

A 50-g soil subsample or a 100-g sample of finely chopped lettuce or witloof-chicory leaves was blended for 3 minutes with 200 ml of a 1:1 mixture of petroleum ether:acetone filtered through a Buchner filter and rinsed with 50 ml of the same solvent mixture.

The extract was transferred to a 1-liter separating funnel and shaken twice with 200 ml H_2O and 25 ml of a saturated NaCl solution. Water layers were discarded and the petroleum-ether phase was dried over anhydrous Na_2SO_4. In most cases the resulting solution was concentrated and directly analyzed by gas chromatography using the 2 percent OV-225 column. Confirmation was obtained on the OV-17—OV-210 column (Fig. 2). Recoveries ranged between 85 and 95 percent. Limits of detection for the normal procedure without concentration were: 0.01 ppm, HCB; 0.02 ppm, PCNB; 0.05 ppm, PCA and PCTA. After a tenfold concentration of the petroleum-ether extract, detection limits were one tenth the rates mentioned above (*5,6*). Dichloran and endosulfan were sometimes detected in soil samples but in much smaller amounts than quintozene and related compounds.

Results and Conclusions

Tables 1 and 2 show the results of the soil analyses and the quintozene dosage rates indicated by the growers. Tables 3 and 4 summarize the results for lettuce and witloof-chicory soils, respectively. Tables 5 and 6 show the results of soil and plant analysis for lettuce and witloof-chicory.

The recommended application rates of active ingredient (a.i.) in lettuce vary according to the references: 0.125-0.2 g m^2 (*10*), 3-4 g m^2 (*2*), and 8-10 g/m^2 (*14*). No actual dosage recommendation is available for witloof-chicory but the general tendency is to apply about 5 g a.i./m^2.

Information obtained from growers indicates that more quintozene is applied each year to witloof-chicory than to lettuce. This is mainly due to the facts that several crops are grown in the same year, each preceded by a quintozene treatment, and that all are grown on the same topsoil. Compounding the higher quintozene residues in witloof-chicory soils are the dark, indoor growing conditions which do not favor decomposition of the fungicide.

A certain amount of information about quintozene breakdown and metabolism has been published (*8,9, 11-13, 15*). The literature indicates that microbiological processes, influenced by temperature, humus, oxygen, and water content of the soil, influence the breakdown.

Physical processes such as evaporation and leaching may affect the rate of disappearance of pesticides from the soil. Wang and Broadbent (*15*) showed that for quintozene, evaporation plays an important part in warm and wet soils. Mainly because of the low solubility of quintozene, leaching is negligible (*13*). Dejonckheere et al. (*7*) concluded that adding organic matter to the soil increases the rate of quintozene decomposition. PCA is produced primarily under anerobic conditions; PCTA is produced under aerobic conditions.

Nevertheless the high soil residues found during the present investigation indicate that quintozene is very persistent and breaks down slowly. HCB, QCB, PCA, and PCTA were also found in easily detectable quantities associated with quintozene. As indicated in Table

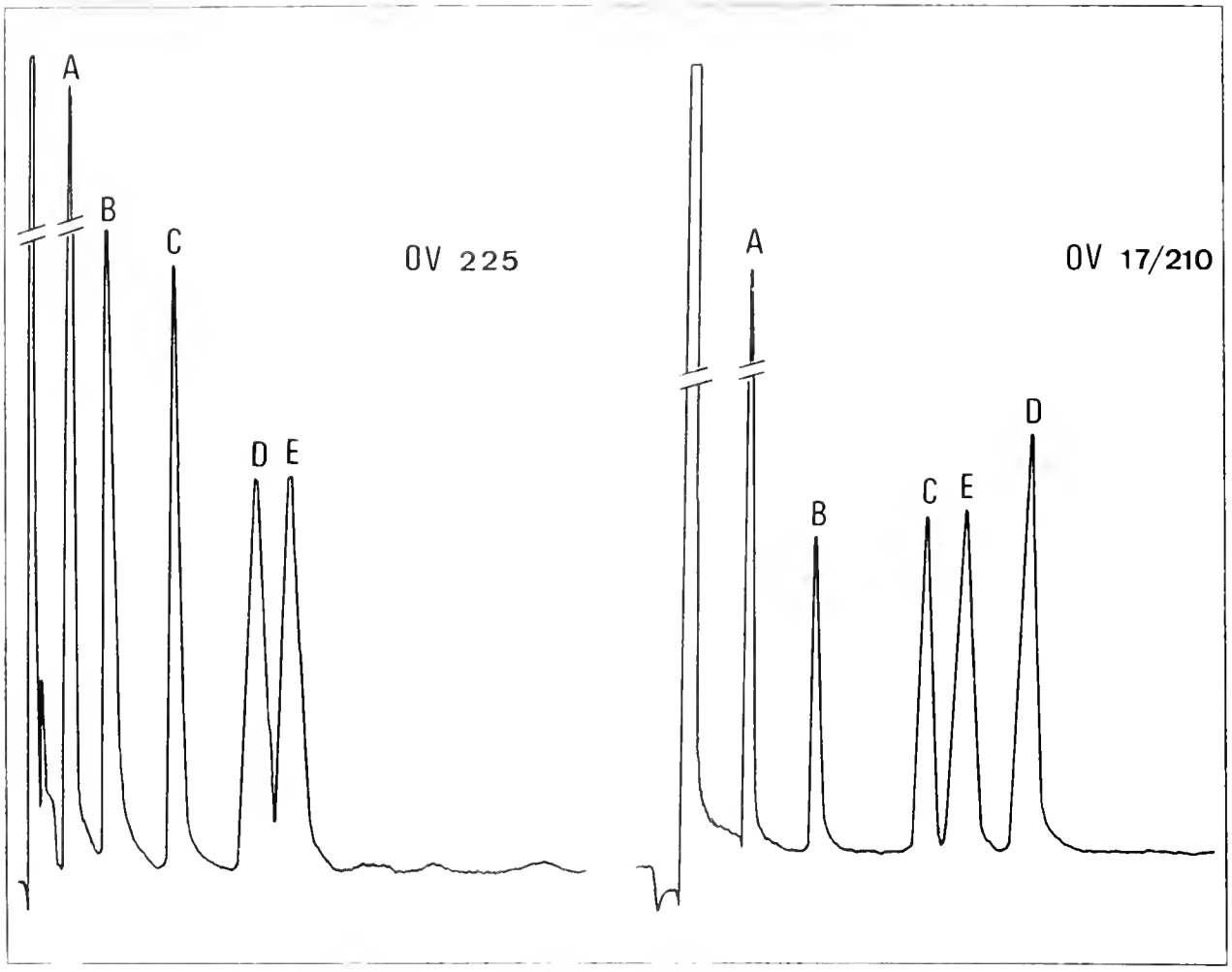

FIGURE 2. *Gas chromatograms of QCB, HCB, PCNB, PCTA, and PCA.*

TABLE 1. *PCNB, HCB, QCB, PCA, and PCTA residues in greenhouse lettuce soil, Belgium—1969–74*

Site	Applied Dose (a.i. g/m²)[1]							Residues, ppm				
	1969	1970	1971	1972	1973	1974	Total	PCNB	HCB	QCB	PCA	PCTA
1	—	1.5	0.75	0.25	1.5	0.75	4.75	4.90	0.79	0.19	1.52	0.28
2	—	—	2.92	4.0	4.0	2.00	12.92	5.80	0.31	0.19	0.98	0.74
3	—	0.46	—	0.69	—	—	1.55	1.15	0.06	0.06	0.10	0.11
4	—	—	—	0.93	—	—	0.93	1.34	0.25	0.24	0.46	0.20
5	—	0.74	0.74	0.74	0.74	—	2.96	4.40	0.38	0.30	0.88	0.55
6	—	—	—	0.93	5	2.5	8.43	0.54	0.12	0.28	0.27	0.09
7	—	4	4	1.86	1.86	0.93	12.65	3.25	1.18	0.51	3.75	1.20
8	—	4	4	4	4	2	18.00	5.10	0.98	0.40	2.06	0.37
9	—	—	3	4.5	4.5	1.5	13.5	1.83	0.23	0.41	0.78	0.11
10	4	4	4	1.6	1.6	0.8	16	5.40	1.62	0.63	1.63	0.28
11	—	2.25	2.25	4.0	4.0	—	12.5	6.40	0.41	0.28	0.94	1.08
12	2	4	4	4	4	[illegible]	18.0	6.80	0.56	0.25	0.55	0.73
13		4	3.6	3.2	3.6	1.56	15.96	8.40	0.98	0.27	0.84	0.92
14			-	-	0.93	-	0.93	0.97	0.08	0.06	0.14	0.15
15			—	0.93	0.93		1.86	1.48	0.10	0.06	0.12	0.26
16	[illegible]	[illegible]	[illegible]	[illegible]			5.0	0.08	0.11	0.03	0.53	0.11
17		2.8	1.86	1.30	1.30		7.26	0.88	0.32	0.26	0.87	0.35
18				0.6	0.6	0.86	2.06	1.50	0.08	0.07	0.36	0.09
19			0.4		0.4		0.8	5.50	0.42	0.42	1.05	1.48
20	[illegible]	[illegible]	[illegible]	[illegible]			40	4.60	1.04	0.70	1.76	1.37
21			1.4	1.4	1.4		4.2	1.50	0.30	0.24	0.60	0.51
22	0.3	[illegible]	0.3	0.3	0.3	0.56	2.06	0.22	0.06	0.06	0.20	0.17
23	0.3	0.3	0.3	0.3	0.3	0.56	2.06	0.14	0.03	0.05	0.10	0.06
24	0.5	0.7	0.6	0.6	0.5	-	2.7	0.63	0.08	0.06	0.66	0.16
						Average		3.03	0.44	0.25	0.84	0.47

NOTE: Blank denotes no application.

[1] Dosage rates are approximations [illegible] by growers.

TABLE 2. *PCNB, HCB, QCB, PCA, and PCTA residues in soil of witloof-chicory forcing beds, Belgium—1969-74*

Site	Applied Dose (a.i. g/m²)[1]							Residues, ppm				
	1969	1970	1971	1972	1973	1974	Total	PCNB	HCB	QCB	PCA	PCTA
1	—	—	—	—	3	—	3	0.76	0.15	0.08	0.34	0.04
2	—	20	20	20	20	—	80	25.50	1.31	1.14	4.10	0.49
3	—	8	8	—	8	—	24	4.90	0.29	0.19	1.10	0.07
4	—	—	17.2	17.2	—	—	34.4	2.35	0.26	0.23	1.60	0.12
5	—	7	7	15	—	—	29	21.60	1.85	0.54	5.10	0.67
6	—	8	8	8	8	—	32	9.00	2.25	0.73	5.60	0.87
7	—	—	8	—	—	—	8	0.78	0.29	0.31	1.80	0.12
8	—	12	12	12	—	—	36	7.50	0.77	0.38	1.70	0.19
9	—	—	—	6	6	—	12	1.60	0.20	0.20	1.00	0.11
10	NI	NI	NI	NI	NI	NI	NI	0.67	0.20	0.14	0.68	0.03
11	NI	NI	NI	NI	NI	NI	NI	2.80	0.21	0.13	0.89	0.07
12	—	—	—	—	5	—	5	3.40	0.45	0.21	1.37	0.14
13	—	8	8	6	6	—	30	2.00	0.34	0.26	1.31	0.07
14	—	16	16	16	16	—	64	10.30	1.10	0.95	0.99	0.36
15	—	—	—	—	10	—	10	6.50	0.74	0.60	5.60	0.53
16	NI	NI	NI	NI	NI	NI	NI	23.60	4.18	1.22	13.60	1.57
17	NI	NI	NI	NI	NI	NI	NI	5.10	0.55	0.39	2.30	0.13
18	—	15	15	15	15	—	60	18.40	2.84	0.57	6.30	0.41
19	NI	NI	NI	NI	NI	NI	2	0.85	0.04	0.03	0.14	0.06
20	—	—	28	28	—	—	56	10.60	1.06	0.74	2.30	0.35
21	—	14	14	14	—	—	42	20.40	1.70	0.94	5.40	0.46
22	NI	NI	NI	NI	NI	NI	NI	6.10	0.95	1.22	0.86	0.28
23	—	5	5	5	5	—	20	2.70	0.61	0.29	2.52	0.09
24	—	5	5	5	—	—	15	3.75	0.22	0.17	1.30	0.08
25	—	4	4	4	4	—	16	3.25	0.27	0.15	0.51	0.04
26	NI	NI	NI	NI	NI	NI	NI	22.50	0.83	0.23	1.07	0.17
27	NI	NI	NI	NI	NI	NI	NI	1.85	0.25	0.21	0.83	0.07
28	—	10	10	10	10	—	40	19.50	1.40	0.72	7.90	1.02
29	—	10	10	10	10	—	40	15.80	0.81	0.43	3.50	0.25
30	—	14	14	14	—	—	42	12.10	1.28	0.70	7.10	0.58
31	—	—	7	7	—	—	14	0.25	0.08	0.04	0.14	0.06
32	—	6	6	6	6	—	24	3.95	0.52	0.38	1.58	0.15
33	—	10	10	10	10	—	40	10.90	0.62	0.20	2.18	0.16
34	—	15	15	15	15	—	60	34.30	2.30	0.48	3.00	0.41
35	—	14	14	14	14	—	56	13.40	1.20	0.67	7.10	0.78
36	—	30	30	30	30	5	125	55.60	2.06	0.56	0.80	0.41
37	—	28.5	14.25	14.25	14.25	—	71.25	10.90	0.40	0.24	1.10	0.12
38	—	—	14.25	14.25	14.25	—	42.75	2.10	0.13	0.11	0.32	0.32
39	—	—	—	—	4.30	—	4.30	0.64	0.12	0.11	0.26	0.05
40	—	—	—	14.25	4.30	—	18.55	0.74	0.40	0.25	1.40	0.10
41	—	—	—	—	8.60	—	8.60	11.80	0.81	0.80	2.20	2.61
42	NI	NI	NI	NI	NI	NI	NI	5.40	0.86	0.33	3.90	0.46
43	—	—	2.90	—	—	—	2.90	6.25	0.85	0.58	2.50	1.86
44	—	—	—	6.2	—	—	6.2	13.60	1.11	1.11	3.05	1.28
45	—	—	—	6.2	—	—	6.2	3.10	0.50	0.73	3.22	0.71
46	—	—	14	7	7	—	28	1.51	0.51	0.64	2.58	0.24
47	14	—	—	4.15	4.15	—	22.30	3.30	0.97	0.49	7.90	1.11
48	—	—	—	12	—	—	12	0.12	0.02	0.02	0.68	0.39
						Average		9.25	0.85	0.46	2.83	0.43

NOTE: Blank denotes no application.
NI denotes no information available.

[1] Dosage rates are approximations supplied by growers.

TABLE 3. *Survey of PCNB, HCB, QCB, PCA, and PCTA residues in greenhouse lettuce soil, Belgium—1969–74*

Samples containing PCNB	Range, ppm	Samples containing: HCB	QCB	PCTA	PCA	Range, ppm
3	0.0— 0.5	6	8	3	1	0.0—0.1
4	0.5— 1.0	3	2	7	5	0.1—0.2
5	1.0— 1.5	2	7	3	1	0.2—0.3
1	1.5— 2.0	6	3	2	2	0.3—0.5
—	2.0— 3.0	1	3	2	4	0.5—0.7
4	3.0— 5.0	3	1	3	6	0.7—1.0
6	5.0— 7.0	2	—	4	1	1.0—1.5
1	7.0—10.0	1	—	—	3	1.5—2.0
		—	—	—	1	2.0—3.0
		—	—	—	1	3.0—5.0
		—	—	—	—	5.0—7.0

NOTE: Blank denotes no samples in the range indicated.

TABLE 4. *Survey of PCNB, HCB, QCB, PCA, and PCTA residues in soil of witloof-chicory forcing beds, Belgium—1969-74*

Samples containing PCNB	Range, ppm	Samples containing: HCB	QCB	PCTA	PCA	Range, ppm
2	0.0— 0.5	3	3	12	—	0.0— 0.1
6	0.5— 1.0	5	8	11	1	0.1— 0.2
4	1.0— 2.0	8	10	3	2	0.2— 0.3
4	2.0— 3.0	4	8	10	2	0.3— 0.5
7	3.0— 5.0	6	8	3	3	0.5— 0.7
7	5.0—10.0	9	7	3	—	0.7— 1.0
8	10.0—15.0	7	4	3	8	1.0— 1.5
3	15.0—20.0	2	—	2	4	1.5— 2.0
5	20.0—30.0	3	—	1	7	2.0— 3.0
1	30.0—40.0	1	—	—	7	3.0— 5.0
1	50.0—60.0	—	—	—	5	5.0— 7.0
		—	—	—	4	7.0—10.0
		—	—	—	1	10.0—15.0

NOTE: Blank denotes no samples in the range indicated.

TABLE 5. *PCNB, HCB, QCB, PCA, and PCTA residues in soil and in lettuce grown in that soil, Belgium—1969-74*

	Residues, ppm									
	Soil					Lettuce				
Site	PCNB	HCB	QCB	PCA	PCTA	PCNB	HCB	QCB	PCA	PCTA
1	4.90	0.79	0.19	1.52	0.28	0.39	<0.005	ND	0.14	ND
3	1.15	0.06	0.06	0.10	0.11	0.10	0.008	ND	0.02	ND
4	1.34	0.25	0.24	0.46	0.20	0.04	<0.005	ND	0.01	ND
5	4.40	0.38	0.30	0.88	0.55	1.51	0.018	ND	0.40	ND
6	0.54	0.12	0.28	0.27	0.09	0.02	<0.005	ND	0.01	ND
7	3.25	1.18	0.51	3.75	1.20	0.63	0.038	ND	0.63	ND
9	1.83	0.23	0.41	0.78	0.11	0.22	0.010	ND	0.13	ND
10	5.40	0.98	8.40	2.06	0.37	0.83	0.037	ND	0.38	ND
11	6.40	0.41	0.28	0.94	1.08	0.61	0.009	ND	0.25	ND
12	6.80	0.56	0.25	0.55	0.73	0.60	0.010	ND	0.24	ND
13	8.40	0.98	0.27	0.84	0.92	0.57	0.010	ND	0.26	ND
14	0.97	0.08	0.06	0.14	0.15	0.75	<0.005	ND	0.31	ND
15	1.48	0.10	0.06	0.12	0.26	1.15	<0.005	ND	0.58	ND
16	0.08	0.11	0.03	0.53	0.11	0.04	ND	ND	0.01	ND
17	0.88	0.32	0.26	0.87	0.35	0.03	<0.005	ND	0.03	ND
19	5.50	0.42	0.42	1.05	1.48	0.10	0.008	ND	0.06	ND
20	4.60	1.04	0.70	1.76	1.37	0.05	0.013	ND	0.05	ND
21	1.50	0.30	0.24	0.60	0.51	0.38	ND	ND	0.21	ND
22	0.22	0.06	0.06	0.20	0.17	0.28	0.007	ND	0.09	ND
23	0.14	0.03	0.05	0.10	0.06	0.72	0.012	ND	0.18	ND
24	0.63	0.08	0.06	0.66	0.16	0.02	<0.005	ND	0.02	ND

NOTE: ND = not detectable.

TABLE 6. *PCNB, HCB, QCB, PCA, and PCTA residues in soil and in witloof-chicory forced in that soil, Belgium—1969-74*

	Residues, ppm									
	Soil					Witloof-Chicory				
Site	PCNB	HCB	QCB	PCA	PCTA	PCNB	HCB	QCB	PCA	PCTA
2	25.50	1.31	1.14	4.10	0.49	0.052	0.030	ND	0.012	ND
3	4.90	0.29	0.19	1.10	0.07	0.016	ND	ND	ND	ND
4	2.35	0.26	0.23	1.60	0.12	0.005	ND	ND	ND	ND
8	7.50	0.77	0.38	1.70	0.19	0.160	0.012	ND	ND	ND
12	3.40	0.45	0.21	1.37	0.14	0.005	ND	ND	ND	ND
14	10.30	1.10	0.95	0.99	0.36	0.023	ND	ND	ND	ND
16	23.60	4.18	1.22	13.60	1.57	0.007	0.010	ND	0.015	ND
17	5.10	0.55	0.39	2.30	0.13	0.010	0.008	ND	0.010	ND
36	55.60	2.06	0.56	3.80	0.41	0.330	0.029	ND	0.040	ND
37	10.90	0.40	0.24	1.10	0.12	0.008	0.002	ND	0.006	ND
38	2.10	0.13	0.11	0.32	0.32	0.005	ND	ND	ND	ND
39	0.64	0.12	0.11	0.26	0.05	0.005	ND	ND	ND	ND
40	0.74	0.40	0.25	1.40	0.10	0.005	0.007	ND	0.017	ND
41	11.8	0.81	0.80	2.20	2.61	0.036	0.005	ND	0.006	ND
42	5.40	0.86	0.33	3.90	0.46	0.056	0.053	ND	0.100	ND
43	6.25	0.85	0.58	2.50	1.86	0.026	0.009	ND	0.014	ND
44	13.60	1.11	1.11	3.05	1.28	0.015	0.007	ND	0.022	ND
45	3.10	0.50	0.73	3.22	0.71	0.005	ND	ND	0.007	ND
46	1.51	0.51	0.64	2.58	0.24	0.005	0.003	ND	0.005	ND
47	3.30	0.97	0.49	7.90	1.11	0.013	0.026	ND	0.130	ND
48	0.12	0.02	0.02	0.68	0.39	ND	ND	ND	ND	ND

NOTE: ND = not detectable.

[illegible] residues (ppm) in lettuce soil for the 6-year period were: PCNB, 3.03; HCB, 0.44; QCB, 0.25; PCA, 0.74; PCTA, 0.17. Corresponding values in witloof chicory soil listed in Table 2 were: PCNB, 9.25; HCB, 0.[illegible]; QCB, 0.46; PCA, 2.83; PCTA, 0.43.

The average PCNB/PCTA ratio was 0.290 in lettuce and 0.305 in witloof chicory soil. The respective values for the PCTA quotient were 0.155 and 0.046. This may indicate that PCTA is produced during lettuce growing and witloof chicory growing, which corresponds with the aerobic conditions of the lettuce field. The calculated average HCB quintozene ratios were 0.145 for lettuce soil and 0.092 for witloof chicory soil. QCB quintozene ratios were 0.082 for lettuce soil and 0.048 for witloof chicory soil. These HCB and QCB ratios seem, especially for lettuce soils, to be higher than the normal impurity content of the formulations applied, which may be explained by the rapid breakdown of quintozene and the slow formation of QCB from quintozene (*7*).

Apart from the general aspect of soil contamination which these residues present, there is also the possibility that these chemicals will be taken up by the crops grown on polluted soils. In an earlier work (*6*) the authors found that the ratio between the quintozene soil residue and the amount present in the lettuce crop at time of harvest averaged 1.34 for an early harvest (average head 143 g) and 0.44 for a late harvest (average head 315 g). For HCB these ratios were 0.97 and 0.36, respectively. The uptake was somewhat higher for low

quintozene soil residues (0.12-0.44 ppm) than for high ones (5.0-6.1 ppm). For witloof-chicory the uptake factor averaged 0.004, much lower than for lettuce.

No QCB or PCTA residues were found in the harvested crops, which confirms previous findings.

The average soil:crop quintozene ratio calculated from the results of this study was 0.15 for lettuce and 0.004 for witloof-chicory. The value for lettuce is clearly lower than that found in previous work (*6*), perhaps in part because crops in the present study were sampled for residue analysis 3-6 months after soil samples had been taken for the same purpose.

The confirmed variability in the soil:crop residue ratio for witloof-chicory may reflect the various degrees of cleanup which the plant receives before analysis. The residue level may depend greatly on the presence or absence of small quintozene-carrying soil particles between the closely packed witloof-chicory leaves.

LITERATURE CITED

(*1*) *Beck, J., and K. E. Hansen. 1974.* The degradation of quintozene, pentachlorobenzene, hexachlorobenzene and pentachloroaniline in soil. Pestic. Sci. 5(1):41-48.

(*2*) *Crop Protection Advisory Services. 1973.* Guide for Disease and Weed Control in Agriculture and Horticulture. Wageningen, Holland.

(*3*) *Dejonckheere, W., W. Steurbaut, and R. H. Kips. 1974.* Pesticide residues in lettuce. II. Winter 1972-1973. Meded. Fac. Landbouww. Rijksuniv. Gent 39(1): 297-300.

(*4*) *Dejonckheere, W., W. Steurbaut, and R. H. Kips. 1974.* Quintozene (PCNB) residues in witloof chicory. Parasitica 30(1):28-36.

(*5*) *Dejonckheere, W., W. Steurbaut, and R. H. Kips. 1975.* The fate of quintozene (PCNB) on lettuce. Meded. Fac. Landbouww. Rijksuniv. Gent 40(2):1033-1038.

(*6*) *Dejonckheere, W., W. Steurbaut, and R. H. Kips. 1975.* Residues of quintozene, hexachlorobenzene, dichloran and pentachloroaniline in soil and lettuce. Bull. Environ. Contam. Toxicol. 13(6):720-729.

(*7*) *Dejonckheere, W., J. Willcox, W. Steurbaut, R. H. Kips, J. P. Voets, and W. Verstraete. 1975.* Changes in the rate of metabolism of quintozene in the soil under varying microbial growth conditions. Meded. Fac. Landbouww. Rikjsuniv. Gent 40(2):1187-1197.

(*8*) *De Vos, R. H., M. C. ten Noever De Brauw, and P. D. A. Olthof. 1974.* Residues of pentachloronitrobenzene and related compounds in greenhouse soils. Bull. Environ. Contam. Toxicol. 11(6):567-571.

(*9*) *Gorbach, S., and U. Wagner. 1967.* Pentachloronitrobenzene residues in potatoes. J. Agr. Food. Chem 15(4):654-656.

(*10*) *Heymands, P., and F. Lickens. 1972.* Crop Protection in Market Gardening. Vegetable Crop Research Station, St. Katelijne-Waver, Belgium.

(*11*) *Kow, H. W., and J. D. Farley. 1969.* Conversion of pentachloronitrobenzene to pentachloroaniline in soil and the effect of these compounds on soil microorganisms. Phytopathology 59(7):64-67.

(*12*) *Kuchar, E. J., F. O. Geenty, W. P. Griffiths, and R. J. Thomas. 1969.* Analytical studies of metabolism of Terrachlor in Beagle dogs, rats and plants. J. Agr. Food. Chem. 17(6):1237-1240.

(*13*) *Leistra, M., and J. H. Smelt. 1974.* Concentrations of quintozene at different depths in bulb growing soils. Bull. Environ. Contam. Toxicol. 11(3):241-243.

(*14*) *Tilemans, E. 1968.* List of Registered Crop Protection Chemicals. Ministry of Agriculture, Brussels, Belgium.

(*15*) *Wang, C. H., and F. F. Broadbent. 1973.* Effect of soil treatments on losses of two chloronitrobenzene fungicides. J. Environ. Quality 2(4):511-515.

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-*endo*-*exo*-5,8-dimethanonaphthalene
AROCLOR 1260	PCB, approximately 60% chlorine
AZINPHOSETHYL (Guthion)	O,O-Diethyl S[4-oxo-1,2,3-benzotriazin-3(4H)ylmethyl] phosphorodithioate
AZINPHOSMETHYL	O,O-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 *gamma* is most active as an insecticide.
CARBOPHENOTHION	S-[[(*p*-Chlorophenyl)thio] methyl] O,O-diethyl phosphorodithioate
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
DDD	See TDE.
DDE	Dichlorodiphenyl dichloro-ethylene (degradation product of DDT) *p,p'*-DDE: 1,1-Dichloro-2,2-bis(*p*-chlorophenyl) ethylene *o,p'*-DDE: 1,1-Dichloro-2-(*o*-chlorophenyl)-2-(*p*-chlorophenyl)ethylene
DDT	Main component (*p,p'*-DDT): α-Bis(*p*-chlorophenyl) β,β,β-trichloroethane. Other isomers are possible and some are present in the commercial product. *o,p'*-DDT: [1,1,1-Trichloro-2-(*o*-chlorophenyl)-2-(*p*-chlorophenyl) ethane]
DIAZINON	O,O-Diethyl O-(2-isopropyl 4-methyl-6-pyrimidyl) phosphorothioate
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-*endo*-*exo*-5, 8-dimethano-naphthalene
DIMETHOATE	O,O-Dimethyl S-(N-methylcarbamoylmethyl) phosphorodithioate
DISULFOTON	O,O-Diethyl S-2(ethylthio) ethyl phosphorodithioate
ENDOSULFAN	6,7,8,9,10,10-Hexachloro-1,5,5a,6,9,9a-hexahydro-6,9-methano-2,4,3-benzodioxathiepin 3-oxide
ENDRIN	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
ETHION	0,0,0',0'-Tetraethyl S,S'-methylene bisphosphorodithioate
FENITROTHION	O,O-Dimethyl O-(4-nitro-*m*-tolyl) phosphorothioate
HEPTACHLOR	1,4,5,6,7,8,8-Heptachloro-3a,4,7,7a-tetrahydro-4,7-*endo*-methanoindene
HEPTACHLOR EPOXIDE	1,4,5,6,7,8,8-Heptachloro 2,3-epoxy-3a,4,7,7a-tetrahydro-4,7-methanoindane
IMIDAN	O,O-Dimethyl S-phthal-imidomethyl phosphorodithioate
LINDANE	Gamma isomer of benzene hexachloride (1,2,3,4,5,6-hexachlorocyclohexane) of 99+% purity
MALATHION	S-[1,2-Bis(ethoxycarbonyl)ethyl] 0,0-dimethyl phosphorodithioate
METHOXYCHLOR	1,1,1-Trichloro-2,2-bis(*p*-methoxyphenyl) ethane
METHYL PARATHION	O,O-Dimethyl O-*p*-nitrophenyl phosphorothioate
METHYL TRITHION	O,O-Dimethyl S-(*p*-chlorophenylthio) methyl phosphorodithioate
MIREX	Dodecachlorooctahydro-1,3,4-metheno-1H-cyclobuta[cd]pentalene
NONACHLOR	1,2,3,4,5,6,7,8-Nonachlor-3a,4,7,7a-tetrahydro-4,7-methanoindan
OXYCHLORDANE	2,3,4,5,6,6a,7,7-Octachloro-1a,1b,5,5a,6,6a-hexahydro-2,5-methano-2H-indeno(1,2-*β*)oxirene
PARATHION	O,O-Diethyl-O-p-nitrophenyl phosphorothioate
PCB'S (POLYCHLORINATED BIPHENYLS)	Mixtures of chlorinated biphenyl compounds having various percentages of chlorine
PHORATE	O,O-Diethyl S-(ethylthio) methyl phosphorodithioate
PHOSPHAMIDON	1 Chloro-diethylcarbamoyl-1-propen-2yl dimethyl phosphate
RONNEL	Dimethyl 2,4,5-trichlorophenyl phosphorothionate
TDE	2,2 Bis (p-chlorophenyl)-1,1-dichloroethane (including isomers and dehydrochlorination products)
TOXAPHENE	Chlorinated camphene (67-69% chlorine); product is a mixture of polychlor bicyclic terpens with chlorinated camphenes predominating
TRIFLURALIN	α,α,α Trifluoro-2,6-dinitro-N,N dipropyl-*p*-toluidine

ERRATUM

Pesticides Monitoring Journal, Volume 10, Number 1, pp. 10-17. In the paper "Nationwide Residues of Organochlorines in Starlings, 1974," Acknowledgments should read:

> Special thanks are extended to the following for their help with starling collections: Donald Donahoo, James Elder, Robert Hillen, Harry Kennedy, David Lenhart, John Peterson, and Larry Thomas. Earlene Swann compiled the tables and Pamela Kramer constructed the map.

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CONTENTS

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RESIDUES IN FISH, WILDLIFE, AND ESTUARIES

Chlorinated Hydrocarbon and PCB Residues in Tissues and Lice of Northern Fur Seals, 1972 [1]

David A. Kurtz [2] and Ke Chung Kim [3]

ABSTRACT

DDT, dieldrin, and PCB contents of tissues and the sucking lice of the northern fur seal (Callorhinus ursinus) *were studied in samples collected in July 1972 in the Pribilof Islands, Alaska. They included the analyses of two nursing cows and their two newborn pups, three 2-month-old pups, and the sucking lice inhabiting these animals,* Antarctophthirus callorhini *and* Proechinophthirus fluctus. *The ΣDDT content of fat tissue was 5.2, 5.6, and 63 μg/g ($\bar{x}$) for cows, newborns, and 2-month-old pups, respectively. Dieldrin appeared at trace levels. PCB residues (Aroclor 1254) were 5.8, 5.5, and 33 μg/g ($\bar{x}$), respectively. The ΣDDT content of blood was less than 0.01 μg/g for cows and newborns and 4.6 μg/g for 2-month-old pups. PCB's were found only in trace amounts in the blood of all animals except one 2-month-old pup which contained 3.4 μg/g. Lice contained 0.2-6 percent, respectively, of the ΣDDT and PCB's detected. All residues were expressed on a wet-weight basis. Two-month-old pups had far higher residue levels than had cows. A high percentage of* ΣDDT occurred *as the DDE metabolite: 60 percent in cows and newborn pups and 90 percent in 2-month-old pups.*

Introduction

Biological concentrations of pesticide residues in harp, harbor, gray, and ringed seals have been reported on a world-wide basis (*1-3, 8-9, 12-15, 21-25*), but they are indicators of generally localized pesticide contamination levels since these species are localized. Anas, in fact, has suggested that harbor seals could be used to locate geographical areas where organochlorine and polychlorinated biphenyl (PCB) concentrations are high (*3*).

The northern fur seals, *Callorhinus ursinus*, on the other hand, are migratory and have an open ocean habitat. They subsist solely on marine fishes and invertebrates. They spend 4-5 months on the Pribilof Islands in Alaska and the remainder in the northern Pacific Ocean ranging from the Bering Sea to areas off the coasts of California and Japan. Analysis of fur seals would thus be an indicator of pesticide concentrations of the neritic seas. Anas and Wilson have studied pesticide concentrations in 30 fur seals collected on the Pribilof Islands in 1968 and off the California cost in 1969 (*4*). ΣDDT concentrations in liver of male and female seals of all ages averaged 0.78 and 0.98 ppm, respectively; they were found in quantities of 0.21 ppm and 0.26 ppm, respectively, in samples of brain tissue. Dieldrin was detected in only three liver samples and in no brain samples. PCB's were not detected. In five samples of liver and brains from seals collected in November 1969 on the Pribilof Islands, Anas and Wilson found 2.21 ppm ($\bar{x}$) and 0.20 ppm ($\bar{x}$) ΣDDT, respectively, no dieldrin, and traces of PCB. In blubber they found 15.9 ppm ($\bar{x}$) ΣDDT, 0.045 ppm ($\bar{x}$) dieldrin, and only traces of PCB (*5*).

This paper reports the accumulation of ΣDDT, dieldrin, and PCB's in tissues and the sucking lice of the northern fur seals, *Callorhinus ursinus*. Two species of the sucking lice, *Antarctophthirus callorhini* and *Proechinophthirus fluctus*, are parasitic on the fur seal. The taxonomy, ecology, and population biology of these lice have been studied by one of the authors (*17-19*). The detection of mercury in the tissues and the sucking lice of these fur seals has also been reported by Kim et al. (*20*).

Materials and Methods

Samples of body tissue and the sucking lice were collected from the northern fur seals on St. Paul Island, Alaska, in July 1972. Fat and blood samples were taken from two nursing cows, two newborn pups, and three 2-month-old pups. Subcutaneous fat samples were taken

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[2] Pesticide Research Laboratory and Graduate Study Center, The Pennsylvania State University, University Park, Pa. 16802. Reprints available from this address.

[3] The Frost Entomological Museum, Department of Entomology, Pennsylvania State University, University Park, Pa.

from the abdominal region and blood was taken directly from the heart. Fat was collected as a single small sample. Anas and Worlund have speculated that this method produces less specific residue levels than does the collection of a larger homogenized sample (6).

Sucking lice of the species *A. callorhini* were collected from all five pups and those of the species *P. fluctus* were collected from only the 2-month-old pups. All samples were stored in glass vials and kept frozen from the time of collection until analysis. The two pregnant cows were caged away from the rookery for study, and samples were taken from these two nursing cows and two newborn pups in captivity for this study.

Blood samples were extracted by vortexing 50 mg with 5 ml hexane four times. Hexane layers were combined, concentrated to 1 ml, and passed through a small florisil column containing 2.3 g florisil. Lice and fat samples were ground in a Duall tissue grinder, size B. Lice samples generally varied from 8 to 29 mg; for one 2-month-old pup the *P. fluctus* sample was 139 mg. Fat samples weighed 200 mg. Each sample was extracted three times with 3 ml acetonitrile each time. The combined acetonitrile layers were extracted once with 5 ml hexane to remove excess fats. To the remainder was added 9 ml water containing 1 percent sodium sulfate and this solution was then extracted three times with 3 ml hexane. The hexane layers were combined, concentrated, and passed through a florisil column containing 2.3 g activated florisil. All solvents were from Burdick and Jackson and were used without further purification. The extraction and cleanup methods follow those of the U.S. Environmental Protection Agency (26).

Quantitative gas-chromatographic (GC) analysis was accomplished using a 160-cm U column of 1.5 percent SP-2250/1.95 percent SP-2401 on 100/120 Supelcoport packing. A Microtek 220 gas chromatograph was operated at an oven temperature of 215°C, the inlet was operated at 240°C, and the detector at 330°C. The flow of nitrogen was 60 ml/min with 20 ml/min detector purge. The electrometer sensitivity was 1.6×10^{9} amp amplitude full scale.

Silicic acid column separations were run on all samples that showed residues greater than trace levels in order to separate PCB compounds from DDT compounds (7). Determinations were confirmed on a 155-cm column of 3 percent DEGS on 80/100 mesh Chromosorb WHP. This column was operated at 200°C, the inlet was operated at 240°C, and the detector at 330°C.

The range of recovery of DDT and metabolites was 55 to 66 percent from seal fat tissue and 56 to 58 percent from blood. The low recoveries from fat tissue were a direct result of an additional partitioning in the extraction steps. Following the original partitioning of the fat with acetonitrile, a second partitioning was performed from the acetonitrile portion with a carefully measured volume of hexane. In this step most of the lipids that were partitioned into the acetonitrile layer then moved into the hexane layer. Concurrently, smaller portions of the DDT metabolites and Aroclor mixtures were partitioned into the hexane layer and were subsequently lost from the recovery as this hexane layer was discarded. Aroclors were also recovered in a similar range, 47 percent from fat and 40 percent from blood. Other recovery data from this laboratory indicated that these data are consistent. Although massive amounts of DDT and metabolites were used for recovery, other data based on much lower added values have shown similar recovery percentages.

Results

The DDT content in fat tissues of the northern fur seals was approximately equal in cows and their newborn pups; total *p,p'*-DDT's were 5.2 μg/g and 5.6 μg/g, respectively (Table 1). Two-month pups selected ran-

TABLE 1. *Pesticide and Aroclor 1254 content in fat samples of the northern fur seal,* Callorhinus ursinus, *1972*

	Residue, μg/g wet weight							
Seal	Aroclor 1254	Dieldrin	*o,p'*-TDE	*o,p'*-DDT	*p,p'*-DDE	*p,p'*-TDE	*p,p'*-DDT	Sum, *p,p'*-DDTs
Nursing cow #2	6.8	0.16	0.4	1.5	3.8	1.0	2.2	7.0
Newborn pup #2	3.8	0.12	0.2	1.0	3.3	0.6	1.4	5.3
Nursing cow #3	4.7	0.07	0.1	0.6	2.0	0.4	0.9	3.3
Newborn pup #3	7.2	TR	0.3	1.0	3.9	0.6	1.3	5.8
Mean								
Cows	5.8	0.12	0.3	1.1	2.9	0.7	1.6	5.2
Pups	5.5	0.06	0.3	1.0	3.6	0.6	1.4	5.6
Pup (2 mo.) #13	16	ND	TR	0.6	98	4.7	3.1	106
Pup (2 mo.) #14	8.1	TR	TR	2.0	70	3.3	3.2	77
Pup (2 mo.) #15	1.3	TR	ND	TR	5.1	0.1	0.1	5.3
Mean	3.3	TR	TR	0.9	58	2.7	2.1	63
Recovery from 0.200 g fat sample (nursing cow #3)								
Added, ng	10^{5}		2000	1500	2000	2000		
Recovered, %	47		51	55	66	60		

NOTE: Analyses for all residues except dieldrin and *o,p'*-TDE were corrected for recovery.
TR = trace (approximately 0.01 μg/g)
ND = no detectable residue (< 0.003 μg/g)

domly, however, had a much higher ΣDDT content. One sample contained only 5.3 μg/g ΣDDT, but the other two had 77 μg/g and 106 μg/g. The average of the three samples was 63 μg/g. The predominant DDT metabolite was DDE which accounted for approximately 60 percent of the total DDT in cows and newborns and over 90 percent in the two-month pups. The difference in the proportion of these isomers between the cows/newborns and the pups may have significance, but the sample size was too small to form any solid conclusions. It may also be significant that although small amounts of *o,p'*-DDT were found, no *o,p'*-DDE occurred in any samples.

PCB's were also found in these samples (Table 1). General GC peak patterns were seen for Aroclor 1254 but none appeared for Aroclor 1242 nor Aroclor 1260. Differential metabolism of the PCB compounds was also noted. The quantitative level found in the fat of most samples revealed that the PCB level was approximately equal to that of total *p,p'*-DDT. The average PCB level in cows was 5.8 μg/g; the average ΣDDT level was 5.2 μg/g. For the newborn, PCB's averaged 5.5 μg/g and DDT averaged 5.6 μg/g. Average PCB residue for one pup was 91 μg/g: ΣDDT averaged 77 μg/g. The Aroclor 1254 content of the other two pups was lower than the ΣDDT content: 16 μg/g vs. 106 μg/g and 1.3 μg/g vs. 5.3 μg/g.

In a recent study by Jones et al. (*16*) the blubber from one newborn fasted harp seal taken from the Gulf of St. Lawrence in 1973 contained amounts of biocide (1.47 ppm ΣDDT and 1.80 ppm PCB's) similar to those in pups who were 8-14 days old: 1.21 ppm ΣDDT and 0.9 ppm PCB's, respectively. The pups' mothers contained 4.41 ppm ΣDDT and 6.1 ppm PCB's. As in fur seals, the biocides passed the placental barrier, though in smaller amounts.

Dieldrin occurred in almost all samples in trace or very low amounts.

Levels of DDT and PCB's in the blood of these animals (Table 2) were much lower than in the fat. Absolute levels of DDT metabolites were not detectable in the cows and newborn, eliminating comparisons. The 2-month-old pups had low ΣDDT values, with a mean of 4.6 μg/g. In two samples ΣDDT was 1-3 percent of that in the fat. In the third sample results were anomalous.

PCB's occurred in blood samples only at a trace level. This suggests that, like DDT, PCB's in the blood do not exceed 3 percent of the PCB's in fat.

Lice inhabiting the bodies of the seals were analyzed; results appear in Table 3. DDT appeared in the low ppm range in lice on the 2-month-old pups. Total *p,p'*-DDT's averaged 4.4 μg/g in *A. callorhini* and 3.6 μg/g in *P. fluctus*. No quantities greater than trace were found in lice of cows or newborns. This amounts to about 6 percent of that found in fat and twice that in blood.

PCB levels in lice were generally about one-fourth of the ΣDDT levels or in the low ppm range. In the 2-month-old pups PCB's averaged 2.0 μg/g and 0.9 μg/g for *A. callorhini* and *P. fluctus*, respectively. ΣDDT and PCB's appeared in equal proportions in *A. callorhini* and *P. fluctus* species. In essentially all cases the level in the *A. callorhini* species just slightly exceeded that in the *P. fluctus* species.

Correlation coefficients for blood-lice and lice-lice relationships determined for the 2-month pups were all highly positive. Blood to *A. callorhini* lice for DDE and the sum of *p,p'*-DDT were 0.93 and 0.92, respectively. Blood to *P. fluctus* lice for DDE and the sum of *p,p'*-DDT were both 0.96. The correlations of *A. callorhini* to *P. fluctus* for PCB's, DDE, and the sum of *p,p'*-DDT were 0.69, 0.99, and 0.99, respectively.

Discussion and Conclusions

The higher ΣDDT and PCB levels of these seals compared with those collected in 1969 (*5*) indicate that

TABLE 2. *Pesticide and Aroclor 1254 content in blood samples of the northern fur seal,* Callorhinus ursinus, *1972*

	Residue, μg/g wet weight							
Seal	Aroclor 1254	Dieldrin	*o,p'*-TDE	*o,p'*-DDT	*p,p'*-DDE	*p,p'*-TDE	*p,p'*-DDT	Sum, *p,p'*-DDT's
Nursing cow #2	TR	0.02	ND	ND	ND	ND	ND	ND
Newborn pup #2	TR	0.02	ND	ND	ND	ND	ND	ND
Nursing cow #3	TR	0.02	ND	ND	ND	ND	ND	ND
Newborn pup #3	TR	0.02	ND	ND	TR	ND	ND	ND
Pup (2 mo.) #13	TR	0.07	ND	ND	2.8	0.2	TR	3.0
Pup (2 mo.) #14	TR	0.06	ND	ND	0.6	0.1	TR	0.7
Pup (2 mo.) #15	3.4	0.05	ND	ND	10	0.3	0.1	10
Mean		0.06			4.5	0.2		4.6
Recovery from 0.05 g blood sample (nursing cow #2)								
Added, ng	4000		400	300	400	400		
Recovered, %	40		58	58	56	57		

NOTE: Analyses were corrected for recovery.
TR = trace (approximately 0.03 μg/g for DDT isomers and 0.3 μg/g for Aroclor 1254).
ND = no detectable residue (< 0.01 for DDT isomers and < 0.1 μg/g for PCB).

TABLE 3. *Pesticide and Aroclor 1254 content in sucking lice samples of the northern fur seal,* Callorhinus ursinus, *1972*

Seal	Lice[1]	Residue, μg/g wet weight: Aroclor 1254	Dieldrin	*o,p'*-DDT	*p,p'*-DDE	*p,p'*-TDE	*p,p'*-DDT	Sum, *p,p'*-DDT's
Newborn pup #2	Ac	TR	TR	ND	TR	ND	TR	TR
Newborn pup #3	Ac	TR	TR	ND	TR	ND	TR	TR
Pup (2 mo.) #13	Ac	0.5	TR	ND	1.9	ND	TR	1.9
	Pf	0.4	TR	TR	1.3	0.01	0.01	1.3
Pup (2 mo.) #14	Ac	2.4	TR	TR	2.9	0.06	0.05	3.0
	Pf	TR	TR	ND	1.7	ND	TR	1.7
Pup (2 mo.) #1	Ac	3.0	TR	TR	8.2	0.04	0.06	8.3
	Pf	2.2	TR	ND	7.9	ND	TR	7.9
Mean	Ac	2.0			4.3	0.03	0.03	4.4
	Pf	0.9			3.6	0.00	0.00	3.6

NOTE: Analyses were not corrected for recovery.
TR = trace (approximately 0.01 μg/g for DDT isomers and 0.4 μg/g for Aroclor 1254).
ND = no detectable residue (< 0.003 μg/g for DDT isomers and < 0.1 μg/g for PCB).
[1]Ac = *Antarctophthirus callorhini* and Pf = *Proechinophthirus fluctus*

the levels of pesticide residues have increased in the oceans in the past several years. Woodwell et al. (*27*) and Cramer (*10*) have proposed global models for DDT in the biosphere. In these models they discussed the various reservoirs and rates of exchange between them. The shallow seas form the last accessible reservoir before DDT which, adsorbed to organic matter, sinks to the ocean abyss. While differing in some aspects of the models, both authors predicted a maximum DDT concentration in the shallow seas in 1971-72.

Because the northern fur seal spends most of its life in the shallow portion of the northern Pacific Ocean, analysis of this animal could be a good test of the validity of Woodwell and Cramer's global DDT model. Samples in the present study were collected at the proposed peak level and, though very few in number, had higher residues than had earlier analyses. The small sampling and wide variability between samples detract from their value in confirming this theory. Further analysis of fur seals seems warranted.

Analyses also indicated that 2-month-old nursing pups had far higher levels than had cows analyzed from the same herd. The diet at this age is predominantly mother's milk (*11*), which contains as much as 50 percent fat (5). This implies a tremendous potential for containment of DDT. The mother herself feeds principally on small fishes and squids (*4*) whose biological loading potential is not so great as seal milk.

This magnification was not evident in the results of Frank et al. in studying harp seals (*12*). On the contrary, their data indicated that the young had lower concentrations than had adult females. Two age groups of young contained 2.4 ppm (n = 19) and 2.6 ppm (n = 10) ΣDDT. Adults from that area and year, however, contained 7.4 ppm (n = 13). In the study of harp seals by Jones et al. similar results were obtained (*16*).

Several factors could explain the differences in results of the harp seal studies and the present authors' fur seal studies. These include the amount of biocide excreted in the milk and the degradation pathways in the seal. Little is known of the levels of biocide excreted by mother harp or fur seals in milk. Fur seal pups after 2 months of suckling ought to have higher levels than harp seal pups after only 2 weeks of feeding providing that other factors, such as the levels in the milk, amount of milk ingested, and body fat contents of the seal body, are similar. Degradation rates and pathways for these biocides in either species are not well known. Harp seals may have a higher rate of DDA formation, which has not been studied, resulting in lower DDT levels than those of fur seals. On the other hand one cannot overlook the possibility that since only two of the three nursed fur seal pups in the present study contained high DDT levels, these could have resulted from feeding from mothers who had unusually high levels themselves.

Another major finding of this study is the high percentage of degradation of the parent DDT molecule to the DDE metabolite. In both cows and newborns, 60 percent of the ΣDDT in the fat tissues was in the form of DDE. In the nursing seals fully 90 percent of the ΣDDT in both fat and blood portions was in the form of DDE. Both *A. callorhini* and *P. fluctus* lice living on 2-month sucklings had 95 percent of the ΣDDT in the DDE form.

In harp seals Jones et al. (*16*) found that DDE was also the major fat-soluble metabolite of DDT. For example, in fat tissue DDE content of mothers and their 8-14-day-old pups was 72 percent and 74 percent, respectively, of the ΣDDT found.

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LITERATURE CITED

(1) *Addison, R. F., S. R. Kerr, J. Dale, and D. E. Sargeant. 1973.* Variation of organochlorine residue levels with age in Gulf of St. Lawrence harp seals (*Pagophilus groenlandicus*). J. Fish. Res. Board Can. 30(5): 596-600.

(2) *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.

(3) *Anas, R. E. 1974.* DDT plus PCB's in blubber of harbor seals. Pestic. Monit. J. 8(1): 12-14.

(4) *Anas, R. E., and A. J. Wilson, Jr. 1970.* Organochlorine pesticides in fur seals. Pestic. Monit. J. 3(4): 198-200.

(5) *Anas, R. E., and A. J. Wilson, Jr. 1970.* Organochlorine pesticides in nursing fur seal pups. Pestic. Monit. J. 4(3): 114-116.

(6) *Anas, R. E., and D. D. Worlund. 1975.* Comparison between two methods of subsampling blubber of northern fur seals for total DDT plus PCB's. Pestic. Monit. J. 8(4): 261-262.

(7) *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.

(8) *Brewerton, H. V. 1969.* DDT in fats of Antarctic animals. New Zealand J. Sci. 12: 194-199.

(9) *Brown, N. J., and A. W. A. Brown. 1970.* Biological fate of DDT in a sub-Arctic environment. J. Wildl. Manage. 34(4): 929-940.

(10) *Cramer, J. 1973.* Model of the circulation of DDT on Earth. Atmos. Environ. 7: 241-256.

(11) *Eddie, B., W. J. L. Sladen, and K. F. Meyer. 1966.* Serologic studies and isolation of bedsonia agents from northern fur seals on Pribilof Islands. Am. J. Epidemiol. 84(2): 405-410.

(12) *Frank, R., K. Ronald, and H. E. Braun. 1973.* Organochlorine residues in harp seals (*Pagophilus groenlandicus*) caught in eastern Canadian waters. J. Fish. Res. Board Can. 30(8): 1053-1063.

(13) *Gaskin, D. E., R. Frank, M. Holdrinet, K. Ishida, C. J. Walton, and M. Smith. 1973.* Mercury, DDT, and PCB in harbour seals (*Phoca vitulina*) from the Bay of Fundy and Gulf of Maine. J. Fish. Res. Board Can. 30(3): 471-475.

(14) *George, J. L., and D. E. H. Frear. 1966.* Pesticides in the Antarctic. J. Appl. Ecol. 3 (suppl.): 155-167.

(15) *Holden, A. V., and K. Marsden. 1967.* Organochlorine pesticides in seals and porpoises. Nature 216: 1274-1276.

(16) *Jones, D., K. Ronald, D. M. Lavigne, R. Frank, M. Holdrinet, and J. F. Uthe. 1976.* Organochlorine and mercury residues in the harp seal. Sci. Total Environ. 5: 181-195.

(17) *Kim, K. C. 1971.* The sucking lice (*Anoplura: Echinophthiriidae*) of the northern fur seal; descriptions and morphologic adaptation. Ann. Entomol. Soc. Amer. 64(1): 280-292.

(18) *Kim, K. C. 1972.* Louse populations of the northern fur seal (*Callorhinus ursinus*). Am. J. Vet. Res. 33(10): 2027-2036.

(19) *Kim, K. C. 1975.* Ecology and morphological adaptation of the sucking lice on the northern fur seal. Proc. Symp. Biol. Seals, University of Guelph, Canada, 1972. Repp. P.-V. Reun. Conf. Int. Explor. Mer. 169: 504-515.

(20) *Kim, K. C., R. C. Chu, and G. P. Barron. 1974.* Mercury in tissues and lice of northern fur seals. Bull. Environ. Contam. Toxicol. 11(3): 281-284.

(21) *Koeman, J. H., W. H. M. Peters, C. J. Smit, P. S. Tjioe, and J. J. M. DeGoeij. 1972.* Persistent Chemicals in Marine Mammals. TNO Nieuws 27: 570-578.

(22) *Koeman, J. G., and H. van Genderen. 1966.* Some preliminary notes on residues of chlorinated hydrocarbon insecticides in birds and mammals in the Netherlands. J. Appl. Ecol. 3 (suppl.): 99-106.

(23) *Robinson, J., A. Richardson, A. N. Crabtree, J. C. Coulson, and G. R. Potts. 1967.* Organochlorine residues in marine organisms. Nature 214: 1307-1311.

(24) *Shaw, S. B. 1971.* Chlorinated Hydrocarbon Pesticides in California Sea Otters and Harbor Seals. Calif. Fish and Game 57(4): 290-294.

(25) *Sladen, W. J. L., C. M. Menzie, and W. L. Reichel. 1966.* DDT residues in Adelie penguins and a crabeater seal from Antarctica. Nature 210: 670-673.

(26) *U.S. Environmental Protection Agency. 1971.* Analysis of Pesticide Residues in Human and Environmental Studies. Perrine Primate Research Laboratory, Perrine, Fla.

(27) *Woodwell, G. M., P. P. Craig, and H. A. Johnson. 1971.* DDT in the biosphere: where does it go? Science 174: 1101-1107.

Organochlorine Pesticide Residues in Plain Chachalacas from South Texas, 1971-72[1]

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ABSTRACT

Plain chachalacas (Ortalis vetula) *from the intensively cultivated and sprayed Lower Rio Grande Valley of Texas were analyzed for pesticide residues during 1971 and 1972. Residues of eight organochlorine pesticides and a polychlorinated biphenyl were identified in fat tissues of specimens collected from four study areas. Chemicals detected in all 24 birds and average residue levels (±SD) in ppm wet weight were: DDT (1.52±4.12), DDE (2.48±2.09), dieldrin (0.23±0.59), endrin (0.13±0.52), and Aroclor 1248 (0.17±0.20). Residue levels varied considerably, but the majority of the fat tissues contained significantly less than 1 ppm of these chemicals.*

Because birds of this species feed primarily on unsprayed native fruits rather than on sprayed crops, they adsorb very few pesticides through their diet. Although birds from exposed areas near cultivated fields had generally higher residues than had birds from less exposed areas, these herbivores generally had much lower residues than would most birds living near heavily treated lands. During the present study there was no evidence that plain chachalacas died as a direct result of exposure to agricultural chemicals, nor was there evidence that eggshells of this species have thinned significantly since 1900.

Introduction

The Lower Rio Grande Valley of Texas is predominantly a semitropical agricultural region with heavy pesticide use, primarily on cotton (*1*). Within this region, plain chachalacas (*Ortalis vetula*) inhabit small, isolated tracts of dense, brushy woodland (5) and feed primarily on small fruits of native plants (*6*). The majority of the chachalacas live close to cultivated fields which are sprayed intensively with agricultural pesticides. Pesticide residue levels in the birds were determined and compared according to the birds' proximity to agricultural activities.

Eggshell thinning in some populations of wild birds has been recognized as a problem associated with environmental contamination by DDE and related chemicals (*9*). To determine whether such a pattern exists in chachalacas, shell thickness of eggs collected during the present study were compared to museum specimens of eggshells collected in South Texas before 1900.

Methods

Fat tissues of 24 birds collected from four study areas in the Lower Rio Grande Valley were analyzed for organochlorine and polychlorinated biphenyl (PCB) residues. Three of the areas, Anzalduas Dam, McManus Farm, and Santa Ana National Wildlife Refuge, are isolated dense brushland in southern Hidalgo County surrounded by fields under intensive cultivation. The Falcon Dam area, a narrow strip of riparian vegetation adjacent to the Rio Grande in western Starr County, was not closely associated with intensive farming.

Of the 24 fat samples analyzed, 10 were from Santa Ana Refuge, 10 from Anzalduas Dam, and 2 each were from McManus Farm and Falcon Dam study areas. For convenience in comparing residue levels, sample collection sites were classified according to proximity and probable exposure to agricultural chemicals. "Central" samples were taken from birds collected more than 400 m from the nearest cultivated fields. Samples from birds collected nearer the adjacent fields were labeled "peripheral." Five samples from central and 5 from peripheral

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locations were analyzed for each of the larger areas, Santa Ana Refuge and Anzalduas Dam. All samples obtained at McManus Farm and Falcon Dam were considered peripheral.

Samples were frozen in 150-ml glass containers and maintained at approximately -18°C. A general pesticide scan for residues of organochlorine pesticides and PCB's was conducted on all fat tissues in laboratories of the Department of Agricultural Analytical Services at Texas A&M University. Analyses were modified slightly from those outlined in Section 211 of a manual by the Food and Drug Administration, U.S. Department of Health, Education, and Welfare (*10*). Each fat sample was thoroughly homogenized in anhydrous sodium sulfate and extracted several times using petroleum ether. A Buchner funnel containing sharkskin filter paper was used to decant supernatant from these extractions into a suction flask. Fat solution was transferred to a tared beaker using small portions of petroleum ether. Petroleum ether was evaporated and the beaker was weighed. Lipid residues were partitioned with acetonitrile saturated with petroleum ether and cleaned with florisil. The cleaned extract was analyzed for pesticide residues by electron-capture gas chromatography with parameters as described by Reynolds (*8*).

Residue levels are reported in parts per million (ppm) on a whole tissue wet-weight basis. Mean residues for all areas were compared using Duncan's new multiple range test (*2*). Mean residues in samples obtained at central and peripheral collection sites were also compared using a t-test (*7*).

Chachalaca eggshells collected during this study were air-dried for several months. Eggshell thickness was determined using a Starrett 1010-m dial gauge calibrated in 0.01-mm units and expressed as the mean of measurements made at three points near the waist of the egg. Chachalaca eggshells collected in southern Texas before 1900 and preserved at the Smithsonian Institution—National Museum of Natural History, Washington, D.C., were similarly measured and the data were statistically compared with those from recent eggshells using a pooled t-test (*7*).

Results and Discussion

Eight organochlorine pesticides including BHC, chlordane, DDT, DDE, dieldrin, endrin, hexachlorobenzene (HCB), and toxaphene were reported in one or more fat samples from collected birds. A polychlorinated biphenyl (PCB), Aroclor 1248, occurred in birds from all collection areas except Anzalduas Dam.

All 24 fat samples contained residues of *p,p'*-DDT and its major metabolite, *p,p'*-DDE. Twenty-one samples contained dieldrin; 12 contained Aroclor 1248. Endrin was found in 8 fat samples, HCB in 3, toxaphene in 2, chlordane in 1, and benzene hexachloride (BHC) in 1.

Mean fat tissue residue levels for 5 major pesticides were generally highest in specimens from Anzalduas, Santa Ana, and McManus Farm, which are closer to agricultural spraying than is Falcon Dam (Table 1). Duncan's new multiple range test revealed no significant differences in residue levels among study areas, except for DDE. Fat in specimens from peripheral areas at Anzalduas Dam and Santa Ana Refuge contained significantly higher mean residues ($P<0.05$) of DDE than did fat from birds at Falcon Dam. The small sample size undoubtedly restricted the power of Duncan's test in detecting these differences.

At Anzalduas and Santa Ana study areas, birds collected in peripheral locations had generally higher residue levels than had those from central locations. Comparisons of these differences yielded nonsignificant t values ($P>0.05$) of 1.03, 1.40, 0.77, 1.19, and 1.06 for Aroclor 1248, DDT, DDE, dieldrin, and endrin, respectively. Once again, the highly variable nature of these residue levels and the relatively small sample size severely restricted

TABLE 1. *Mean residue levels of five pesticides in fat tissues of plain Chachalacas, Lower Rio Grande Valley, Texas—1971-1972.*

Study Area	No. Samples	Mean Pesticide Residues, ppm wet weight				
		Aroclor 1248	*p,p'*-DDT	*p,p'*-DDE	Dieldrin	Endrin
Falcon Dam	2	0.14±0.06 (0.10–0.18)	0.03±0.02 (0.01–0.04)	0.07±0.02 (0.05–0.08)	0.00	0.00
Anzalduas						
Peripheral	5	0.00	5.46±8.49 (0.72–20.53)	1.89±0.79 (0.86–2.86)	0.79±1.22 (0.0–2.86)	0.53±1.13 (0.0–2.55)
Central	5	0.00	0.54±0.51 (0.09–1.35)	0.99±0.79 (0.17–2.12)	0.03±0.03 (0.0–0.04)	0.04±0.07 (0.0–0.16)
Santa Ana						
Peripheral	5	0.42±0.13 (0.24–0.58)	0.69±0.53 (0.19–1.54)	4.25±2.22 (1.78–6.98)	0.08±0.04 (0.04–0.14)	0.02±0.04 (0.0–0.10)
Central	5	0.22±0.24 (0.18–0.49)	0.39±0.16 (0.22–0.64)	3.65±2.65 (1.54–8.17)	0.17±0.19 (0.06–0.50)	0.00
McManus Farm	2	0.28±0.01 (0.27–0.29)	0.50±0.06 (0.46–0.54)	2.77±0.78 (2.21–3.32)	0.05±0.03 (0.03–0.07)	0.00
Mean		0.17±0.20 (0.0–0.58)	1.52±4.12 (0.01–20.53)	2.48±2.09 (0.05–8.17)	0.23±0.59 (0.0–2.86)	0.12±0.52 (0.0–2.55)

the power of this statistical test in detecting these differences. Quantities of pesticides in tissues are generally related to food habits and history of exposure (*3*). Chachalacas which were close to cultivated fields were presumably more heavily exposed to agricultural chemicals than were birds and vegetation some distance from intensive farming; so, too, was their food supply. Although not statistically significant, residue levels in fat of birds from peripheral locations were higher than those from central locations; but overall, these birds had remarkably low pesticide residue levels.

Residue levels in chachalacas were much lower than in ring-necked pheasants (*Phasianus colchicus*) from highly agricultural areas. Pheasants feed in agricultural fields, creating a direct dietary pathway for pesticides to enter their bodies. In rice-growing areas of the Sacramento Valley, California, fat tissues of ring-necked pheasants contained an average of 123 ppm DDT and its metabolites; the maximum level was 5,448 ppm. Mean concentration of dieldrin in fat of these birds was 0.8 ppm (*4*). Even higher levels have been reported for pheasants in California. In 1962, the same investigators reported that fat from four hen pheasants in a treated agricultural area contained 1,236-2,930 ppm DDT, 306-717 ppm DDE, and 0.1-25 ppm dieldrin; considerably lower levels were found in birds from untreated areas (*3*).

Chachalaca eggshells are thicker than those of other gallinaceous birds. Sixty-three eggshells collected in southern Texas before 1900 had a mean thickness of 0.57±0.12 mm; the range was 0.49-0.74 mm. This was slightly higher than the average thickness (0.50±0.06 mm, range 0.41-0.66 mm) of 72 eggshells collected during the present study. The difference in eggshell thickness between pre-pesticide eggs and recent ones was not significant ($t=1.87$, $P>0.05$) and there was little evidence to suggest that pesticides caused this slight difference.

Acknowledgments

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LITERATURE CITED

(*1*) *Burns, J.E. 1974.* Organochlorine pesticide and polychlorinated biphenyl residues in biopsied human adipose tissue—Texas, 1969-72. Pestic. Monit. J. 7(3/4):122-126.

(*2*) *Duncan, D. B. 1955.* Multiple range and multiple F tests. Biometrics 11(1):1-42.

(*3*) *Dustman, E. H., and L. F. Stickel. 1969.* The occurrence and significance of pesticide residues in wild animals. Ann. New York Acad. Sci. 160(1):162-172.

(*4*) *Keith, J. O., and E. G. Hunt. 1966.* Levels of insecticide residues in fish and wildlife in California. Trans. N. Am. Wildl. Nat. Resour. Conf. 31:150-177.

(*5*) *Marion, W. R. 1974.* Status of the Plain Chachalaca in south Texas. Wilson Bull. 86(3):200-205.

(*6*) *Marion, W. R. 1976.* Plain Chachalaca food habits in south Texas. The Auk 93(2):376-379.

(*7*) *Ostle, B. 1963.* Statistics in Research: Basic Concepts and Techniques for Research Workers. Iowa State Univ. Press, Ames. 583 pp.

(*8*) *Reynolds, L. M. 1969.* Polychlorobiphenyls (PCB's) and their interference with pesticide residue analysis. Bull. Environ. Contam. Toxicol. 4(3):128-143.

(*9*) *Stickel, L. F., and L. J. Rhodes. 1970.* The thin eggshell problem. Pages 31-35 *in* J. W. Gillett, ed. The biological impact of pesticides in the environment. Oregon State Univ. Press, Corvallis. 210 pp.

(*10*) *U.S. Department of Health, Education, and Welfare, Food and Drug Administration. 1972.* Pesticide analytical manual. Vol. I.

Insecticide Residues on Stream Sediments in Ontario, Canada[1]

J. R. W. Miles

ABSTRACT

Insecticide residues on suspended and bottom sediments of streams of Ontario, Canada, have been studied in a tobacco-growing and a vegetable muck area. The proportion of TDE to DDT was <1 in water and >1 in bottom sediments. The ratio of TDE to DDT in bottom material increased linearly from the contamination point at stream source to the mouth of Big Creek in Norfolk County, Ontario. Bed load samples contained three to six times greater concentrations of insecticides than bottom material. Adsorption of insecticides on suspended sediment decreased in order DDT > TDE > dieldrin > diazinon, which is consistent with the water solubility of these compounds.

Introduction

Insecticide analyses of environmental water samples are usually performed on the whole unfiltered sample (5). Because the whole water, including sediment, is the environment of fish, crustaceans, and aquatic insects, analysis of the whole-water sample produces data pertinent to biological significance of insecticides. Whole-water analyses combined with water discharge data also are used to calculate transport of insecticides from a stream to the receiving body of water. However, the state of an insecticide, i.e., whether pure particles, adsorbed on sediment, or dissolved in water, can affect biological action because some organisms prefer to feed on sediments (*3*) and because insecticides adsorbed on suspended sediment are eventually deposited and become part of the bottom material (*6*). In the study reported here the author has analyzed insecticide presence in whole-water samples, suspended sediments, bed load, and bottom material of streams in Ontario, Canada.

Methods

Water samples were collected in 1100-ml narrow-neck bottles clamped to an 8-m aluminum pole. Depth integration was achieved by moving the bottle from just below the surface to within 30 cm of the bottom while the bottles were filling with water. Bottles were sealed with tin-foil-lined caps for transport to the laboratory. Contents of two bottles were combined as one sample in a tared 2-liter florence flask (Fig. 1) and the weight of flask plus samples was recorded. Walls of the two sample bottles were rinsed with the same 10-ml acetone which was transferred to the florence flask. A second acetone rinse of 7 ml was also transferred to the flask. A 35-mm magnetic stirring bar was inserted, 50 ml 1:1 hexane/benzene was added, and the flask neck was covered with aluminum foil previously rinsed with hexane. The flask was stirred 15 minutes using enough torque that the vortex pulled the extracting solvent completely into the water. The flask was removed and

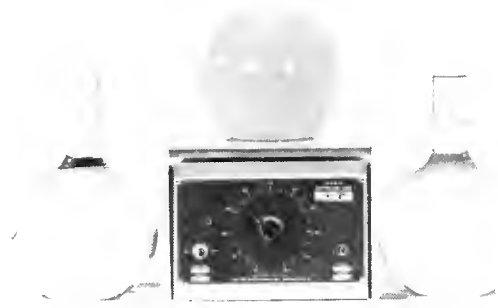

FIGURE 1. *Equipment for extracting insecticide residues from water samples*

[1] Contribution No. 648, Research Institute, Agriculture Canada, University Sub P.O., London, Ontario, Canada N6A 5B7.

left standing 15 minutes. The separated extract layer was transferred to a 250-ml separatory funnel with a Teflon stopcock by a suction tube adapter fitted into the separatory funnel neck. Three extractions were made using fresh hexane:benzene and the three extracts were combined in the separatory funnel. The lower aqueous layer was discarded. The extract was dried by adding 10 g anhydrous sodium sulfate prerinsed with benzene and hexane and poured from the neck of the separatory funnel through a filter funnel containing glass wool which had been rinsed with hexane into a 500-ml round-bottom flask for concentration on a rotary evaporator. Recoveries of insecticides from fortified distilled water were all >90 percent.

SEDIMENT SEPARATION

Water samples for sediment separation were collected at the same time and in the same manner as those for whole-water analysis. The sediment was separated by filtration through a Millipore filter apparatus using 4.25-cm-diameter Whatman GF/C fiber glass papers with nominal porosity of 0.45 μm. Residues were extracted from the filtered sediment with acetone, followed by 1:1 hexane:benzene in a conical flask. Three successive extractions were completed and the combined extracts were dried with anhydrous sodium sulfate before fractionation (9). A separate 4-liter sample of water was also taken and filtered through a tared filter paper to obtain the weight of the sediment loading.

Bottom material samples were collected using a sampler designed by the author; it consisted of a steel can, 8.5 cm in diameter and 4.5 cm deep, attached to the end of an 8-m aluminum pole. The can was permitted to settle on the bottom of the stream in inverted position. On rotation of 180° the can sampled a 6-cm-deep portion of bottom material. Five samples of mud were taken from near the bank to mid-stream, and combined into one sample. After the standing water was poured off, the mud was mixed in a pyrex glass tray. Three hundred grams of the mixed sample was placed in a 900-ml narrow-neck glass bottle. One hundred ml of acetone was added and the bottle was swirled to mix. Four hundred ml hexane was added and the bottle was stoppered and tumbled end over end for 1 hour. The supernatant liquid was poured into a 1-liter separatory funnel, the acetone was removed by several distilled water washes, and the hexane extract was dried with anhydrous Na_2SO_4. The moisture content of a 50-g sample of the mud was determined so that results could be reported on a dry-weight basis. Bed load samples were taken with a Bogardi T3 bed load sampler (Fig. 2; 2). The sampler was lowered from a bridge to the stream bottom and left in position 4 hours. The fluid sample was filtered and extracted as described above for separation of sediment from water samples. Fractionation of extracts on florisil has been described previously (9,10).

GAS CHROMATOGRAPHY

Two model 1400 and one model 1200 Varian Aerograph gas chromatographs were used. All columns were 2 m long by 2 mm ID and operated at 180°C. Two 1400 models were equipped with ^{3}H electron-capture detectors. The column of one model was packed with 5 percent XE60; the other used a liquid phase mixed before coating, 3 percent DC 200/4.5 percent QF-1. The column of the model 1200 was also packed with mixed DC 200/QF-1 but this instrument was equipped with ^{3}H electron-capture detector in series with Rb_2SO_4 alkali flame ionization detector.

Results and Discussion

BOTTOM MATERIAL

An earlier article (11) reported that although in water the ratio of TDE to DDT is $<<1$, in practically all analyses of bottom mud the ratio is >1. This indicates that the process of dechlorination of *p,p'*-DDT to *p,p'*-TDE was occurring in the bottom material. These findings are consistent with data of Hill and McCarty (7) who report that DDT is degraded more readily under anaerobic than aerobic conditions.

If the ratio of TDE to DDT is calculated from the data on bottom mud published earlier (11), there is a steady increase in the ratio from spring through summer to fall. For Muskoka River bottom mud from May through September 1971, the TDE:DDT values were 1.6, 1.9, 1.9, 2.4, and 5.4. Since DDT was banned from use in

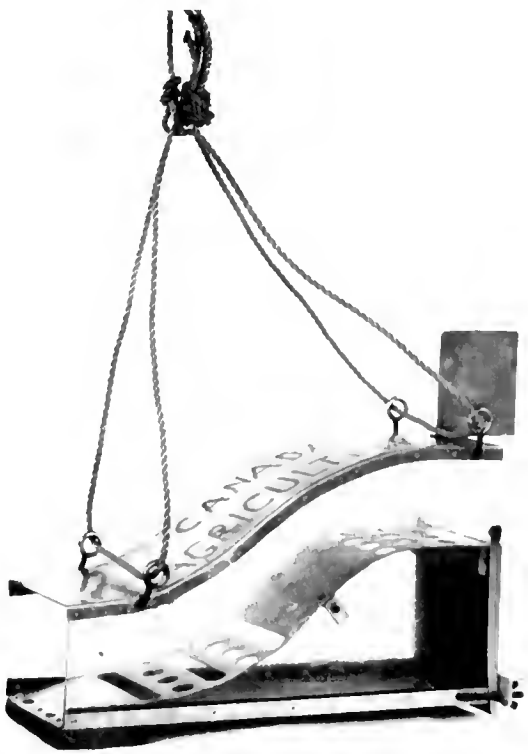

FIGURE 2. *Bogardi bed load sampler*

Ontario in 1970 the above data could mean that DDT on eroded soil incorporated in the bottom mud in the spring was gradually converted to TDE by microorganism activity from May through September.

Because it requires time for bottom material to move downstream the author sampled a stream for bottom material from source to mouth all in the same day to assess any differences in residue content and ratios. The stream selected was Big Creek in Norfolk County, Ontario, previously described (*10,11*). Big Creek drains a tobacco-growing area; DDT-contaminated soil averaging about 3.5 ppm Σ DDT (*4*) erodes into the upper reaches of the stream. Residues found at the six sampling stations from source to mouth in 1972 are shown in Table 1. Dieldrin concentrations increased gradually from source to mouth but there appears to be no regularity in actual DDT concentration in the bottom material of these six stations. However, there is a regular increase in ratio of *p,p'*-DDE to *p,p'*-DDT and an even more pronounced increase in ratios of *p,p'*-TDE to *p,p'*-DDT from stream source to mouth. Overall change in TDE:DDT from source to mouth is 20 times! The increase in ratio of TDE to DDT can be explained by the longer contact time of adsorbed DDT residues with anaerobic microorganisms as they move from the source down to the mouth, a distance of about 42 km. Since the DDE:DDT ratio also increased steadily from source to mouth one must assume that the bottom material also harbors organisms containing dehydrochlorinase. A repeat of the above experiment at four locations in 1973 revealed the same trend but the range of values was not quite so dramatic: from source to mouth TDE:DDT ratios were 0.2, 0.4, 0.5, and 0.6.

TABLE 1. *Insecticide residues on bottom material at six stations from source to mouth of Big Creek, Ontario—1972*

Sampling Stations	Residues, ppb dry weight		Residue Ratios		
	Σ DDT	Dieldrin	*p,p'*-TDE	*p,p'*-DDE	*p,p'*-DDT
1 Stream source	23.8	<0.3	0.1	0.2	1
2	58.5	0.8	0.2	0.2	1
3	6.9	<0.3	0.8	0.7	1
4	13.0	0.6	1.0	0.9	1
5	26.1	1.3	1.2	1.0	1
6 Stream mouth	34.2	1.4	2.0	1.5	1

BED LOAD

Simultaneous bed load and bottom material samples were taken at monthly intervals from June through October 1973 (Table 2). With one exception, August 14, all residues on bed load samples were much greater than those in the bottom material. In fact, average DDT in the bed load was three times that in the bottom material. Dieldrin was also three times greater and endosulfan was six times greater in the bed load. The bed load is the shifting mass of detritus and sediment which forms the interface between the water and bottom material and provides the environment of benthic organisms. The

TABLE 2. *Insecticide residues on bed load and bottom material of Big Creek, Norfolk County, Ontario—1973*

Sampling Date	Residues, ppb dry weight					
	DDT		Dieldrin		Endosulfan	
	Bed Load	Bottom Material	Bed Load	Bottom Material	Bed Load	Bottom Material
June 26	198	30	6	1.2	2	<0.1
July 10	45	26	4	1.3	<1	<0.1
Aug. 14	21	27	1	1.7	3	0.7
Sept. 25	100	35	8	1.3	3	0.2
Oct. 2	30	18	2	1.1	1	0.6
Oct. 16	62	18	2	0.7	1	0.2

NOTE: Bed Load = shifting mass of detritus and sediment collected with the Bogardi bed load sampler.
Bottom Material = more permanent bottom mud

above data would indicate that animals living in the bed load may be exposed to more insecticide than would be suggested by analysis of bottom material alone. The average ratio of TDE to DDT in bottom material was 1.24; in the bed load the ratio was 0.38. This again indicates that the DDT residues in the bottom material have had a longer period under anaerobic conditions, producing more TDE.

SUSPENDED SEDIMENT

Residues on suspended sediment in Big Creek in 1973 ranged from 8 to 100 percent of the whole-water analyses, as shown in Table 3. Residues in sediment expressed as percent of the whole-water analysis are generally proportional to the sediment load. Although TDE and dieldrin concentrations in water samples were significant, up to 2.0 ng/liter and 2.7 ng/liter, respectively, only traces of TDE and dieldrin were found on the sediment. This is consistent with the solubility of the two chemicals, i.e., 3 times and 13 times that of *p,p'*-DDT (*1*). In some instances, namely, April 10, May 1, 8, 22, and June 12, the percent of Σ DDT on sediment was much less than that of *p,p'*-DDT or *p,p'*-DDE (Table 3). This was because TDE, present in the whole-water sample, contributed to Σ DDT but no TDE was detected on the sediment. The average value for Σ DDT expressed as ppm dry weight of sediment is 0.11 ppm. This value is 4.2 times the average ppm in the bottom material samples from Big Creek during the same sampling period. Since DDT residues in the bottom material are only one-fourth those on the sediment one must conclude that considerable dilution with uncontaminated bottom material occurs upon deposit of sediment and/or the DDT degrades more quickly in the bottom material.

Comparable data on residues in sediment as percent of whole-water analyses for three streams in the Holland Marsh, which contains organic soil used for vegetable production, are shown in Table 4. Concentrations in water and mud of this region are much greater than those of Big Creek, as demonstrated by the greater quantities of insecticides on the sediment. These are

TABLE 3. *Insecticide residues on suspended sediment of Big Creek, Ontario—1973*

Sampling Date	Sediment Load, mg/liter	Residues[1]							
		Σ DDT		*p,p'*-DDT		*p,p'*-DDE		Dieldrin	
		%	ppm	%	ppm	%	ppm	%	ppm
March 27	0.0600	68	0.07	68	0.05	67	0.02	16	<0.01
April 3	0.0825	81	0.19	72	0.11	97	0.04	29	0.01
10	0.0543	63	0.08	89	0.06	97	0.02	ND	ND
17	0.0430	90	0.13	100	0.07	76	0.13	ND	ND
24	0.0364	45	0.10	40	0.06	88	0.04	ND	ND
May 1	0.0440	70	0.10	85	0.05	83	0.05	ND	ND
8	0.0222	51	0.13	85	0.08	48	0.05	ND	ND
15	0.0222	33	0.07	36	0.04	60	0.03	ND	ND
22	0.0082	29	0.15	33	0.09	63	0.06	ND	ND
June 12	0.0330	64	0.09	90	0.05	100	0.04	ND	ND
July 17	0.0082	8	0.06	19	0.06	ND	ND	17	0.04
Sept 12	0.0182	53	0.17	32	0.05	ND	ND	ND	ND
Oct 9	0.0116	42	0.10	69	0.10	ND	ND	ND	ND

NOTE: ND = none detected
TDE was present in whole-water analyses from trace to 2 ng/liter but only traces were detected on suspended sediments
Dieldrin after April 3 was present in whole water from 0.7 to 2.7 ng/liter but only traces were detected on suspended sediment, except July 17
[1]Residues expressed as percent of whole-water analysis and as ppm on dry weight of sediment.

TABLE 4. *Insecticide residues on suspended sediment of streams in Holland Marsh, Ontario—1973*

Sampling Date	Sediment Load, mg/liter	Residues[1]											
		Σ DDT		*p,p'*-DDT		*o,p'*-DDT		*p,p'*-DDE		*p,p'*-TDE		Dieldrin	
		%	ppm	%	ppm	%	ppm	%	ppm	%	ppm	%	ppm
Stream A													
Mar 22	0.0044	38	13.4	36	8.6	42	2.3	47	1.8	39	0.7	8	0.5
29	0.0076	75	12.9	79	9.8	72	1.8	73	0.9	40	0.3	13	0.5
Apr 5	0.0083	89	14.0	90	10.3	96	2.1	75	0.9	77	0.7	42	0.5
12	0.0026	35	11.5	38	8.7	30	1.2	41	0.9	19	0.8	5	0.5
Stream B													
Mar 29	0.0028	44	17.9	43	12.4	45	2.4	43	1.3	57	1.9	8	0.6
Apr 5	0.0068	47	8.9	48	6.0	49	1.4	46	0.8	42	0.7	11	0.4
12	0.0040	32	4.7	35	3.2	30	0.6	37	0.5	18	0.4	3	0.2
Stream C													
Mar 22	0.0148	88	1.5	86	1.0	96	0.2	90	0.1	91	0.3	18	0.1
29	0.0247	85	0.9	96	0.6	93	0.1	78	0.1	57	0.1	10	<0.1
Apr 5	0.0203	79	1.3	86	0.9	95	0.2	67	0.1	35	0.1	9	<0.1
12	0.0142	65	1.2	70	0.8	90	0.1	60	0.1	46	0.2	13	0.1
AVERAGE		62		64		67		60		47		13	

[1]Residues expressed as percent of whole-water analysis and as ppm on dry weight of sediment.

much greater than the residues found in the bottom material which contained *p,p'*-DDT, *p,p'*-DDE, and *p,p'*-TDE in parts per billion range. This agrees with the above discussion of data from the Big Creek study. The percentages of insecticides on the sediment are again roughly proportional to the sediment load. It is significant that *p,p'*-DDT, *o,p'*-DDT, and *p,p'*-DDE were all ~60 percent adsorbed on the sediment, but the more water soluble *p,p'*-TDE averaged 47 percent adsorption and dieldrin averaged 13 percent, ranging from 9 to 42 percent. These ranges may appear wide but this was not a controlled laboratory sediment experiment; composition of sediments could vary between sampling dates, greatly affecting adsorption. Since both sediments and insecticides determined in stream samples are allochthonous, great variability can be expected.

Diazinon was present in all whole-water samples (≤80 ng/liter) but was not detected on any suspended sediment samples. It is soluble to 40 ppm (*12*) in water and evidently remains in solution rather than adsorbing onto the sediments. Four samples reported in Table 4, all from stream A, contained parathion in the whole-water samples ranging from 13 to 19 ng/liter, but no parathion was detected in the sediments. Parathion has a water solubility of 24 ppm (*12*) so presumably it would also be in solution and not adsorbed to the sediment. Ethion, which has a solubility of 0.6 ppm in water as determined by this laboratory, was present in three whole-water samples in quantities as high as 33 ng/liter. No ethion was detected in the filtered sediment.

This author has observed that some laboratories studying environmental water samples have analyzed only the filtered water. Since plant and animal life are exposed to the whole water including sediment (*3,8*), such an approach is unrealistic. The study of stream sediments reported herein has been performed in considerable

detail, including separation of sediment-borne insecticide residues from the whole-water samples and separate analyses of suspended sediment, bed load, and bottom material. The study demonstrates that concentrations of insecticide residues on stream sediments vary with the type of sediment and its location in the stream. Even residues of the supposedly recalcitrant DDT are in a state of change, with the ratios of metabolites DDE and TDE varying in proportion to the parent DDT on the different sediments and on the same sediment at different locations upstream or downstream.

Acknowledgments

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LITERATURE CITED

(1) *Biggar, J. W., and R. L. Riggs. 1974.* Apparent solubility of organochlorine insecticides in water at various temperatures. Hilgardia 42(10):383-391.

(2) *Bogardi, J. 1942.* Vizfolyasok hordalekmerese [Sediment measurements on watercourses]. Hidrologiai Kozlony 7-12. Budapest.

(3) *Coker, R. E. 1954.* Streams, Lakes and Ponds. Harper and Row, New York, p. 139.

(4) *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.

(5) *Hartung, R. 1975.* Accumulation of chemicals in the hydrosphere. Page 189 *in* R. Haque and V. H. Freed, ed. Environmental Dynamics of Pesticides. Plenum Press, N.Y.

(6) *Hassett, J. P., and G. F. Lee. 1975.* Pesticides in the aqueous environment. Page 180 *in* R. Haque and V. H. Freed, ed. Environmental Dynamics of Pesticides. Plenum Press, N.Y.

(7) *Hill, D. W., and P. L. McCarty. 1967.* Anaerobic degradation of selected chlorinated hydrocarbon pesticides. J. Water Pollut. Control Fed. 39(8):1259-1277.

(8) *Jones, J. R. E. 1964.* Fish and River Pollution. Butterworths, London, p. 5.

(9) *Miles, J. R. W. 1972.* Conversion of DDT and its metabolites to dichlorobenzophenones for analysis in the presence of polychlorinated biphenyls. J. Ass. Offic. Anal. Chem. 55(5):1039-1041.

(10) *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.

(11) *Miles, J. R. W., and C. R. Harris. 1973.* Organochlorine insecticide residues in streams draining agricultural, urban-agricultural, and resort areas in Ontario, Canada—1971. Pestic. Monit. J. 6(4):363-368.

(12) *Spencer, E. Y. 1973.* Guide to the Chemicals Used in Crop Protection. Pub. No. 1093 6th ed. Research Branch, Agriculture Canada, Ottawa. 542 pp.

Chronology of Organochlorine Compounds in Lake Michigan Fish, 1929-66

William J. Neidermyer and Joseph J. Hickey [1]

ABSTRACT

Museum specimens of six species of Lake Michigan fish collected from 1929 through 1966 were analyzed for dieldrin, polychlorinated biphenyls (PCB's), and DDT analogs. Dieldrin first appeared in the 1955 specimens. Residues were low and exhibited no trend with time. PCB's and DDT analogs appeared in 1949 in the same samples. Both PCB's and ΣDDT increased progressively through 1965. PCB residues showed no decreasing trend. ΣDDT peaked in 1965. PCB's and DDE were always detected together. The ratio of PCB to DDT showed no trend from 1949 to 1966.

Introduction

Insecticide residues in Great Lakes fish have been monitored since 1965 by the Great Lakes Fishery Laboratory of the Fish and Wildlife Service, U.S. Department of Interior (*8*). Lake Michigan fish contain the highest concentrations of organochlorine insecticides of all Great Lakes fish. The high residue levels are in part the result of the widespread usage of these compounds in the watershed and the disproportionately brief flushing period and low biomass density of Lake Michigan, according to Veith (*9*). Veith has established baseline concentrations of DDT and polychlorinated biphenyls (PCB's) in Lake Michigan fish in 1971. The present report presents an historical profile of chlorinated hydrocarbon residues in Lake Michigan fish from 1929 to 1966. Historical residue levels of DDT analogs and PCB's have been reported for a marine fish species (*6*), marine sediments (*4*) , and membranes of peregrine falcon (*Falco peregrinus*) eggshells (*7*) in other ecosystems.

Sampling Procedures

Specimens were obtained from the Museums of Zoology at the University of Michigan and at the University of Wisconsin in Madison. At the time of acquisition the specimens were preserved in glass jars filled with ethyl alcohol. Some specimens had been preserved originally in formalin before being transferred to ethyl alcohol by the museum staff. Authors obtained whole fish when available. From large fish a sample of the epaxial muscle was analyzed. All samples were placed in glass jars with aluminum-foil-lined caps and were frozen until analysis. The following common and scientific names of the six species of fish examined are from the list published by the American Fisheries Society (*2*): emerald shiner (*Notropis atherinoides*), fourhorn sculpin (*Myoxocephalus quadricornis*), rainbow smelt (*Osmerus mordax*), kiyi (*Coregonus kiyi*), bloater (*Coregonus hoyi*), and alewife (*Alosa pseudoharengus*).

Analytical Methods

The WARF Institute, Inc., in Madison, Wis., used gas chromatography to analyze all samples for dieldrin, PCB's, DDT, TDE, and DDT. Large samples were homogenized with the aid of a Hobart food chopper. Small samples were snipped finely with tissue scissors. A portion of the sample was weighed into a 150-ml beaker. The sample was ground with about 30 g anhydrous sodium sulfate and dried 48-72 hours. The sample was placed in a 33-by-94-mm Whatman extraction thimble and extracted for 8 hours on a Soxhlet extractor with 70 ml ethyl ether and 170 ml petroleum ether. The solvent was reduced to near dryness on the steam bath and placed in a 40°C oven for 4 hours. The beaker was removed from the oven, contents were desiccated, weighed, and the amount of lipid in the sample was calculated.

An aliquot of the sample was cleaned on a standardized florisil column. Typical elutions were 150 ml 5 percent ethyl ether in petroleum ether, followed by 240 ml 15 percent ethyl ether in petroleum ether. After florisil cleanup the resulting solutions were concentrated on a 5-10-ml steam bath and made to 25 ml with hexane.

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The first elutions from the florisil were injected on a gas chromatograph to determine the approximate amount of PCB interference. An aliquot of this solution ≤5 μg DDE and 20 μg PCB was run through a silicic acid / celite column according to the Armour-Burke method for separating PCB's from DDT and its analogs (*1*). Each resulting solution was chromatographed and the amounts of the various pesticides were determined. A Barber-Colman model 5400 gas chromatograph with a 4-ft-by-3-mm glass column packed with 5 percent DC-200 on 80/100-mesh Gas-Chrom Q was used for the gas chromatography. The carrier gas, nitrogen, was maintained at 80 ml/min; the injector, column, and detector temperatures were 215°, 200°, and 245°C, respectively.

Recovery rates of PCB (Aroclor 1254), dieldrin, DDE, TDE, and DDT were 60-80, 65-95, 86-96, 80-90, and 75-95 percent, respectively. The detection limit for dieldrin and DDT analogs was 0.01 ppm; for PCB's, 0.1 ppm. No confirmatory tests were performed.

Results and Discussion

Because the years of storage in formalin and ethyl alcohol had dehydrated fish tissues, residues are expressed on a lipid basis (Table 1). Gibbs et al. reported that formalin, ethyl alcohol, and isopropyl alcohol affected the concentrations of heavy metals in specimens of myctophid fish (*3*). MacGregor (*6*) reported that formalin had no effect on the residues of DDT and its metabolites and PCB's in specimens of myctophid fish preserved from 1949 to 1972. Authors do not know whether formalin and ethyl alcohol affected the specimens used in this study. Reinert (*8*) has shown that lipid content, size of fish, and season of capture may affect considerably the concentration of chlorinated hydrocarbons observed in tissue. Although such effects were not controlled in the present analyses, authors believe that the data represent the magnitude of the residue levels present at time of analysis.

Dieldrin first appeared in two samples from 1955. No trends in residue levels of dieldrin during subsequent years could be determined. Levels were usually low, ranging from 0.20 to 2.39 ppm (Table 1).

Commercial manufacture of PCB's began in the United States in 1929 (*5*). No PCB's were detected in museum samples until 1949, when the kiyi had 5.17 ppm and the alewife had 4.85 ppm (Table 1). Hom et al. found that the deposit of PCB's in marine sediments from the Santa Barbara basin began about 1945 (*4*). They associated this finding with the rapid increase in PCB use during World War II as electrical-insulating fluids and paint additives, and in a variety of miscellaneous applications which release these compounds into the environment. Presumably Lake Michigan began receiving PCB deposits about the same time, although a critical gap in Lake Michigan data from 1943 to 1948 prevents an absolute statement to this effect.

Levels of PCB's in Lake Michigan fish show a progressive increase from 1949 through 1966. Hom et al. (*4*) found a similar increase through 1967 in marine sediments. MacGregor (*6*) found no trend with time in the concentrations of PCB's in a myctophid fish off southern California between 1949 and 1966. Veith (*9*) established baseline concentrations for 1971 in Lake Michigan fish of 70.80 ppm and 30.00 ppm PCB's (lipid basis) in alewife and bloater, respectively. These concentrations are

TABLE 1. *Concentrations of organochlorines in Lake Michigan fish, 1929-66*

Species[1]	Year	Percent Lipid[2]	Residues, ppm lipid weight					PCB: Σ DDT Ratio
			Dieldrin	PCB	DDE	TDE	DDT	
Emerald shiner	1938	0.26	ND	ND	ND	ND	ND	
Fourhorn sculpin	1936	1.69	ND	ND	ND	ND	ND	
	1949	0.11	ND	ND	ND	ND	ND	
	1951	3.66	ND	3.40	8.54	5.19	5.66	0.18
	1955	7.02	0.20	4.39	9.31	13.70	5.48	0.15
	1965	1.20	ND	24.88	37.32	43.54	6.22	0.29
	1966	2.17	ND	17.43	38.02	0.83	34.25	0.24
Rainbow smelt	1931	0.35	ND	ND	ND	ND	ND	
	1942	0.35	ND	ND	ND	ND	ND	
	1942	0.54	ND	ND	ND	ND	ND	
	1960	0.34	ND	59.31	11.86	ND	ND	5.00
	1966	10.03	0.55	12.34	30.91	14.09	11.91	0.22
Kiyi	1949	4.88	ND	5.17	7.31	3.24	3.03	0.38
Bloater	1929	0.18	ND	ND	ND	ND	ND	
	1961	3.87	1.09	7.85	4.96	2.31	2.18	0.83
	1965	12.03	0.93	43.96	34.67	29.96	2.89	0.65
	1966	14.24	1.34	39.36	38.03	22.44	4.61	0.60
Alewife	1949	23.95	ND	4.85	2.18	1.68	ND	1.26
	1951	24.65	ND	1.02	4.14	3.71	ND	0.13
	1952	27.76	ND	3.50	6.98	1.64	2.62	0.31
	1953	31.27	ND	5.78	6.57	2.54	0.53	0.60
	1954	20.39	ND	1.85	6.34	4.07	ND	0.18
	1955	10.57	2.39	5.37	13.98	12.12	3.72	0.18
	1965	0.13	ND	79.69	25.81	13.07	19.36	1.37

NOTE: ND = not detected.

[1]Scientific names of species sampled: emerald shiner, *Notropis otherinoides*; fourhorn sculpin, *Myoxocephalus quadricornis*; rainbow smelt, *Osmerus mordax*; kiyi, *Coregonus kiyi*; bloater, *Coregonus hoyi*; alewife, *Alosa pseudoharengus*.

[2]Results expressed on liquid basis because prolonged storage of museum specimens in formalin and ethyl alcohol dehydrated fish tissues

slightly lower than the values found in the present study: 79.69 ppm in alewife in 1965, and 39.36 ppm in bloater in 1966 (Table 1). Reinert reported increasing levels of PCB's in Lake Michigan coho salmon (*Oncorhynchus kisutch*) and lake trout (*Salvelinus namaycush*) from 1972 through 1974, and stable levels in bloaters during the same time period (R. E. Reinert, Great Lakes Fishery Laboratory, U.S. Department of Interior, 1975: personal communication). Thus it appears that the concentrations of PCB's in Lake Michigan fish remain high despite the restriction of sales to closed-system users in 1971 by Monsanto Company, St. Louis, Mo., the sole producer of PCB's in the United States.

Among museum specimens, PCB's were never detected in the absence of DDE. The ratio of PCB's to ΣDDT should be important in reflecting the trend of concentrations of these compounds. Data from the present study show no trend from 1949 through 1966. Values range from 0.13 to 5.00 (Table 1).

DDT and its analogs were first detected in 1949. They appeared in the same specimens in which PCB's were first detected: kiyi, 13.58 ppm; alewife, 3.86 ppm (Table 1), and progressively increased to 1965. Hom et al. (*4*) reported that DDE in marine sediments deposited off the California coast progressively increased from about 1952 through 1967; MacGregor (*6*) reported increasing DDT metabolites in California myctophid fish from 1949 through 1970; and Peakall (*7*) reported DDE in the membranes of peregrine falcon eggshells at least as early as 1948. These four independent studies agree in their determination of the time that DDT and its metabolites began accumulating in the environment. That date corresponds closely with the increase in the manufacture and use of DDT during and immediately after World War II. However, the critical years of 1946 and 1947 are not represented in the samples of these four studies. Establishing the presence of DDE in these two years is important to the phenomenon of eggshell thinning attributed to the presence of DDE (*5*).

Data for alewives and bloaters (Figure 1) indicate that the concentration of ΣDDT in Lake Michigan fish peaked in 1965. These data and results from the Great Lakes Fishery Laboratory suggest that residues have been decreasing since the late 1960's. R. E. Reinert reports a continued decrease of ΣDDT through 1974 in Lake Michigan bloaters, coho salmon, and lake trout (personal communication: see previous allusion).

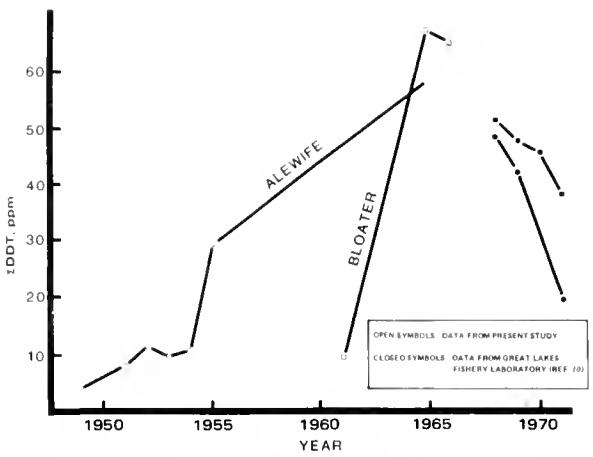

FIGURE 1. *Trend of ΣDDT concentrations in Lake Michigan alewives and bloaters, 1949-71.*

Acknowledgments

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LITERATURE CITED

(*1*) *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.

(*2*) *Bailey, R. M., J. E. Fitch, E. S. Herald, E. A. Lachner, C. C. Lindsey, C. R. Robins, and W. B. Scott. 1970.* A list of common and scientific names of fishes from the United States and Canada. 3rd ed. Amer. Fish. Soc. Spec. Publ. 6. Ann Arbor, Mich. 150 pp.

(*3*) *Gibbs, R. H. Jr., E. Jarosewich, and H. L. Windom. 1974.* Heavy metal concentrations in museum fish specimens: effects of preservatives and time. (Science 184 (4135):475-477.

(*4*) *Hom, W., R. W. Risebrough, A. Soutar, and D. R. Young. 1974.* Deposition of DDE and polychlorinated biphenyls in dated sediments of the Santa Barbara basin. Science 184(4142):1197-1199.

(*5*) *Hubbard, H. L. 1964.* Chlorinated biphenyl and related compounds. *In* R. E. Kirk and D. F. Othern, eds. Encyclopedia of Chemical Technology 5:289. Second rev. ed.

(*6*) *MacGregor, J. S. 1974.* Changes in the amount and proportions of DDT and its metabolites, DDE and DDD, in the marine environment off southern California, 1949-72. Fishery Bull. 72(2):275-293.

(*7*) *Peakall, D. B. 1974.* DDE: its presence in peregrine eggs in 1948. Science 183(4125):673-674.

(*8*) *Reinert, R. E. 1970.* Pesticide concentrations in Great Lakes fish. Pestic. Monit. J. 3(4):233-240.

(9) *Veith, G. P. 1975.* Baseline concentrations of polychlorinated biphenyls and DDT in Lake Michigan fish, 1971. Pestic. Monit. J. 9(1):21-29.

(10) *Tait, H. D. 1972.* Progress in Sport Fishery Research 1971. Great Lakes Fishery Laboratory, U.S. Department of Interior, pp. 86-120.

Preliminary Study of the Occurrence and Distribution of DDT Residues in the Jordan Watershed, 1971[1]

Jacob D. Paz[2]

ABSTRACT

Data obtained from the Jordan watershed in 1971 revealed the presence of DDT and its metabolites at various levels along the food chain. Detectable levels of ΣDDT in water of the Jordan River and two fish ponds ranged from 0.019 to 0.500 ppb, which is 1/10 to 1/500 the maximum level permitted in water by the U.S. Government. Mean residue in phytoplankton was 0.906 μg/g; in zooplankton the mean was 6.49 μg/g. ΣDDT residue in fish of the Jordan watershed averaged 0.37 mg/kg in carp, 2.59 mg/kg in benith, and 3.34 mg/kg in sardines.

Introduction

This study investigated the presence of DDT residues in the Jordan watershed. No previous studies have been conducted on DDT and its residues in that body of water.

The area of the Jordan watershed is 2,730 km². Its major components are the Jordan River and its tributaries: the Dan, the Snir, and the Hermon Rivers. The water level is sustained by spring and effluent discharges as well as by runoff.

Most of the 100,000 inhabitants of the watershed live in villages and towns, where they are employed in agriculture and industry.

The watershed discharges $9 \cdot 10^8 m^3$ of water annually into the Sea of Galilee (Lake Kinneret). This includes approximately $1.4 \cdot 10^7$ m³ of domestic sewerage effluent, $5.4 \cdot 10^7 m^3$ of fish pond effluent, and $1.4 \cdot 10^7 m^3$ drainage from agricultural fields (7).

Most of the effluents flow directly into the Sea of Galilee. The Hula Valley in northern Israel, which was once a swamp, is also drained by the Jordan River. This valley is intensely cultivated and has received extensive applications of DDT and other pesticides. Runoff and wind are mechanisms by which various pesticide residues likely find their way to the Jordan River.

Sampling

Samples were collected at the three sites labeled in Figure 1: two fish ponds in Dafna, northern Israel, near the source of the Dan River; the Huri bridge at the southern end of the Hula Valley; and a spot 500 feet from the tip of the Jordan River before it enters the Sea of Galilee.

SITE 1

Surface water samples were collected at the edge of each pond and 30 feet within the ponds. Subsamples were placed in 1-liter polyethylene bottles.

Phytoplankton was collected with No. 63 mesh nets and refrigerated in 1-liter bottles. Carp (*Cyprinus carpio*) were caught in nets within 25 feet of the ponds' edges.

SITES 2 AND 3

Water samples were collected at the edge of the river and midriver. Presumably the current provided good mixing. One liter of water consisting of three subsamples was placed in a bottle.

Phytoplankton was collected midriver and at the edge of the river with No. 63 mesh nets, and refrigerated in bottles.

Zooplankton was caught midriver and at the bank with No. 230 mesh nets. Samples were refrigerated in 1-liter bottles.

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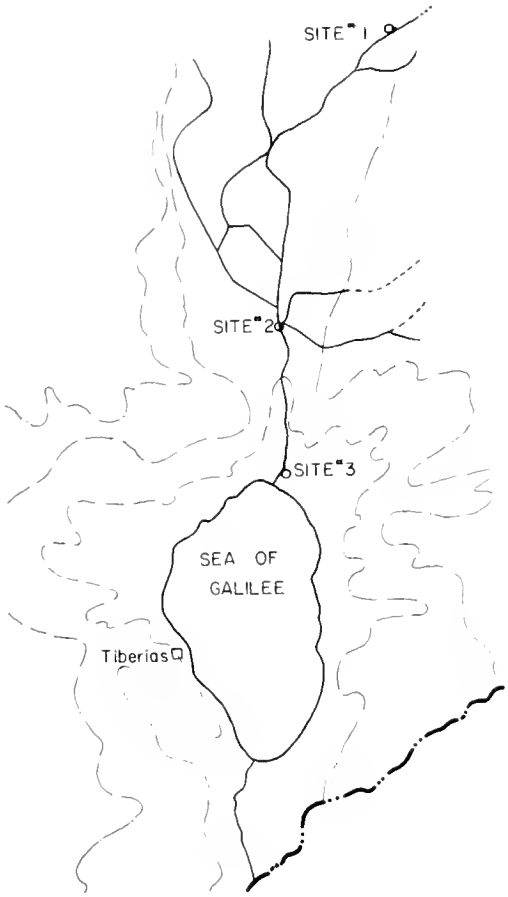

FIGURE 1. *Sites in Jordan watershed sampled for DDT residue, 1971*

Benith (*Barbus longiceps*) and sardines (*Acanthobrama terrae-sanctae*) which inhabit the Jordan River were caught by the net and refrigerated at 4°C.

Analytical Procedures

EXTRACTION

Water—One liter of water was filtered through Whatman No. 4 filter paper. Samples were extracted with hexane as described in *Standard Methods for Examination of Water and Wastewater* (*8*).

Phytoplankton—The sample was filtered through fiber glass cloth and ground mechanically. Extraction was carried out with acetonitrile and the sample was re-extracted with 10 ml hexane. The concentration of phytoplankton was determined on a dry-weight basis (*4*).

Zooplankton—The sample was filtered through Whatman No. 4 filter paper, dried under silica gel, and weighed. Zooplankton was ground mechanically. Extraction was carried out with 10 ml hexane. The sample was filtered and stored for further cleanup.

Fish—The extraction procedure followed the Extraction of Lean Tissue with Hexane recommended in the *Guide to the Analysis of Pesticide Residues* (*9*).

Ten to twenty g tissue from the midbellies of fish was placed in a homogenizer with 10 g sand-washed acid and anhydrous Na_2SO_4. This was ground to a fine powder. The sample was extracted with 50 ml hexane in a 250-ml beaker on a steam bath of 50°C and subsequently vacuum-filtered. The sample was re-extracted three times with 20 ml hexane and transferred to 100 ml in a volumetric flask. The volume was adjusted to 100 ml with hexane to compensate for loss from evaporation. The volumetric flask with its contents was placed at 4°C for 1 hour to precipitate the bulk of the fat. For further cleanup 25 ml of extract was taken (*2*).

CLEANUP

Liquid partition was followed as described by de Faubert Maunder et al (*2*).

To remove traces of fatty acids which could interfere with gas chromatography, an activated alumina column was used (*1*). Alumina was heated for 1 hour at 450°C and cooled in a desiccator. Ten percent water was added. Ten g activated alumina anhydrous hexane was transferred to a chromatographic column in the form of a slurry, which was allowed to settle. A 5-cm layer of anhydrous sodium sulfate was added. The hexane extract was poured completely through and washed three times with 90 ml hexane. The eluate was concentrated to the desired volume by evaporation in a water bath (*6*).

QUANTITATIVE ANALYSIS

A model 1200 Varian Aerograph gas chromatograph (GC) with an electron-capture detector and an all-glass column was used for pesticide quantification. Operating conditions were:

Column	8 feet long, 1 mm by 3 mm
Column Packing	3 percent QF-1 as a liquid support on solid support Varaport No. 39
Carrier Gas	N_2
Initial Pressure	60 psi
Gas Flow	30 ml/min

Column Temperature	180°C
Detector Temperature	225°C

Residues were reported as ΣDDT (DDT+DDE+TDE). Concentration of DDT was determined by a series of standards injected into the GC. Means of the peaks were plotted against the concentration of DDT. No attempts were made to isolate and identify another peak that appeared on the GC.

Retention times for the various pesticides were, in minutes: DDE, 4.2; *p,p'*-DDT, 4.4; TDE, 5.2; *o,p'*-DDT, 5.5.

Results

WATER

Table 1 shows pesticide concentrations of DDT residues in water of Dafna fish ponds and the Jordan River at various locations. Quantities ranged from $^1/_{10}$ to $^1/_{500}$ the level permitted by the U.S. Government in a water supply (*10*).

PHYTOPLANKTON

Concentrations of ΣDDT residue in phytoplankton varied from 0.1 to 3.7 μg/g dry weight (Table 2). ΣDDT residues in the Daphna fish ponds were much lower than in the Jordan River, perhaps because DDT runoff from agricultural uses finds its way to the river.

TABLE 1. *DDT concentrations in water of Jordan River and Daphna fishponds, Israel—1971*

	RESIDUES, PPB		
SAMPLE	DDE	DDT	ΣDDT
POND 10			
1			ND
2	0.032		0.032
3			ND
POND 11			
4	0.038		0.038
5	0.02		0.02
6	0.073		0.073
7	0.02		0.02
Mean			0.026
JORDAN RIVER			
8	0.019		0.019
9	0.500		0.500
10		0.024	0.024
11		0.02	0.02
12			ND
13			ND
Mean			0.08
14	0.032	0.04	0.076
15	0.09		0.090
16	0.02		0.020
17			ND
18			ND
19			ND
20	0.04		0.040
Mean			0.032

NOTE: See map, Figure 1, for sampling sites.
ND = not detected (<0.2 ppb).
No significant differences observed among Daphna fish ponds and locations along Jordan River from which samples were taken.

TABLE 2. *DDT concentrations in pyhtoplankton of Jordan watershed, Israel—1971*

	RESIDUES, μG/G DRY WEIGHT		
SAMPLE	DDE	*p,p'*-DDT	ΣDDT
POND 10			
20			ND
21			ND
22			ND
POND 11			
23	0.3		0.3
24	0.25		0.25
25	0.15		0.15
JORDAN RIVER			
26	0.19	0.23	0.42
27	0.3	0.16	0.46
28	0.75	0.27	1.02
29	0.75	1.25	2.00
30	3.00	0.79	3.79
31	1.10	1.20	2.30
32	0.40	0.80	1.20
33	0.70	0.90	1.60
34	0.53		0.53
35	0.09	0.4	0.49
Mean [1]			0.906

NOTE: See map, Figure 1, for sampling sites.
ND = not detected (<0.2 ppb)
[1] SD of mean = 0.906±1.05

ZOOPLANKTON

In zooplankton samples from the Jordan River ΣDDT concentrations varied from 3.4 to 17.0 μg/g in the forms of DDE and *p,p'*-DDT (Table 3). High concentration of ΣDDT may be due to difference in metabolism of DDT and absorption directly from water, and from zooplankton's feeding on phytoplankton.

FISH

As indicated in Table 4, carp from fish pond 10 which had been spawned April 1971 weighed 30-50 g. ΣDDT residue ranged from 0.18 to 0.82 mg/kg. Carp from pond

TABLE 3. *DDT concentrations in zooplankton of Jordan watershed, Israel—1971*

	RESIDUES, μG/G DRY WEIGHT			
SAMPLE	DDE	*p,p'*-DDT	TDE	ΣDDT
50	4.8	0.41		5.21
51	2.0	1.4		3.4
52	16.0	1.0		17.0
53	1.7	1.7		3.4
54	4.0	3.2		7.2
55				ND
56	7.2			7.2
57				ND
58	12.5			12.5
59		3.7	1.2	4.9
60	3.2	5.6		8.8
61	2.0	5.0		7.0
Mean [1]				6.49

NOTE: See map, Figure 1, for sampling site
ND = not detected (<0.1 μg g).
[1] SD of mean = 6.49±4.64

TABLE 4. *DDT concentrations in carp from Israeli ponds, 1971*

Sample	Weight, g	Residues, mg/kg wet weight				
		DDT	*p,p'*-DDT	*o,p'*-DDT	TDE	Σ DDT
Pond 11						
100	860					ND
101	1,010	0.14			0.7	0.34
102	300					ND
103	300					ND
104	400	0.25				0.25
105	950					ND
106	700	3.9			0.46	4.36
Pond 10						
107	51					0.18
108	52				0.47	0.47
109	40	0.05			0.44	0.49
110	45					ND
111	32					ND
112	30					ND
113	31	0.1	0.2	0.1		0.4
114	45					lost
115	51	0.1				0.2
116	50	0.16	0.66		0.1	0.82
117	51	0.18				0.18
Mean[1]						0.37

NOTE: See map, Figure 1, for sampling sites.
ND = not detected (<0.01 mg/kg).
[1] SD of mean = 0.37±0.21.

11 had been spawned April 1970 and weighed 300-1,000 g. ΣDDT residue ranged from 0.25 to 4.36 mg/kg.

Benith from the Jordan River (Table 5) weighed between 150 and 1,035 g. ΣDDT residue ranged from 0.1 to 8.78 mg/kg. Sardines from the river (Table 6) ranged from 12 to 108 g. ΣDDT residue ranged from 0.1 to 16.6 mg/kg.

The high DDT residues in benith and sardines might be attributed to the fact that both fish are at the top of the food chain; ΣDDT increases along the chain. DDT concentration increased with age and weight of the fish

TABLE 5. *DDT concentrations in benith of Jordan River, Israel—1971*

Sample	Weight, g	Residues, mg/kg wet weight				
		DDT	*p,p'*-DDT	*o,p'*-DDT	TDE	ΣDDT
119						
120	150	0.1				0.1
121	260	0.5	0.9		1.3	2.6
122	190					ND
123	190	0.7				ND
124	160	0.9				ND
125	270	3.0	0.31			1.81
126	403	1.17	0.9			1.8
127	1,035	0.25	2.57			8.78
128	470	8.8	1.76			4.24
129	254		2.0		0.6	2.95
130	163	1.42	1.0		0.6	2.4
131	430	0.60				ND
132	380	1.0	3.53			4.95
136	396	0.3	0.32		0.10	1.42
138	163					1.70
139	150		0.7			1.50
144	210		1.81			1.81
Mean[1]						2.59

NOTE: ND = not detected (<0.01 mg/kg).
[1] SD of mean = 2.59±2.56.

TABLE 6. *DDT concentrations in sardines of Jordan River, Israel—1971*

Sample	Weight, g	Residues, mg/kg wet weight				
		DDE	*p,p'*-DDT	*o,p'*-DDT	TDE	ΣDDT
145	12		0.1			0.1
146	85		2.77	3.0	3.05	8.82
147	15			1.18	0.9	2.09
148	15					ND
149	49	4.8	2.8	7.0	2.0	16.6
150	40	0.1	1.6			1.7
154	14	0.3	0.1	0.3	0.4	1.1
156	79	1.2	0.9	0.9		3.0
160	108	1.33	1.61	0.11	0.1	3.16
161	97	0.62	2.81	3.12		6.55
162	76	2.55	1.77	0.2	0.1	4.62
163	84	3.6	1.1	0.3	1.52	6.26
164	42	0.1	0.96	0.1	0.4	1.56
Mean[1]						3.34

NOTE: ND = not detected (<0.01 mg/kg)
[1] SD of mean = 3.34±2.54

(Figure 2). Based on scale studies, highest concentration ranges occurred in fish 3-5 years old.

Discussion

Primary evidence demonstrates that DDT residue in the lentic environment of the Jordan watershed has been absorbed into the food chain and has increased from one trophic level to the next. Thus a mechanism based upon absorption and solubility difference regulates concentration levels in various components of the lentic environment. The partition coefficient for DDT between water and fish was $4.6 \cdot 10^4$. The partition coefficient is as follows: the ratio uptake of DDT occurs from one trophic level to the next. Partition coefficients can be shown in the following ratios (concentrations are expressed as the mean values):

$$\frac{\text{DDT concentration in phytoplankton}}{\text{DDT concentration in water}} = 1.4 \cdot 10$$

$$\frac{\text{zooplankton}}{\text{phytoplankton}} = 9.5$$

$$\frac{\text{fish}}{\text{zooplankton}} = 2.2 \cdot 10^2$$

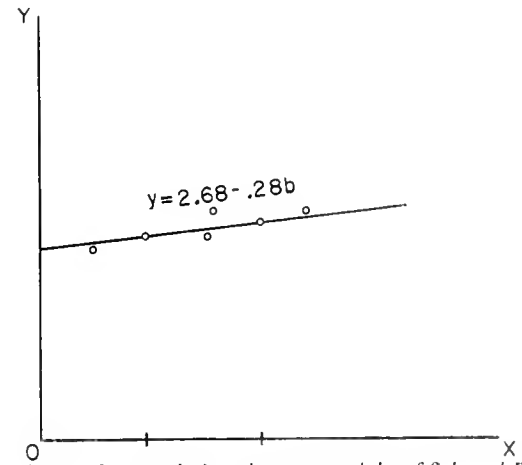

FIGURE 2. *Correlations between weight of fish and DDT residue in Jordan watershed, 1971*

Various degrees of partition coefficients have been published. Hamelink (*4*) reported partition coefficients of $1.0 \cdot 10^{4}$ between water and fish. Gunther (*3*) reported various coefficients: 10^{3}, 10^{4}, 10^{5}, 10^{6}, 10^{7}. These partition coefficients depend upon such factors as the amount of DDT in each trophic level, and metabolism and temperature.

Sources of DDT in the Jordan watershed are agricultural uses in the Hula and the upper Galilee Valleys. Pesticides are transported to the Jordan River by wind and runoff from rain. The Jordan watershed discharges annually $9 \cdot 10^{8} m^{3}$ water into the Sea of Galilee, which supplies a third of Israel's water. It is quite feasible that DDT finds its way to the lake. Although the amount of ΣDDT residue in this study does not exceed the 42 ppb deemed acceptable by the United Nations World Health Organization, Lahav (*5*) reported that TDE and *o,p'*-DDT in the Sea of Galilee exceed the WHO permissible level by a factor of 100.

DDT and its metabolites were concentrated in fish tissues at various levels. Differences in feeding habits and age may explain the variation in residue levels among the three species within a body of water.

Mean ΣDDT residue was 0.37 ppm in carp, 2.59 ppm in benith, and 3.34 ppm in sardines. Residues found in the tissues included DDT and its metabolites DDE, TDE, *p,p'*-DDT, and *o,p'*-DDT. The level of 5 mg/kg DDT permitted by WHO was exceeded in sardines by a factor as large as three.

These data obtained in the summer of 1971 show that agricultural contamination of the Jordan watershed warrants concern for fish, fish-consuming populations, and the affected environment. Further study should be conducted to investigate the full impact of DDT and other pesticides on the Jordan watershed.

LITERATURE CITED

(*1*) *Beynon, K. Y., and K. E. Elgar. 1966.* The analysis for residues of chlorinated insecticides and pesticides. Analyst 91(1080):143-175.

(*2*) *de Faubert Maunder, M. J., H. Egan, E. W. Godly, E. W. Hammond, J. Roburn, and J. Thomson. 1964.* Clean-up of animal fats and dairy products for the analysis of chlorinated pesticide residues. Analyst 89(1056):168-174.

(*3*) *Gunther, F. A., W. E. Westlake, and P. S. Jaglan. 1968.* Reported solubilities of 738 pesticide chemicals in water. Residue Rev. 20:1-148.

(*4*) *Hamelink, J. L., R. C. Waybrant, and R. C. Ball. 1971.* Proposal: exchange equilibriums control the degree chlorinated hydrocarbons are biologically magnified in lentic environments. Trans. Am. Fish. Soc. 100(2):207-214.

(*5*) *Lahav, N., and Y. Kahanovitch. 1974.* Occurrence of pesticides in selected water sources in Israel. Environ. Sci. Technol. 8:762-765.

(*6*) *Pionke, H. B., J. G. Konrad, G. Chesters, and D. E. Armstrong. 1968.* Extraction of organochlorine and organophosphate insecticides from lake waters. Analyst 93 (107):363-367.

(*7*) *Shuval, H. T. 1970.* Developments in Water Analysis Research. Ann Arbor Press. 7 pp.

(*8*) *Standard Methods for Examination of Water and Wastewater. 1971.* Chlorinated hydrocarbon pesticides. Amer. Public Health Assoc., 13th ed., pp. 100-107.

(*9*) *U.S. Department of Health, Education, and Welfare. 1965.* Extraction of lean tissue with hexane. Guide to Analysis of Pesticide Residues, Vol. 1, Sec. II (A.5.a).

(*10*) *U.S. Department of Interior. 1968.* Water Quality Criteria—Report of the National Technical Advisory Committee to the Secretary of the Interior. Federal Water Pollution Control Administration. 233 pp.

Occurrence of Pesticide Residues in Four Streams Draining Different Land-Use Areas in Pennsylvania, 1969-71[1]

John F. Truhlar[2] and Lloyd A. Reed[2]

ABSTRACT

Samples of water, streambed material, fish, and soil were collected in four small drainage basins in Pennsylvania in 1969-71 and analyzed to determine the concentrations of chlorinated hydrocarbon insecticides. Water samples were also analyzed for phenoxy-acid herbicides. Each basin studied represents a predominant land use: forest, general farms, residential areas, and orchards.

All water and fish samples showed pesticide concentrations less than the maximum level recommended by the Public Health Service, U.S. Department of Health, Education, and Welfare. However, no fish were found in the orchard stream.

DDT or one of its metabolites was the most frequently occurring insecticide and was detected in all media sampled except the forest soil. The highest combined concentration of DDT and its metabolites in storm-runoff samples was 11.4 µg/liter in a sample collected from the residential area stream, but the median was higher (0.12 µg/liter) in the orchard than in the residential area (0.02 µg/liter).

A sample of the top 0.5 inch (13 mm) of orchard soil contained 40,000 µg/kg DDT and its metabolites, even though DDT had not been used in the orchards for several years prior to this study. Maximum concentrations detected in other orchard media are 330 µg/kg in streambed material and 3.45 µg/kg in storm runoff.

Dieldrin was the second most frequently occurring insecticide. Other insecticides detected were chlordane, heptachlor epoxide, lindane, and a trace of aldrin in one fish sample. Each stream contained at least one of the following herbicides: 2,4-D, silvex, or 2,4,5-T.

Introduction

This study was conducted to determine the degree of pesticide contamination in four small drainage basins and to determine whether pesticide residues were present in amounts that could be hazardous to humans or to aquatic life. Each basin was chosen to represent a single land use: forest, general farms, residential area, or orchards.

The four basins were selected according to the percentage of drainage area in the desired land-use category and the ease of collecting data during storms. Areas selected are shown in Figure 1. The areas are (1) a 46.2 mi² (119.7 km²) forested area situated in northern Clinton, eastern Potter, and western Lycoming Counties drained by Young Womans Creek; (2) a 15.0 mi² (38.8 km²) general farming area in western Perry County drained by Bixler Run; (3) a 1.85 mi² (4.79 km²) residential area in Dauphin County drained by an unnamed tributary of Spring Creek; (4) a 1.26 mi² (3.26 km²) orchard area in Adams County drained by an unnamed tributary of Latimore Creek.

Samples of streambed material and water were collected periodically from each of the four areas from February 1969 to April 1971 and analyzed for chlorinated hydrocarbon insecticides. Water samples were analyzed for phenoxy-acid herbicides. Insecticide concentrations in local soils and fish, except in the orchard area, were determined once in each area. Data were collected also on streamflow, suspended sediment concentration, and water chemistry.

Sampling and Analysis

Most soil samples were collected from the top 3 inches (76 mm) from different locations in each of the areas and composited into single samples for analysis. Soil samples from the orchard area were divided into three categories:

[1] Originally printed in cooperation with the Pennsylvania Department of Environmental Resources, State Conservation Commission, as Water Resources Investigations 6-75, U.S. Geological Survey, Harrisburg, Pa.

[2] U.S. Geological Survey, Box 1107, Harrisburg, Pa. 17108. Reprints available from this address.

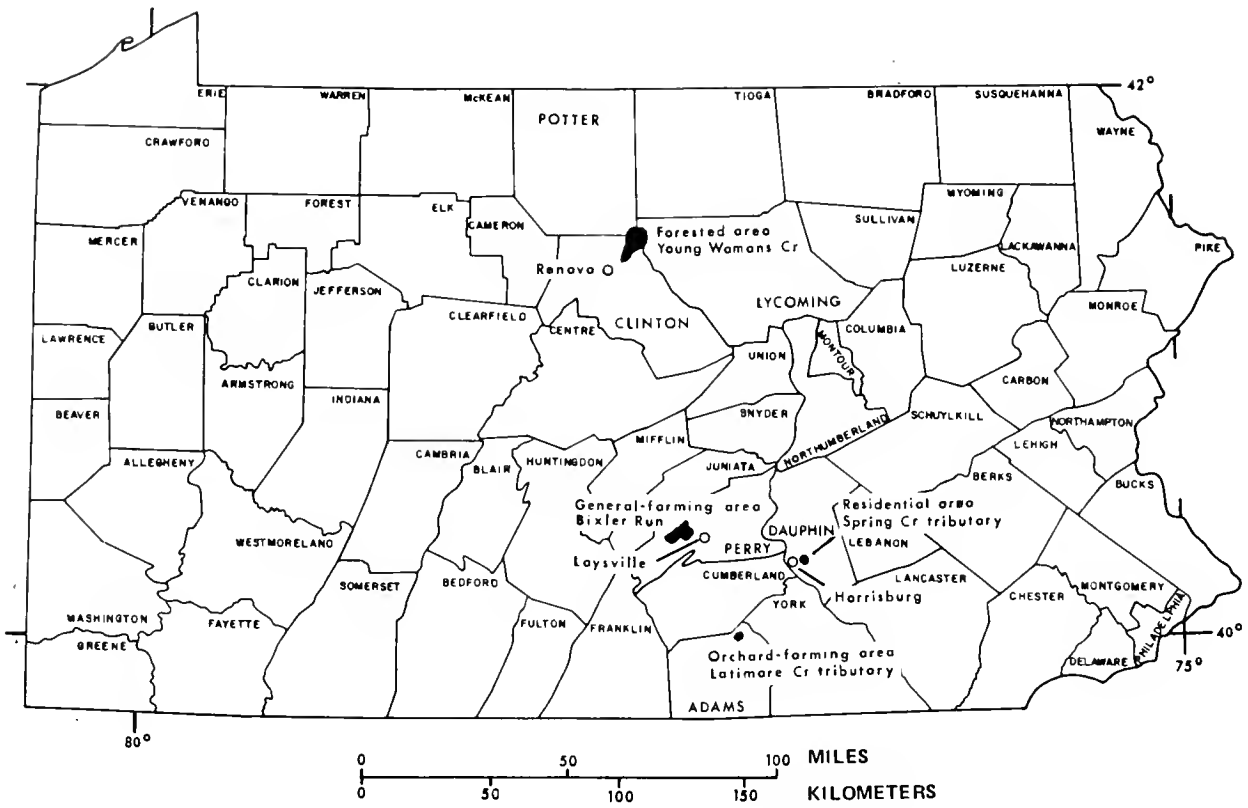

FIGURE 1. *Locations in Pennsylvania sampled for pesticide residues, 1969-71*

the area in open fields and woods, the top 0.5 inch (13 mm) of orchard soil, and the orchard soil 0.5 to 3 inches (13 to 76 mm) deep. Samples were collected from the top 2 inches (51 mm) of the streambed where fine material had been deposited. Samples were collected from different locations in the channel and composited into a single sample for analysis.

Water samples were collected both during base flow periods when streams were normally clear, and during storms when streams were highly turbid. Suspended sediment samples were collected using standard depth-integrating sediment samplers (6), and samples for pesticide analyses were collected by wading and sampling, with a container of teflon or glass, throughout the vertical section. Samples for pesticide and suspended sediment concentration were collected simultaneously. Analyses were run on each individual water sample; no composites were made. Pesticide analyses were performed on the whole water sample, including suspended sediment.

Fish samples were collected and separated according to species and age, and frozen. Analyses were performed on the whole fish.

Streamflow data were collected using the existing gauging station records for Young Womans Creek and Bixler Run and by using staff gauges and storm hydrograph recorders installed during the study on the tributaries of Spring and Latimore Creeks.

The basic analytical procedures utilized in the pesticide analyses, and the pesticides which can be detected by these methods, have been described by Goerlitz and Brown (4). A list of the pesticides that were detected is shown below. Subsequent tables show only those pesticides that were detected in each medium. Polychlorinated biphenyls (PCB's) were separated from the chlorinated hydrocarbon insecticides by the scheme described by Goerlitz and Law (5). The reported values are not corrected for recovery. Mass spectrometry was used for residue confirmation.

Description of Study Areas

FOREST

Nearly 100 percent of the forested area, which is drained by Young Womans Creek, is State forest lands which have light duty roads, hunting camps, and lodges. Water,

chemical, and sediment discharge data have been collected since December 1964 at the Young Womans Creek gauging station near Renovo as part of the Geological Survey hydrologic benchmark station network.

No known pesticide has been applied directly to this forest. The nearest large-scale pesticide application was in 1965 when a part of the Kettle Creek basin north of the Young Womans Creek basin was aerially sprayed with DDT at the rate of 0.5 lb/a. (0.5 kg/ha.) to control fall cankerworm.

GENERAL FARMS

The general farming area, which is drained by Bixler Run, supports dairy farms typical of those located in the valley and ridge sections of the State. Nearly all the crops grown, primarily corn, oats, mixed hay, and alfalfa, are fed to dairy cattle. Water, chemical, and sediment discharge records have been collected since 1954 at the Bixler Run gauging station near Loysville.

Pesticides are used especially to control weeds in corn and insects in alfalfa; application rates and quantities were not determined for the study.

RESIDENTIAL AREA

The residential area is in Dauphin County east of Harrisburg. The land is used primarily for suburban housing in 0.25- to 1-acre (0.1-0.4 ha.) lots. Pesticides are used to control insects and diseases on trees and shrubbery, and to control weeds, undesirable grasses, and insects in lawns. Application rates vary greatly from house to house and year to year. A random survey of homeowners in this area indicated that herbicides, usually applied with a fertilizer, are used more frequently than are insecticides.

Spring Creek tributary which drains this area occasionally received domestic sewage during storms. This sewage, in addition to overland runoff during storms, may be a source of some pesticide residues found in the stream. Pesticides enter the sewers when homeowners wash their spraying equipment or dispose of pesticides directly into sewers.

ORCHARDS

Orchards occupy nearly 70 percent of the area drained by Latimore Creek tributary at the sampling location. Apples are the major crop, but cherries and peaches are also grown.

Pesticide applications for most apples begin in April and continue almost daily, covering the entire orchard area in about a 1-week period. Spraying is discontinued 2-3 weeks before harvest in September or October. Pesticides are applied mainly to control insects and fungus; however, small quantities are used to control rodents and limit the growth of grass and weeds. Most spraying is done by the individual farmer using tractor-towed orchard sprayers equipped with fans to propel the pesticide mist to the interior areas of the trees. Dieldrin and endrin were the only chlorinated hydrocarbon insecticides applied during the period studied here. Exact records of the pesticides used in previous years are not available; however, the operator of the orchards has not used DDT for several years.

Occurrence of Pesticides

DDT or one of its metabolites was found in all areas and in each medium sampled except for soil in the forested area. Dieldrin was the second most commonly detected insecticide. Figure 2 shows where and in which media insecticides were detected.

One or more of the herbicides 2,4,-D, silvex, or 2,4,5-T was detected at least once in each stream. Herbicides in soil, bed material, or fish samples were not analyzed.

SOILS

Results of insecticide analyses of composited soil samples are shown in Table 1. Highest insecticide concentrations were detected in soils from the orchard area. Samples were separated into three composite groups as previously described because higher concentrations were anticipated in this area than in the others. The combined concentration of DDT and its metabolites in the top 0.5 inch (13 mm) of orchard soil was 40,000 μg/kg. The calculated concentration of DDT and its metabolites in the top 3 inches (76 mm) of orchard soil was 14,000 μg/kg, and corresponding values for the residential and general farming soils were 55 μg/kg and 1.7 μg/kg, respectively. No insecticide residues were found in forest soil samples.

The fact that high concentrations of DDT and its metabolites were found in the top 0.5 inch (13 mm) of

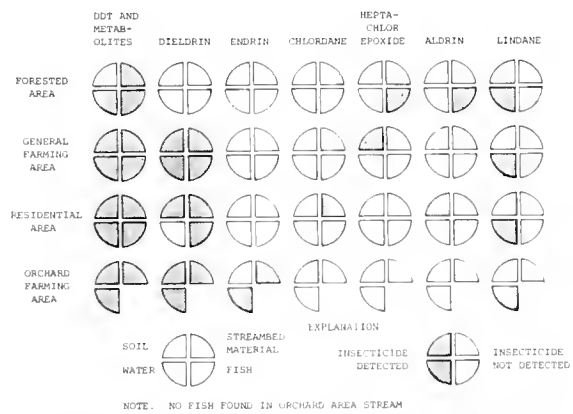

FIGURE 2. *Occurrence of insecticides in soil, streambeds, water, and fish samples from four different land-use areas, Pennsylvania—1969-71*

TABLE 1. *Insecticide residues in soil samples from stream basins draining four different land-use areas, Pennsylvania—1969-71*

Collection Date	Sample Depth	Residues, µg/kg				
		TDE	DDE	DDT	Dieldrin	Heptachlor epoxide
Forests						
10-15-70	Top 3 inches (76 mm)	0.0	0.0	0.0	0.0	0.0
General Farms						
5-1-69	Top 3 inches (76 mm)	0.0	1.7	0.0	2.4	0.6
Residential Area						
2-27-69	Top 3 inches (76 mm)	4.0	0.0	5.1	1.7	0.0
Orchards						
2-27-69	Top 0.5 inch (13 mm)	6,200	6,300	28,000	6,100	0.0
2-27-69	0.5 to 3 inches (13 to 76 mm)	690	1,900	6,200	3,600	0.0
2-27-69	Top 3 inches (76 mm) in adjacent open fields and woods	2.1	1.7	7.7	8.8	0.0

TABLE 2. *Insecticide residues in streambed samples from four different land-use areas, Pennsylvania—1969-71*

Collection Date	Residues, µg/kg					
	Chlordane	TDE	DDE	DDT	Dieldrin	Endrin
Forests						
6-10-68	0	0.5	0.1	0.5	0.0	0.0
11-27-68	0	0.5	0.0	0.5	0.0	0.0
5-20-69	0	0.0	0.6	0.0	0.0	0.0
7-10-69	0	0.0	0.0	0.0	0.0	0.0
10- 2-69	0	0.2	0.0	0.0	0.0	0.0
11-18-70	0	0.0	0.0	0.0	0.0	0.0
4-15-71	0	0.8	0.9	0.5	0.0	0.0
Mean	0	0.3	0.2	0.2	0.0	0.0
Median	0	0.2	0.0	0.0	0.0	0.0
General Farms						
2-27-69	0	0.0	0.0	0.0	0.5	0.0
7- 9-69	0	0.0	0.0	0.0	0.0	0.0
10-15-70	0	0.0	0.0	0.0	0.0	0.0
4-13-71	0	0.4	0.5	0.5	0.3	0.0
Mean	0	0.1	0.1	0.1	0.2	0.0
Median	0	0.0	0.0	0.0	0.0	0.0
Residential Area						
4-30-69	0	7.4	6.9	9.1	0.0	0.0
7- 8-69	0	1.1	1.0	1.5	0.0	0.0
8-28-69	0	1.0	0.0	2.5	TR	0.0
10-15-70	0	47	10	5,900	0.0	0.0
4-13-71	250	5.2	11	5.7	0.2	0.0
Mean	50	12	5.8	1,200	0.0	0.0
Median	0	5.2	6.9	5.7	0.0	0.0
Orchards						
2-27-69	0	59	30	53	0.0	0.0
4-30-69	0	37	23	50	10	0.0
7- 8-69	0	19	14	31	0.0	0.0
10-15-70	0	190	41	54	7.7	55
4-13-71	0	230	60	37	10	120
Mean	0	110	34	45	5.7	35
Median	0	59	30	50	7.7	0.0

NOTE: TR = trace.

orchard soil even though DDT has not been used for several years, indicates that residues of this insecticide remain primarily in the uppermost soil layers, which contain organic material and clay-size soil particles.

STREAMBEDS

Samples were collected on at least four occasions from streambeds and analyzed for insecticides (Table 2). Ranges observed in the concentration of DDT and its metabolites from each of the four basins are shown in Figure 3. Lowest concentrations were observed in the streams draining the forest and farming areas, and highest concentrations were observed in the streams draining the residential and orchard areas. The sample collected from a residential area near Spring Creek tributary October 15, 1970, had 5,900 μg/kg DDT. This could reflect a slug discharge which passed through the sewer system during a recent storm. Separate sanitary and storm sewers were installed within the residential area during the study period but were not finished until after the study. Prior to completion of the separate sewer system, residential sewage was flushed by direct runoff through storm sewers into Spring Creek tributary.

One streambed sample typical of those analyzed was collected at each area for size analysis. Particle size distributions of these samples are shown below. No sample contained material larger than sand although the materials in all except the residential area streambed are predominantly cobble-sized.

	Sand, %	Silt, %	Clay, %
Forest	63	24	13
General farm	73	12	15
Residential area ..	53	28	19
Orchards	63	24	13

WATER

More than 80 water samples were analyzed for pesticide concentrations (Table 3). Twenty percent were collected during base flow periods when sediment concentrations were low; the remainder were collected during storms when sediment concentrations were high. It was anticipated that pesticide residues observed during storm runoff would be higher than during base flow due to the increased suspension of sediment and organic detritus with which pesticides are associated.

Very low pesticide concentrations were observed in the four base flow and six storm-runoff samples collected from Young Womans Creek. Pesticides were detected in only one base flow and one storm-runoff sample. Bixler Run, like Young Womans Creek, showed very low

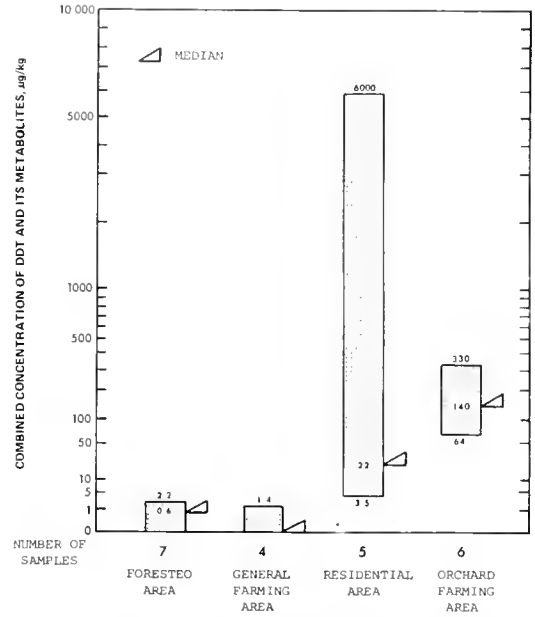

FIGURE 3. *Range in concentration of DDT and its metabolites in streambed samples collected from streams draining four different land-use areas, Pennsylvania - 1969-71*

concentrations. Pesticides were detected in only one of four base flow samples and in seven of ten storm-runoff samples.

Spring Creek tributary was sampled 3 times during base flow and 23 times during storms. Pesticides were not detected in any of the base flow samples. However, nearly all the storm-runoff samples contained pesticide residues. The highest observed concentration of a single pesticide residue in any water sample was the 11.0 μg/liter of DDT found in a storm-runoff sample collected at this sampling site in June 1970.

Latimore Creek tributary was sampled 6 times during base flow and 27 times during storms. Pesticides were detected in three of the base-flow and in all but two of the storm-runoff samples. The highest observed concentration of a single pesticide detected at this sampling site was the 2.50 μg/liter of DDT found in a storm-runoff sample collected May 9, 1969.

The maximum, minimum, and median concentrations of DDT and its metabolites observed in the water samples from each of the four streams are illustrated in Figure 4. The lowest concentrations were observed in the forest and farms; the highest concentrations were observed in the residential area and the orchard. The combined concentration of 11.4 μg/liter of DDT and its metabolites observed in Spring Creek tributary on June 3, 1970, may

TABLE 3. *Pesticide residues in streams draining four different land-use areas, Pennsylvania—1969-71*

Collection Date	Collection Time	Instantaneous Discharge, CFS	Sediment Concentration, mg/liter	Residues, µg/liter								
				TDE	DDE	DDT	Dieldrin	Endrin	Lindane	2,4-D	Silvex	2,4,5-T
Young Womans Creek (forest)												
2-27-69	—	20	BF	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
4-15-69	1200	171	15	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
4-15-69	1730	285	88	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
4-15-69	1935	340	108	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
4-15-69	2,200	351	65	0.01	0.01	0.01	0.00	0.00	0.00	0.00	0.00	0.01
4-16-69	0705	392	25	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
7-10-69	1315	10	BF	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
8-14-69	1730	10	BF	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
10-12-69	—	4	BF	0.00	0.01	0.02	0.00	0.00	0.01	0.00	0.00	0.00
11-18-70	1200	288	—	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Base flow	Mean			0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
	Median			0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Storm runoff	Mean			0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
	Median			0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Bixler Run (general farms)												
2-27-69	1045	6.9	BF	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
4-15-69	1545	20	20	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
4-15-69	2100	76	48	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.02
5-1-69	1430	8.0	BF	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
5-19-69	1230	32	—	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.02	0.00
7-9-69	1200	2.9	BF	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
7-23-69	0650	104	900	0.00	0.00	0.00	0.00	0.00	0.00	TR	0.00	0.30
7-23-69	0825	71	399	0.01	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.07
7-23-69	1440	123	277	0.00	0.00	0.00	0.00	0.00	0.00	—	—	—
8-27-69	1315	2.5	BF	0.00	0.00	0.13	0.00	0.00	0.00	—	—	—
7-10-70	1135	96	37	0.08	0.05	0.14	0.08	0.00	0.02	0.00	0.00	0.00
2-22-71	1210	341	838	0.00	0.00	0.00	0.00	0.00	0.00	0.02	0.00	0.00
2-22-71	1640	427	342	0.00	0.00	0.00	0.00	0.00	0.00	0.01	0.00	0.00
2-22-71	1910	328	307	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Base flow	Mean			0.00	0.00	0.03	0.00	0.00	0.00	0.00	0.00	0.00
	Median			0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Storm runoff	Mean			0.01	0.01	0.01	0.01	0.00	0.00	0.00	0.00	0.04
	Median			0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Spring Creek Tributary (residential area)												
4-10-69	1755	11	2,000	0.02	0.00	0.08	0.00	0.00	0.00	0.36	0.04	0.04
4-10-69	1908	4.1	550	0.02	0.00	0.03	0.00	0.00	0.00	0.20	0.00	0.03
4-30-69	1550	0.4	BF	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
5-9-69	0838	36	1,220	0.01	0.00	0.06	0.00	0.00	0.00	0.91	0.05	0.25
6-2-69	2205	1.5	205	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
6-2-69	2255	13	760	0.03	0.00	0.20	0.00	0.00	0.00	0.00	0.00	0.00
6-2-69	2340	19	1,030	0.02	0.00	0.12	0.00	0.00	0.00	0.00	0.00	0.00
7-8-69	1815	0.3	BF	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
7-23-69	0600	115	—	—	—	—	—	—	—	0.00	0.00	0.00
7-23-69	1235	25	98	—	—	—	—	—	—	0.00	0.00	TR
8-28-69	—	0.4	BF	0.00	0.00	0.00	0.00	0.00	0.00	—	—	—
9-8-69	1410	13	600	0.00	0.00	0.00	0.00	0.00	0.00	—	—	—
9-8-69	1500	14	860	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
10-12-69	1545	12	660	0.00	0.00	0.07	0.00	0.00	0.02	—	—	—
10-12-69	1608	24	446	0.17	0.00	0.18	0.00	0.00	0.00	—	—	—
10-12-69	1628	41	2,470	0.00	TR	0.12	0.00	0.00	0.02	—	—	—
10-12-69	1645	36	1,526	0.00	0.00	0.00	0.00	0.00	0.00	—	—	—
4-12-70	0545	78	300	0.00	0.00	TR	0.00	0.00	0.01	—	—	—
6-3-70	2025	47	2,970	0.36	0.09	11.0	0.00	0.00	0.34	—	—	—
7-2-70	1000	3.4	32	0.00	0.00	0.01	0.00	0.00	TR	—	—	—
7-9-70	1445	13	275	0.01	0.01	0.08	0.00	0.00	0.01	0.00	0.00	0.00
9-27-70	1045	25	536	0.00	0.00	0.02	0.00	0.00	0.00	0.01	0.02	0.02
12-17-70	0055	10	221	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
2-22-71	0915	7.2	44	0.00	0.00	0.01	0.00	0.00	0.00	0.01	0.00	0.00
2-22-71	1420	25	332	0.00	0.00	0.00	0.00	0.00	0.00	0.02	0.00	0.00
2-22-71	1755	14	90	0.00	0.00	0.00	0.00	0.00	0.00	0.02	0.00	0.00
Base flow	Mean			0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
	Median			0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Storm runoff	Mean			0.03	0.00	0.57	0.00	0.00	0.02	0.10	0.01	0.02
	Median			0.00	0.00	0.02	0.00	0.00	0.00	0.00	0.00	0.00

(continued next page)

TABLE 3 (cont'd.). *Pesticide residues in streams draining four different land-use areas, Pennsylvania—1969-71*

Collection Date	Collection Time	Instantaneous discharge, cfs	Sediment concentration, mg/liter	Residues, µg/liter								
				TDE	DDE	DDT	Dieldrin	Endrin	Lindane	2,4-D	Silvex	2,4,5-T
Latimore Creek Tributary (orchards)												
2-27-69	1530	0.8	BF	0.00	0 00	0.00	0 00	0.00	0 00	0.00	0.00	0.00
4-10-69	1740	2.4	166	0.09	0.08	0 23	0.00	0.00	0 00	0 00	0.00	0 00
4-10-69	1840	1.9	58	0.03	0.00	0.02	0 00	0.00	0 00	0.00	0 00	0.00
4-30-69	1230	0.8	BF	0.00	0.00	0.00	0 00	0.00	0 00	0.00	0.00	0.00
5- 9-69	0720	3.1	2,670	0.05	0 02	0.08	0.00	0.00	0.00	0.03	0.00	0.00
5- 9-69	0750	3.1	1,450	0.55	0 28	0.64	0.00	0.00	0 00	0.06	0 00	0 01
5- 9-69	0810	4.0	1,660	0.58	0.30	2.50	0 00	0.00	0.00	0.05	0 00	0 00
5- 9-69	0855	2.9	325	0.14	0.09	0.07	0.00	0.00	0.00	0.02	0 00	0.00
5-20-69	1410	0.8	BF	0.04	0.00	0.04	0 00	0.00	0.00	0.00	0 00	0.00
6- 2-69	2050	0.4	62	0.02	0.03	0.02	0 00	0.00	0.00	0.00	0 00	0 00
6- 2-69	2110	1.2	390	0.04	0.04	0.07	0 00	0.00	0.00	0.00	0 00	0 00
6-16-69	1030	0.8	BF	0.04	0.01	0.03	0.05	0.00	0 00	0.00	0 00	0.00
7- 8-69	1300	0.3	BF	0 04	0.01	0.01	0.04	0.00	0 00	0.00	0.00	0.00
7-12-69	1545	2.4	872	0 67	0.71	2.07	0.33	0.00	0.00	0.00	0 00	0.00
7-12-69	1600	2.1	523	0.50	0.50	1 45	0 14	0.00	0.00	0.00	0 00	0 00
7-12-69	1700	1.9	119	0 13	0 09	0.23	0 09	0.00	0.00	0 00	0 00	0 00
8-28-69	1115	0.7	BF	0 00	0 00	0.00	0 00	0.00	0.00	—	—	—
9- 7-69	2140	4 4	140	0.00	0.00	0.00	0.00	0.00	0 00	—	—	—
9- 7-69	2205	4.4	179	0 00	0.00	0.00	0.01	0.00	0.00	—	—	—
10- 2-69	1500	4 4	107	0 00	0.00	0.15	0.00	0.00	0 00	—	—	—
10- 2-69	1600	14	1,310	0.00	0.00	0.00	0.00	0.00	0.00	—	—	—
10- 2-69	1920	7.2	41	0 00	0.00	0.12	0.00	0.00	0 00	—	—	—
4- 2-70	1210	39	482	0.30	0.11	0.30	0 00	0.00	0.01	—	—	—
6- 3-70	2135	17	624	0 60	0.21	0.51	0.16	0.00	0.00	—	—	—
7- 2-70	0905	2.7	4	0 06	0.02	0.03	TR	0.00	0.00	—	—	—
7-10-70	1000	11	57	0.00	0.00	0 01	0.00	0.00	0 00	0 08	0 00	0.00
9-27-70	1145	2.9	87	0 04	0 01	0.01	0 00	0.00	0.00	0 02	0.00	0.00
12-16-70	2300	5 3	210	0.02	0.00	0.00	0.00	0.04	0.00	0 00	0.00	0.00
12-16-70	2345	6.1	315	0 04	0.00	0.00	0.00	0.08	0.00	0 01	0.00	0.00
12-17-70	0225	15	431	0.06	0.00	0.00	0 00	0.15	0 00	0.01	0.00	0.00
12-17-70	0310	14	296	0.07	0.00	0.00	0 00	0.19	0.00	0.00	0 00	0.00
2-22-71	1015	13	701	0 07	0.05	0.12	0.00	0.00	0 00	0.00	0 00	0.00
2-22-71	1520	11	161	0.01	0.03	0.04	0 00	0.00	0.00	0 00	0.00	0.00
Base flow	Mean			0 02	0.00	0 01	0.02	0.00	0 00	0 00	0.00	0 00
	Median			0 02	0.00	0.00	0.00	0.00	0 00	0.00	0 00	0.00
Storm runoff	Mean			0.15	0.10	0.32	0 03	0.02	0 00	0.01	0.00	0 00
	Median			0.05	0.03	0.07	0.00	0.00	0 00	0 00	0 00	0.00

NOTE: BF = base-flow sample
TR = trace
— = no analysis performed
[1] To convert cfs to m^3 multiply by 0.02832.

have resulted from a slug discharge. Subsequent samples show approximately the same concentrations observed previously.

None of the pesticide residues detected in the water samples exceeded the maximum permissible concentration (Table 4) recommended by the Public Health Service (*7*). The highest combined concentration of DDT and its metabolites detected in water samples was 11.4 µg/liter, or 27 percent of the maximum permissible concentration. This level was found in a sample collected from Spring Creek tributary on June 3, 1970. The highest combined concentration in Latimore Creek tributary was 3.45 µg/liter, or 8 percent of the maximum permissible concentration, in a sample collected July 12, 1969.

Endrin was detected at a concentration of 0.19 µg/liter, or 19 percent of the maximum permissible concentration, in a water sample collected in Latimore Creek tributary on December 17, 1970. No other pesticides were detected in excess of 2 percent of the recommended maximum permissible concentration for pesticides in public water supplies.

FISH

Fish were collected in March 1970 from three of the four streams investigated. No fish could be found during this sampling period in Latimore Creek tributary, although fish had been observed the previous fall. The fish were separated by species and age, except for the blacknose dace (*Rhinichthys atratulus*, Table 5), and analyzed for insecticides.

Only one compound, DDE, was found in each of the fish samples. It was observed in approximately equal concentrations in the same species of fish from Young Womans Creek and Bixler Run, and in concentrations approximately 10 times greater in the same species from Spring Creek tributary. The highest concentration of DDT and its metabolites in fish samples was 590 µg/kg, or about 12 percent of the recommended maximum (5,000 µg/kg in the edible portion) for food fish (Public

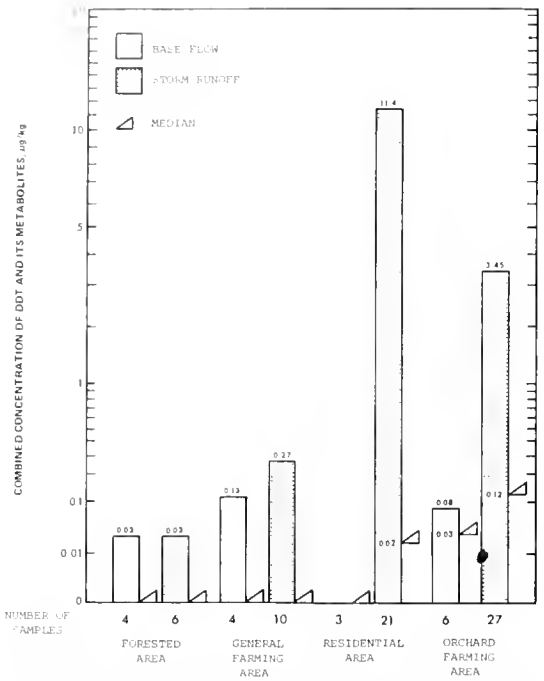

FIGURE 4. *Range in concentration of DDT and its metabolites in streams draining four different land-use areas, Pennsylvania - 1969-71*

Health Service, U.S. Department of Health, Education, and Welfare, 1974; written communication).

Relation of Pesticides to Suspended Sediment

Correlation between suspended sediment concentration and the combined concentration of DDT and its metabolites was examined for each site. No correlation was apparent for either Young Womans Creek or Bixler Run, where only very low concentrations of pesticides were found. The general relationship, showing low pesticide concentrations at base flow and high concentrations only when suspended sediment concentrations were relatively high, was apparent for Spring Creek tributary, but considerable scatter was observed. A fair correlation was found for Latimore Creek tributary, where combined concentration of DDT and its metabolites ranged from 0 to 3.45 µg/liter, with a corresponding range in suspended sediment concentrations of 50 mg/liter to more than 2,000 mg/liter. Figure 5 shows this correlation. DDT is no longer used in the orchards so its only source is the soil; therefore, input to the stream should reflect storm intensity, erosion, and sediment transport.

Particle size distribution was analyzed in five suspended sediment samples from Latimore Creek tributary that were collected simultaneously with samples analyzed for

TABLE 4. *Maximum pesticide concentrations recommended in drinking water supplies, Public Health Service* [1]

Pesticide	Maximum concentration, µg/liter [2]
Endrin	1
Aldrin	17
Dieldrin	17
Lindane	56
Toxaphene	5
Heptachlor	18
Heptachlor epoxide	18
DDT	42
Chlordane	3
Methoxychlor	35
Total organophosphorus and carbamate compounds [3]	100
2,4,5-TP	Individual limits = 100 µg/liter. Sum of any combination of chlorinated phenoxy alkyl pesticides = 100 µg/liter.
2,4-D [4]	

[1] U.S. Department of Health, Education, and Welfare.
[2] For long-term exposures
[3] Expressed in terms of parathion equivalent cholinesterase inhibitions
[4] Short period limit only: 2 to 3 days, no more than once or twice a year

TABLE 5. *Pesticide residues in fish samples from streams draining three different land-use areas, Pennsylvania—1969-71*

Collection Date	Fish	No. in Sample	Age, yr	Residues, µg/kg				
				Aldrin	TDE	DDE	DDT	Dieldrin
			Young Womans Creek (forest)					
	Blacknose dace [1]	47	—	0.0	0.0	32	0.0	0.0
3-5-70	Northern creek chub [2]	5	1	0.0	0.0	22	0.0	0.0
	Northern creek chub	1	2	0.0	0.0	17	0.0	0.0
	White sucker	4	2	TR	0.0	15	0.0	0.0
		8	3	0.0	0.0	17	0.0	0.0
			Bixler Run (general farms)					
	Blacknose dace	100+	—	0.0	8.6	31	0.0	0.0
3-11-70	White sucker	10	2	0.0	4.6	16	0.0	0.0
	White sucker	10	3	0.0	0.0	23	0.0	7.1
			Spring Creek Tributary (residential area)					
	Blacknose dace	100+	—	0.0	60	350	0.0	9.0
3-11-70	Northern creek chub	13	1	0.0	69	250	0.0	6.8
	Northern creek chub	18	2	0.0	50	250	0.0	7.7
	White sucker	1	2	0.0	110	110	370	8.9

NOTE: TR = trace
[1] *Rhinichthys atratulus*
[2] *Semotilus atromaculatus*
[3] *Catostomus commersoni*

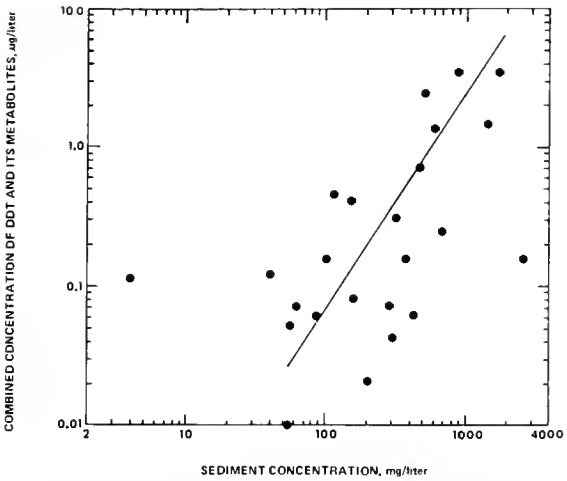

FIGURE 5. *Correlation between suspended sediment concentration and combined concentration of DDT and its metabolites in Latimore Creek tributary, Pennsylvania - 1969-71*

TABLE 6. *Particle size distribution and ΣDDT content of suspended sediment samples from Latimore Creek tributary, Pennsylvania—1969-70*

Collection Date	Sand, %	Silt, %	Clay, %	Suspended sediment concentration: Total, mg/liter	Suspended sediment concentration: Clay, mg/liter	ΣDDT µg/liter
4-10-69	1	53	46	166	76	0.40
7-12-69	0	29	71	523	371	3.45
4- 2-70	34	46	20	482	96	0.71
6- 3-70	7	50	43	624	269	1.32
12-17-70	11	65	24	431	103	0.06

pesticide residues. These data are shown in Table 6 with the computed clay concentrations and the combined concentration of DDT and its metabolites found in corresponding pesticide samples. Except for the sample collected December 17, 1970, the concentration of DDT and its metabolites shows a better correlation with the computed clay concentration than with the total suspended sediment concentration.

Effects of Pesticides on Aquatic Life

Both the residential area and orchard streams occasionally contain temporary pesticide residue concentrations that might be toxic to some fish exposed for 96 hours (*1-3*). The maximum concentrations observed in these streams occurred during storms when suspended sediment concentrations were also at a maximum, and probably never persisted for more than a half hour. However, pesticide concentrations safe for aquatic life under continuous exposure are considerably less than 96 hours (*8*). The effects of these exposures in addition to chronic low-level exposure are practically impossible to evaluate, but it appears possible that there is occasional damage to fish populations in both the residential area and orchard streams.

Aquatic insects are more susceptible than fish to chlorinated hydrocarbon insecticides. Damage to insect populations probably occurs in both the residential area and orchard streams, because these insects spend part of their life cycles in the streambed where pesticide concentrations are higher than in the water. An attempt was made to collect fish in the orchard stream, and the streambed was examined for macroinvertebrates, but neither fish nor macroinvertebrates were found. The lack of fish food, rather than a direct fishkill, may account for the fact that no fish were found. However, pesticides may occasionally be discharged in highly concentrated slugs that could decimate both insect and fish populations. Since it is unlikely that any of the samples were collected exactly at the time of highest residue concentration, higher concentrations may have occurred.

Discussion

Pesticide residues were detected in Young Womans Creek even though none were detected in soil of the basin. Lindane was detected in all four streams but in no other environmental component. A possible explanation for this is that the detection limits for pesticides in water are lower than in other media.

Higher DDT concentrations were observed in one streambed sample and one storm runoff sample from Spring Creek tributary than in any of the samples from Latimore Creek tributary, even though DDT concentrations in the soil were much lower in the residential area drained by Spring Creek than in the orchards drained by Latimore Creek tributary. Slug discharges, possibly through the sewerage system, may account for the high concentrations. High DDT concentrations in the Spring Creek tributary may also result from storm runoff following recent applications of DDT in the residential area. No DDT has been used in the orchards for several years; thus the only source of DDT in Latimore Creek tributary is residue in orchard soils. Slug discharges of other pesticides may sometimes occur in the orchard because parts of the orchards are sprayed almost daily and summer storms sometimes occur unexpectedly, washing off recently applied pesticides.

The high DDT concentrations in soil samples from the orchards were not reflected in streambed or storm runoff samples. This suggests that most DDT remains fixed in the soil and is not easily leached. Soil that enters the streams as sediment appears to be the dominant transport mechanism of pesticide residues, indicating that effective erosion control could decrease the pesticide load in streams.

Analysis of streambed or storm runoff samples appears to be the most expedient and definitive way to determine the degree of pesticide contamination in a stream. Base flow samples contain little or no pesticide residue regardless of those present in basin soils. Fish, though they may be good indicators of pesticide contamination, are more difficult to collect and analyze.

There may be occasional damage to insect and fish populations in Spring Creek and Latimore Creek tributaries, but no water or fish samples contained pesticides above the maximum concentration for public water supplies or food fish recommended by the Public Health Service.

LITERATURE CITED

(1) *Fish and Wildlife Service, U.S. Department of Interior. 1963.* Pesticide-Wildlife Studies—A Review of Fish and Wildlife Service Investigations During 1961 and 1962. FWS Circ. 167. 109 pp.

(2) *Fish and Wildlife Service, U.S. Department of Interior. 1964.* Pesticide-Wildlife Studies, 1963—A Review of Fish and Wildlife Service Investigations During the Calendar Year. FWS Circ. 199. 130 pp.

(3) *Fish and Wildlife Service, U.S. Department of Interior. 1965.* The Effects of Pesticides on Fish and Wildlife. FWS Circ. 226. 77 pp.

(4) *Goerlitz, D. F., and E. Brown. 1972.* Methods for analysis of organic substances in water. U.S. Geol. Survey Techniques Water-Resources Inv., book 5, chap. A3. 40 pp.

(5) *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.

(6) *Guy, H. P., and V. W. Norman. 1970.* Field methods for measurement of fluvial sediment. U.S. Geol. Survey Techniques Water-Resources Inv., book 3, chap. C2. 59 pp.

(7) *Public Health Service, U.S. Department of Health, Education, and Welfare. 1969.* Manual for Evaluating Public Drinking Water Supplies. PHS Pub. 1820. 62 pp.

(8) *Tarzwell, C. M. 1959.* Pollutional effects of organic insecticides. Twenty-fourth North Am. Wildl. Conf. Trans., Mar. 2-4, 1959, pp. 132-142.

RESIDUES IN SOIL

Mercury and 2,4-D Levels in Wheat and Soils from Sixteen States, 1969

J. A. Gowen,[1] G. B. Wiersma,[2] H. Tai[3]

ABSTRACT

Mercury and 2,4-D levels were determined for soil and wheat from 16 States. Mercury was detected in all samples; 2,4-D was found in eight percent of the soil samples and six percent of the wheat samples analyzed.

Introduction

In 1969 wheat and its associated soil were sampled at harvest in 16 major wheat-producing States to determine levels of mercury, 2,4-D, and certain chlorinated hydrocarbon and organophosphate pesticides. Results of the mercury and 2,4-D analyses are reported here; the chlorinated hydrocarbon and organophosphate data have been published (*3*).

Materials and Methods

Wheat and associated soil were sampled from a total of 100 fields randomly selected in 16 States (Table 1). Sample sites were allocated to States and then counties in proportion to the acres of wheat grown. Each soil sample was a composite of nine cores 5.1 cm in diameter by 7.6 cm in depth spaced uniformly over a 231m² area. The sample was passed three times through a 6.3-mm mesh screen and a 2.3-liter subsample was retained and packed in a steel can for shipment. After the wheat was loaded from the combine into a truck, a composite wheat sample was collected by taking small amounts throughout the load until a 2.3-liter can was filled. Records of pesticide use during the year of sampling were obtained from growers.

Samples were sent to the Pesticides Monitoring Laboratory, Gulfport, Miss. (now located at Bay St. Louis, Miss.), where all samples were analyzed for 2,4-D on gas chromatographs equipped with electron-capture detectors. A subsample of 50 soil samples and related wheat samples were chosen randomly for mercury analyses at the Syracuse University Research Corporation, Syracuse, N.Y. The procedure used was essentially that described by Hatch and Ott (*1*).

TABLE 1. *Numbers of wheat and soil samples from sixteen States, 1969*

State	Number of Samples	
	Wheat	Soil
Colorado	4	4
Idaho	4	4
Illinois	5	5
Indiana	4	4
Kansas	22	22
Michigan	4	3
Missouri	4	4
Montana	8	8
Nebraska	8	8
North Dakota	8	8
Ohio	4	4
Oklahoma	6	3
Oregon	4	4
South Dakota	4	4
Texas	5	5
Washington	6	6
TOTAL	100	96

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TABLE 2. *Mercury and phenoxy compounds applied to sampled wheatfields of 16 States, 1969*

Compounds Applied	Percent of Farms Using Compound	Mean Application Rate, kg/ha
MERCURY COMPOUNDS		
Ethylmercury *p*-toluene sulfonamide	10.1	0.0095
Methylmercury acetate	1.0	0.0045
Methylmercury dicyandiamide	29.3	0.0061
Methylmercury quinolinolate	1.0	0.0045
Phenylmercury urea	1.0	0.0045
All mercury compounds	42.4	0.0068
PHENOXY HERBICIDES		
2,4-D	25.3	0.2705
2,4-DB	1.0	0.0045

NOTE: Total sites sampled = 90
Application data reported by landowners and/or operators

Results

Pesticide use records were obtained from farmers for 99 of the 100 sites (Table 2). The phenoxy herbicide 2,4-D was applied to 25 percent of the sites at rates of 0.113 to 0.680 kg/ha., and an undetermined amount was applied to one site as a spot treatment. One wheat grower reported using 2,4-DB, a compound capable of undergoing β-oxidation in many plants to form 2,4-D (*2*).

Mercury compounds were reportedly used as seed treatments on 42 percent of the fields in amounts ranging from 0.005 to 0.01 kg/ha. active ingredient. Methylmercury dicyandiamide was the most commonly used mercury compound, followed by ethylmercury *p*-toluene sulfonamide. The reported use of mercury compounds may have been conservative, because seeds in some cases had been treated prior to purchase and the seed dressings applied were not known.

TABLE 3. *Mercury and 2,4-D levels in soil and wheat of 16 States, 1969*

	Residues, ppm dry weight						
	Arithmetic Mean	Geometric Mean	95% Confidence Limits		Extremes	Percent of Sites with Residues	Number of Samples
			Lower	Upper			
MERCURY							
Soil							
Mercury compounds used	0.12	0.098	0.080	0.119	0.05-0.29	100.0	24
Mercury compounds not used	0.13	0.105	0.079	0.139	0.05-0.36	100.0	24
All soil samples	0.12	0.101	0.086	0.120	0.05-0.36	100.0	48
Wheat Grain							
Mercury compounds used	0.27	0.247	0.204	0.300	0.07-0.59	100.0	24
Mercury compounds not used	0.31	0.266	0.212	0.332	0.11-1.06	100.0	25
All wheat samples	0.29	0.257	0.222	0.296	0.07-1.06	100.0	49
2,4-D							
Soil							
Phenoxy herbicides applied	0.02	0.005	0.001	0.012	0.00-0.20	20.0	25
Phenoxy herbicides not applied	0.01	0.001[1]	0.001	0.003	0.00-0.75	4.2	71
All soil samples	0.01	0.002	0.001	0.004	0.00-0.75	8.3	96
Wheat Grain							
Phenoxy herbicides applied	0.01	0.001	0.001	0.004	0.00-0.05	8.0	25
Phenoxy herbicides not applied	0.01	0.001	0.001	0.002	0.00-0.12	5.4	74
All wheat samples	0.01	0.001	0.001	0.002	0.00-0.12	6.0	100[2]

[1] Difference significant at the 5 percent level as determined by t test of log transformed data

[2] Pesticide application unknown for one site

Mercury levels in soil and grain from sites where mercury compounds had been used were not significantly different from those where no mercury was applied (Table 3). Levels of 2,4-D in soil where phenoxy herbicides had been applied were significantly higher than levels in soil from sites which received no application ($p < 0.05$). However, no significant difference was found between levels of 2,4-D in wheat from application sites and those in wheat from nonapplication sites.

LITERATURE CITED

(1) *Hatch, W. R., and W. L. Ott. 1968.* Determination of submicrogram quantities of mercury by atomic absorption spectroscopy. Anal. Chem. 40:2085-2087.

(2) *Melnikov, N. N. 1971.* Chemistry of Pesticides. Springer-Verlag, New York. 480 pp.

(3) *Wiersma, G. B., P. F. Sand, and R. L. Schutzmann. 1971.* Chlorinated hydrocarbon and organophosphate residues in wheat and soil. USDA Agricultural Research Service. ARS 81-44.

Pesticide Levels in Hay and Soils from Nine States, 1971

J. A. Gowen,[1] G. B. Wiersma,[2] H. Tai,[3] and W. G. Mitchell[3]

ABSTRACT

In 1971 hay and soil samples were collected in 9 States to determine the incidence and levels of pesticide residues in hayfields. Residues were detected in 8 percent of the soil samples and 29 percent of the hay samples. DDT and its metabolites, DDE and TDE, were contained in 2 soil samples and 21 hay samples. Heptachlor epoxide and chlordane were detected in 1 soil sample, dieldrin in 5 soil samples, and diazinon in 4 hay samples.

Introduction

Chlorinated hydrocarbons have been the primary contaminant of animal feed in the past (*2*). Levels of these and other pesticides in hay, which is a major feed source for meat and dairy animals (*7*), is a cause for concern.

In alfalfa, pesticide residues have been found principally on the leaves and are bound to the plant cuticle (*1,2*). King et al. (*6*) found residues of heptachlor and its epoxide to be greater in the crown and roots of alfalfa plants than in the tops, suggesting year-to-year accumulation. Windblown contaminated dust, rain-splashed soil, and drift from agricultural applications of insecticides during the growing season have been suggested as possible sources of pesticide residues in this crop (*10*). Another source of residues may be the soil in which the alfalfa is grown. Beall and Nash (*3*) found evidence of DDT, dieldrin, endrin, and heptachlor translocation in alfalfa seedlings grown in five soil types. However, soil contact during harvest was not a major source of heptachlor and its epoxide in alfalfa (*6*).

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The present study was undertaken in 1971 because residues of DDT, DDE, TDE, and other chlorinated hydrocarbons were detected in soil and field-collected hay samples in the National Soils Monitoring Program for Pesticides in both 1969 and 1970 (*5,11;* also Wiersma, Tai, and Sand, 1969: unpublished data). The objective of the present study was to determine pesticide residue levels associated with hay cultivation in nine States during 1971.

Materials and Methods

Soil and hay samples were collected from sites in nine major hay-producing States (Table 1). Sampling sites were allocated among States and counties in proportion to acreages of hay harvested (*9*) and were randomly distributed within counties among hayfields of 10 acres or more. A 231-m^2 sampling area was designated in each field. Sixteen soil cores, each 5.1 cm in diameter by 7.6 cm in depth, were collected on a uniform grid over each

TABLE 1. *Sites sampled in nine hay-producing States in 1971*

State	Hay	Soil	Hay/Soil
	Sites Sampled	Sites Sampled	Sites Sampled
Iowa	9	8	8
Kansas	7	7	7
Minnesota	10	10	10
Missouri	9	9	9
Nebraska	13	13	13
New York	6	7	6
North Dakota	12	12	12
South Dakota	10	13	10
Wisconsin	11	11	10
TOTAL	87	90	85

231-m² site. The cores were composited and screened and a 2.3-liter subsample was packed in a steel can which had been rinsed with isopropyl alcohol.

Cuttings of the standing crop of hay were collected in the immediate vicinity of each soil core, air-dried, and thoroughly mixed. A 1.4-kg sample was retained for analysis and placed in a plastic bag inside a cloth bag for shipment. The types of hay sampled included alfalfa, 76 percent; mixed hay, 21 percent; clover, 2 percent; and grass, 1 percent.

In addition to the soil and crop samples, pesticide application data for the 1971 crop year, and names of any pesticides known to have been used in the previous 5 years, were obtained for each site wherever possible.

Samples were analyzed at the EPA Pesticides Monitoring Laboratory, Gulfport, Miss. (now located at Bay St. Louis, Miss.). Detailed analytical procedures are outlined by Carey et al. (*4*) for crop samples and Wiersma et al. (*11*) for soil samples. Because of possible PCB contamination of hay samples by the plastic bags which held them, PCB's were accounted for in analyses but were not considered as part of this investigation.

Results

Pesticide application data were reported by the landowners or operators for 80 of 91 sites. Only 10 percent of the respondents reported using pesticides during the 1971 crop year. The pesticides used were atrazine, chloramben, 2,4-D, diazinon, malathion, and methoxychlor. Atrazine was reportedly applied to four fields; 2,4-D to two; and chloramben, diazinon, malathion, and methoxychlor to one field each. Pesticides were applied to 30 percent of the 80 sites during the 6-year period prior to sampling.

All residues are expressed on a dry-weight basis (Tables 2,3). The data were not normally distributed, but tended to fit a log normal distribution. Thus the geometric mean was utilized to provide a better estimate of central tendency. Geometric means were calculated for the variable $(x+0.01)$, where x is the residue determination. Adjusted geometric means are the calculated geometric means minus 0.01. Arithmetic means are also presented.

Of 90 soil samples analyzed, 8 percent contained detectable levels of pesticides. The compounds indentified were chlordane, *o,p'*-DDE, *p,p'*-DDE, *o,p'*-DDT, *p,p'*-DDT, *p,p'*-TDE, dieldrin, and heptachlor epoxide (Table 1). DDTR (DDE+DDT+TDE) occurred in two soil samples, heptachlor epoxide and chlordane in one, and dieldrin in five. Organophosphates were not detected in any soil samples analyzed. The pesticides identified in hay, occurring in 29 percent of 87 samples, were *p,p'*-DDE, *o,p'*-DDT, *p,p'*-DDT, *p,p'*-TDE, and diazinon (Table 2). DDTR was detected in 21 hay samples; diazinon was detected in four.

Discussion

On most sites where pesticides were detected, respondents claimed that the pesticides in question had not been applied within the six years immediately preceding sampling. Unreported use or spray drift from insecticide applications to other crops might account for some residues in hay and soil. Considering the persistent nature of the organochlorine pesticides (*8,11*), the residues detected in soil might also have originated from applications prior to 1966. In hay, other possible residue sources are translocation from the soil (*3*) and volatilization of the compounds from the soil surface with subsequent reabsorption by the cuticle of the leaves (*1,2*).

TABLE 2. *Pesticide residues detected in hayfield soils of nine States, 1971*

Compound	Residue Levels, ppm dry weight				Sites with Residues, %
	Arithmetic Mean	Adjusted Geometric Mean	95% Confidence Limits for Adjusted Geometric Mean	Maximum	
Chlordane	<0.01	*	- -	0.04	1.1
o,p'-DDE	<0.01	*	- -	0.02	1.1
p,p'-DDE	<0.01	0.001	<0.001-0.002	0.27	2.2
o,p'-DDT	0.01	*	- -	0.84	1.1
p,p'-DDT	<0.01	*	- -	0.37	1.1
p,p'-TDE	<0.01	*	- -	0.15	1.1
DDTR	0.02	0.001	<0.001-0.002	1.54	2.2
Dieldrin	<0.01	0.001	<0.001-0.002	0.12	5.6
Heptachlor Epoxide	<0.01	0.001	<0.001-0.002	0.15	1.1

NOTE: Total sites sampled = 90.
Minimum detectable level was 0.01 for all compounds
* = Geometric mean estimate not calculated when less than two positive values were present

TABLE 3. *Pesticide residues detected in hay from nine States, 1971*

Compound	Residue Levels, ppm dry weight				Sites with Residues, %
	Arithmetic Mean	Adjusted Geometric Mean	95% Confidence Limits for Adjusted Geometric Mean	Maximum	
p,p'-DDE	< 0.01	0.001	<0.001-0.001	0.04	18.4
o,p'-DDT	< 0.01	0.001	<0.001-0.002	0.05	5.7
p,p'-DDT	0.01	0.004	0.002-0.007	0.20	21.8
p,p'-TDE	<0.01	0.001	<0.001-0.002	0.03	6.9
DDTR	0.02	0.006	0.003-0.009	0.28	24.1
Diazinon	0.02	0.001	<0.001-0.003	1.32	4.6

NOTE: Total sites sampled = 90
Minimum detectable level was 0.01 for all compounds

The only pesticide detected in both hay and soil samples was DDTR. Of 85 hay samples, 24 percent contained DDTR residues compared with 2 percent of the 85 corresponding soil samples. This difference might be accounted for by spray drift to the hay from other fields. Another possibility is that DDTR was present in soils below the level of detection, 0.01 ppm, but was detected in the corresponding hay samples because a given weight of hay has a larger surface area available for absorption than has the equivalent weight of soil.

LITERATURE CITED

(1) *Archer, T. E. 1968.* Location, extraction, and removal of endrin residues on alfalfa hay. J. Dairy Sci. 51 (10):1606-1611.

(2) *Archer, T. E., and D. G. Crosby. 1967.* Extraction and location of selective chlorinated hydrocarbon residues in alfalfa hay. Bull. Environ. Contam. Toxicol. 2(4):191-206.

(3) *Beall, M. L., Jr., and R. G. Nash. 1969.* Crops seedling uptake of DDT, dieldrin, endrin, and heptachlor from soils. Agron. J. 61(4):571-575.

(4) *Carey, A. E., G. B. Wiersma, H. Tai, and W. G. Mitchell. 1973.* Organochlorine pesticide residues in soils and crops of the Corn Belt Region, United States—1970. Pestic. Monit. J. 6(4):369-376.

(5) *Crockett, A. B., G. B. Wiersma, H. Tai, W. G. Mitchell, P. F. Sand, and Ann E. Carey. 1974.* National soils monitoring program for pesticide residues—FY 1970. Pestic. Monit. J. 8(2):69-97.

(6) *King, R. L., N. A. Clark, and R. W. Hemken. 1966.* Distribution, movement, and persistence of heptachlor and its epoxide in alfalfa plants and soil. J. Agr. Food Chem. 14(1):62-65.

(7) *Naber, E. C., and A. C. Waldron. 1972.* Pesticide residues in feedstuffs: are they a problem? Md. Univ. Nutr. Conf. Feed Manufacturers Proc., pp. 69-72.

(8) *Nash, R. G., and E. A. Woolson. 1967.* Persistence of chlorinated hydrocarbon insecticides in soils. Science 157(3791):924-927.

(9) *U.S. Bureau of the Census. 1967.* Census of Agriculture, 1964. Vol. 1, Statistics for the States and Counties. Parts 7, 14, 15, 16, 17, 18, 19, 20, and 21. U. S. Government Printing Office, Washington, D. C.

(10) *Ware, G. W., B. J. Estesen, and W. P. Cahill. 1968.* An ecological study of DDT residues in Arizona soils and alfalfa. Pestic. Monit. J. 2(3):129-132.

(11) *Wiersma, G. B., H. Tai, and P. F. Sand. 1973.* Pesticide residue levels in soils, FY 1969—National Soils Monitoring Program. Pestic. Monit. J. 6(3):194-228.

APPENDIX

Chemical Names of Compounds Discussed in This Issue

ALDRIN	1,2,3,4,10,10-Hexachloro-1,4,4a,5,8,8a-hexahydro-exo-1, 4-*endo*-5,8-dimethanonaphthalene, not less than 95%
AMIBEN	3-Amino-2,5-dichlorobenzoic acid
ATRAZINE	2-Chloro-4-ethylamino-6-isopropyl-amino-1,3,5-triazine
BHC (BENZENE HEXACHLORIDE)	1,2,3,4,5,6-Hexachlorocyclohexane (mixture of isomers)
CHLORAMBEN	See amiben.
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
2,4-DB	4-Chloro-2-oxobenzothiazolin-3-ylacetic acid
DDE	Dichlorodiphenyl dichloro-ethylene (degradation product of DDT) *p,p'*-DDE: 1,1-Dichloro-2,2-bis(*p*-chlorophenyl) ethylene *o,p'*-DDE: 1,1-Dichloro-2-(*o*-chlorophenyl)-2-(*p*-chlorophenyl) ethylene
DDT	Main component (*p,p'*-DDT): α-Bis(*p*-chlorphenyl) β,β,β-trichloroethane Other isomers are possible and some are present in the commercial product. *o,p'*-DDT: [1,1,1-Trichloro-2-(*o*-chlorophenyl)-2-(*p*-chlorophenyl) ethane]
DIAZINON	O,O-Diethyl O-(2-isopropyl 4-methyl-6-pyrimidyl) phosphorothioate
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-*endo*-*exo*-5,8-dimethanonaphthalene
ENDOSULFAN	6,7,8,9,10,10-Hexachloro-1,5,5a,6,9,9a-hexahydro-6,9-methano-2,4,3-benzodioxathiepin 3-oxide
ENDRIN	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
ETHION	0,0,0',0'-Tetraethyl S,S'-methylene bisphosphorodithioate
ETHYLMERCURY *p*-TOLUENE SULPHONAMIDE	$C_{15}H_{17}HgNO_2S$
HCB	Hexachlorobenzene
HEPTACHLOR EPOXIDE	1,4,5,6,7,8,8-Heptachloro 2,3-epoxy-3a,4,7,7a-tetrahydro-4,7-methanoindan
LINDANE	*Gamma* isomer of 1,2,3,4,5,6-hexachlorocyclohexane
MALATHION	S-[1,2-bis(ethoxy-carbonyl)ethyl] O,O-dimethyl phosphorodithioate
METHOXYCHLOR	1,1,1-Trichloro-2,2-bis(*p*-methoxyphenyl) ethane
METHYLMERCURY DICYANDIAMIDE	$CH_3HgNH.C(:NH)NH.CN$
PARATHION	O,O-Diethyl O-*p*-nitrophenyl phosphorothioate
PCB'S (POLYCHLORINATED BIPHENYLS)	Mixtures of chlorinated biphenyl compounds having various percentages of chlorine
SILVEX	2-(2,4,5-Trichlorophenoxy) propionic acid
2,4,5-T	(2,4,5-Trichlorophenoxy) acetic acid
TDE	2,2-Bis(*p*-chlorophenyl)-1,1-dichloroethane
TOXAPHENE	Chlorinated camphene (67-69% chlorine); product is a mixture of polychlor bicyclic terpenes with chlorinated camphenes predominating.

The *Pesticides Monitoring Journal* welcomes from all sources qualified data and interpretative information on pesticide monitoring. The publication is distributed principally to scientists, technicians, and administrators associated with pesticide monitoring, research, and other programs concerned with pesticides in the environment. Other subscribers work in agriculture, chemical manufacturing, food processing, medicine, public health, and conservation.

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PESTICIDES IN PEOPLE

Organochlorine Compounds in Human Blood Plasma and Milk[1]

Z. W. Polishuk,[2] M. Ron,[3] M. Wassermann,[4] Simi Cucos,[4] Dora Wassermann,[4] and C. Lemesch[4]

ABSTRACT

Organochlorine insecticides and polychlorinated biphenyls (PCB's) were assessed in human blood plasma and milk collected from Israeli mothers 2-4 days after childbirth during 1975.

The concentration of total DDT (ΣDDT) was similar in whole plasma and milk (74 ppb versus 72 ppb) and higher in plasma-extracted lipids than in milk-extracted lipids: 15.12 ppm versus 5.77 ppm.

Levels of γ-BHC, dieldrin, and heptachlor epoxide were higher in whole plasma and plasma-extracted lipids than in whole milk or in milk-extracted lipids.

PCB's had similar concentrations in extracted lipids of plasma and milk but were significantly higher in whole milk than in whole plasma.

Higher percentages of organochlorine insecticides and PCB's were excreted in milk from mothers between 20 and 29 than between 30 and 39, although the younger group had lower levels of these compounds in plasma.

Overweight women excreted lower quantities of organochlorine insecticides and PCB's than did women of normal weight.

Introduction

A broad spectrum of environmental toxic compounds has been reported in human milk. The accumulation of xenobiotics may reach levels dangerous to breast-fed babies. Skin disorders and some deaths occurred in children of nursing mothers who had eaten hexachlorobenzene-treated wheat seed in Turkey in 1956 (*38*). Yusho disease in Japan, associated with accidental ingestion of polychlorinated biphenyls (PCB's), had such symptoms as stillbirth or intrauterine growth retardation, abnormal pigment and desquamation of skin and mucous membranes, early appearance of teeth, calcification of the skull, exophthalmos and gingival hypertrophy (*58*). Monkeys which were experimentally given PCB's showed reduced fertility, and pregnancies which produced small infants (*4*). Mercury and lead have also been transmitted in milk at levels which can be toxic to babies (*38*). In 8 of 101 milk samples, the concentration of mercury exceeded the permissible level of 0.010 ppm. All 8 donors had helped to prepare grain for sowing during pregnancy (*32*).

Organochlorine insecticides have reached unusually high levels in mother's milk in Central America and Japan. In areas of Guatemala where cotton was intensively cultivated, DDT reached 4.07 ppm in whole milk, compared with 1.83 ppm and 2.15 ppm outside the cotton-growing regions (*59*). Safety precautions seem to be very poor among small farmers using insecticides (*16*). High levels of organochlorines were also found in milk from areas subjected to malaria control programs (*29*). In Guatemala the levels of DDT in human milk proved to be 25-30 times the average level found in the United States, England, and Sweden, and hundreds of times higher than the maximum permissible level established by WHO for cow's milk (*44*). In Japan, β-BHC proved to be the most hazardous organochlorine insecticide. In 1971 the average 6-month-old baby in Nagasaki ingested an average of 1.2288 mg BHC (*48*). In other prefectures, β-BHC in whole milk reached levels up to hundreds of ppb. Beta-BHC had been used extensively as a pesticide in ricefields of Japan. The rice straw served as cow feed. High values of pesticides were found in cow's milk from the western region of Japan where these compounds were used in large amounts. In a survey conducted in 1970-71 in Aichi, Japan, total BHC in cow's milk ranged from 10 to 1,100 ppb (*55*).

1 This investigation supported in part by a grant from the Ministry of Health, Jerusalem, and a research agreement from the United Nations—World Health Organization, International Agency for Research on Cancer, Lyon, France

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Thus cow's milk and beef were the main source of β-BHC residues in human milk from Japan.

These circumstances led to the banning of β-BHC in Japan in 1971. Studies carried out in 1972 showed a 40-50 percent decrease of BHC since the ban (*57*). The banning of some organochlorine insecticides in Sweden was followed by a decrease of these xenobiotics in milk. Average PCB levels in human milk in that country increased, however, due to the consumption of fish from the Baltic Sea where industrial waste had been discarded (*80*).

In noncotton regions of Guatemala, cow's milk averaged 0.025 ppm compared with 2.15 ppm in human milk; in this case, cow's milk and beef were not the main source of organochlorines in humans (*59*). Generally, cow's milk contained less than one tenth the quantity of total DDT (Σ DDT) found in human milk. Nearly 83 percent of 168 dairy samples investigated contained less than 20 ppb DDT (*14*). One cause for such differences, in addition to the degree of exposure, is that human mothers excrete in milk approximately 125 percent of the estimated DDT intake, but cows excrete only about 1.5 percent of their DDT intake. Human mothers apparently have a negative DDT balance while lactating (*38*).

Tables 1-6 summarize reports on residues of organochlorine compounds, i.e., some organochlorine insecticides and PCB's, in whole milk and in milk-extracted lipids in several countries.

The importance of studies providing assessment of milk contamination in a region at a given time is that figures obtained in one region can be compared with those from other regions or with subsequent studies in the area after improvement of environmental conditions.

TABLE 1. *Organochlorine residues in extracted lipids of human milk from ten nations*

Literature References	Nation	Residues, ppm						Sampling Year
		Σ DDT	BHC	Dieldrin	Heptachlor Epoxide	HCB	PCB's	
Westöö and Norén 1968 (*81*)	Sweden	2 2800-5 7100		0 0-0 2000				1968
Tuinstra 1971 (*77*)	Netherlands	2 5000	0 3000	0 1200	0 0600			1969
Engst and Knoll 1971 (*14*)	Germany	8 2000						1970
Acker and Schulte 1971 (*1*)	Germany	3 8000	0 5400			5 3000	3 5000	1971
Luquet et al. 1974 (*45*)	France	3 2400	1 7700	0 2300	0 2800	0 9800		1971-1973
Kontek et al 1971 (*41*)	Poland	12 8700	0 3750					1971
Bogusz 1972 (*8*)	Poland	12 8700						1972
Denes and Tarjan 1969 (*11*)	Hungary	9 5000						1962-1963
Damaskin 1965 (*10*)	USSR	1 2200-4 8800						1965
Kroger 1972 (*42*)	USA	2 4000	0 0800		0 1600			1972
Quinby et al 1965 (*62*)	USA	0.5000-10 5000						1965
Suzuki et al 1973 (*71*)	Japan, Akita	3 5300	0 8700	0 3800				1970
Osaka Pref 1973 (*60*)	Japan, Osaka	2 8110		0 0800				1971
Oura et al 1972 (*61*)	Japan Toyama						1 1000	1972
Miller and Fox 1973 (*50*)	Australia urban	16 9000				1.2300		1973
	Australia rural	8 6000				2 2000		1973

TABLE 2. *Organochlorine residues in human whole milk from ten European nations*

Literature References	Nation	Residues, ppb					Sampling Year
		Σ DDT	BHC	Dieldrin	HCB	PCB's	
Bjerk 1972 (*7*)	Norway	50 0-100 0				10 0	1972
Westöö and Noren 1968 (*81*)	Sweden	113 0					1968
Westöö et al 1970 (*82*)	Sweden	120 0					1967-1969
Egan et al 1965 (*13*)	England	130 0	13 0	6 0			1965
Heyndrickx and Maes 1969 (*27*)	Belgium	130 0					1969
Engst and Knoll 1971 (*14*)	Germany	230 0					1969
	Germany	130 0					1970
Engst and Knoll 1972 (*15*)	Germany	160 0					1970
Acker and Schulte 1971 (*1*)	Germany	112 0	18 0		153 0	3 0	1970
Knoll and Jayaraman 1973 (*36*)	Germany	320 0					1971
Knoll and Jayaraman 1973 (*37*)	Germany	300 0	70 0			0 0	1973
Kontek et al 1971 (*41*)	Poland	280 0					1971
Bogusz 1972 (*8*)	Poland	670 0					1972
Gracheva 1969 (*20*)	USSR	0-1000 0					1964
Gracheva 1970 (*21*)	USSR	250 0					1966-1968
Komarova 1970 (*40*)	USSR	100 0					1970
	USSR	190 0					1970
Unterman and Sirghie 1969 (*78*)	Romania	560 0					1969
Mandrolu and Jordáchescu 1971 (*46*)	Romania		0-560 0				1971
Adamović et al 1969 (*2*)	Yugoslavia	207 5	5 0				1969
Adamović et al 1971 (*3*)	Yugoslavia		14 0	79 0			1971
Graca et al 1974 (*19*)	Portugal Lisbon	326 0					1972
	whole country	9 0-1044 0					1972

Organchlorine insecticides and PCB concentrations have been measured in human whole milk, milk-extracted lipids, or both. Knowing the levels of such compounds in whole milk facilitates calculation of the amount of organochlorine insecticides and PCB's ingested by the baby, and comparison of these figures with acceptable daily intakes established by legislation. Levels of organochlorine insecticides and PCB's in milk seem to vary with the lactation period (*22,37*). Most reports do not mention the period of milk sampling; others state results of sampling over a long period of lactation but do not give partial averages according to months of lactation.

The organochlorine insecticide and PCB content of human milk seems to be related to the degree of exposure. Japanese studies showed higher contamination in milk from the western prefectures of Japan where pesticides were used extensively (*25*). Seasonal variations sometimes occur. Higher residue levels are found in winter, probably because winter food contains large amounts of fat (*3*). Several studies reported higher values of organochlorine insecticides in nonfarming families; BHC and dieldrin were higher in the milk of urban mothers than of rural mothers (*24,31,39,73*). There was some correlation between organochlorine insecticide levels in milk and the daily intake of cow's milk and beef which were consumed in higher quantities by urban families (*24,66*). No significant differences between rural and urban DDT levels in mother's milk were found by Komarova (*40*). Organochlorine insecticide and PCB residues were higher in milk samples from underweight and normal-weight women than from overweight ones (*36,37*). The residues increased with age of the lactating women (*36*). Mothers who had nursed three or more babies had DDT concentration in the milk fat below the average (*42*).

This paper reports levels of organochlorine compounds in milk and plasma of Israeli mothers sampled during the first four days after delivery. Samples of blood and milk were taken on the same day.

TABLE 3. *Organochlorine residues in human whole milk, North and Central America*

Literature References	Nation	Residues, ppb					Sampling Year
		Σ DDT	BHC	Dieldrin	Heptachlor Epoxide	PCB's	
Musial et al. 1974 (*53*)	Canada: New Brunswick	35.0					1974
	Nova Scotia	19.0					
Laug et al. 1951 (*43*)	USA	130.0					1951
Quinby et al. 1965 (*62*)	USA: pool	170.0					1960-1961
	individual	120.0					
West 1964 (*79*)	USA	0-370.0					1962
Curley and Kimbrough 1969 (*9*)	USA	70.0	7.0	6.0			1967
Savage et al. 1973 (*63*)	USA	7.0-495.0	0-38.0	0-11.0	0-5.0	40.0-100.0	1971
Hagyard et al. 1973 (*22*)	USA	326.0					1973
Wilson et al. 1973 (*83*)	USA	170.0					1973
Lofröth 1971 (*44*)	Central America	3100.0					1971
Olszyna-Marzys et al. 1973 (*59*)	Guatemala: cotton region	4070.0	0-100.0				1973
	noncotton region	1830.0					

TABLE 4. *Organochlorine residues in human whole milk, Africa*

Literature References	Nation	Residues, ppb				Sampling Year
		Σ DDT	BHC	HCB	PCB's	
Gejvall et al. 1972 (*18*)	Ghana	29.0	30.0	86.0	5.0	1972

TABLE 5. *Organochlorine residues in human whole milk, Oceania*

Literature References	Nation	Residues, ppb				Sampling Year
		Σ DDT	BHC	Dieldrin	HCB	
Newton and Greene 1972 (*56*)	Australia	142.0			52.5	1970
Stacey and Thomas 1975 (*68*)	Australia	78.0	25.0	5.0		1970-1971
Siyali 1973 (*67*)	Australia	64.0		5.0	15.6	1973
Hornabrook et al. 1972 (*29*)	New Guinea	29.0-95.9				1972

TABLE 6. *Organochlorine residues in human whole milk, Japan*

Literature References	Prefecture	Residues, ppb					Sampling Year
		Σ DDT	BHC	Dieldrin	Heptachlor Epoxide	PCB's	
Tokutsu et al 1970 (*74*)	Wakayama	71 0	105 0				1970
Narafu 1971 (*55*)	Aichi		20 0-400 0				1970-1971
Takeshita and Inuyama 1970 (*73*)	Shimane: farmers	79 0	142 9	0-12 9			1970
	nonfarmers	66 0	250 9	0-43 0			1970
Kato et al 1971 (*34*)	Kanagawa	19 0-105 0	18.0-74 0	0-12 0			1971
Hayashi 1972 (*24*)	24 prefectures: farmers	56 3	92 6	3 7			1971
	nonfarmers	63 5	143 4				1971
Hayashi 1972 (*25*)	24 prefectures	60 7	125 9	3 7			1971
	36 prefectures	62 6	100 9	3 4	1 1		1971-1972
Hayashi 1974 (*26*)	38 prefectures	63 0	105 0	3 4	1 1		1971-1972
Nishimoto et al. 1972 (*57*)	Kochi & Nangoku					30 0	1971-1972
Yamagishi et al 1972 (*85*)	Toyko: colostrum	30 0	25 0	7 0			1971
	milk	44 0	41 0	2 0			1971
Kojima et al 1971 (*39*)	Akita I: farmers	52 0	63 0	<1 0			1971
	nonfarmers	50 0	55 2	<1 0			1971
	Akita II: farmers	39 0	14 0				1971
	nonfarmers	38 0	62 0				1971
Mori et al 1971 (*52*)	Mie	5 0-12 0	19 0-86 0	1 0-5 0			1971
Matsuda et al 1971 (*47*)	Ethime: farmers	4 0	71 0	2 0			1971
	nonfarmers	4 0	92 0	1 0			1971
Shimizu 1974 (*65*)	Saga		0 0-390 0				1971
			190 0				after ban
Shirakawa 1974 (*66*)	Wakayama	435 9	345 1	5 8			1971
BHC and DDT 1972 (*6*)	36 prefectures	60 2	115 4			3 4	1971
		56 2	96 0		1 1	3 1	1972
Osaka prefecture 1973 (*60*)	Osaka	21 0	161 5	1 0			1971
		43 0	180 0	2 0			1972
Kawai et al 1973 (*35*)	Ebetsu	78 0	32 0				1971-1972
	Ebetsu & other cities	108 0	40 0				1971-1972
	Muroran	133 0	54 0				1971-1972
	Sapporo	100.0	49 0				1971-1972
Oura et al. 1972 (*61*)	Toyama	33 0	49 0			30 0	1972
Hidaka et al 1972 (*28*)	Kyoto	95 0	120 0	5 0		50 0	1972
Totton Pref 1972 (*76*)	Totton	124 0	109 3	4 7	1 0		1972
Kamata 1972 (*33*)	Hiroshima	90 0-180 0	70 0-160 0				1972
	Shimane						
	Okayama						
Nagai 1972 (*54*)	Oshima	20 0	190 0				1972
	Nagato	31 0	219 0				1972
	Yanai	12 0	94 0	2 0-4 0			1972
	Assa	33 0	247 0				1972
Takano 1972 (*72*)	Iwate	58 7	78 0	3 6	0 4		1971-1973
Yamanashi Prefecture 1972 (*86*)	Yamanashi rural	10 0-53 0	21 0-81 0	2 0-4 0	1 0-4 0		1972
	urban	7 0-77 0	17 0-75 0	1 0-5 0	0 0-1 0		1972
Matsushima 1972 (*48*)	Nagasaki		1288 0				1972
Hara et al 1972 (*23*)	Gumma	6 0-39 0	7 0-22 0	2 0-12 0			1972
Study group 1972 (*70*)	Tokyo		33 0-440 0	4 0			1972
Inuyama and Takeshita 1973 (*31*)	Shimane	89 4	103 3	5 1			1973
Shimamoto et al. 1973 (*64*)	Matsuyama	65 0	109 0	2 0			1973
Yamada and Sakamoto 1973 (*84*)	Hiroshima	39 0	40 0				1973
Status quo 1974 (*69*)	Saga	40 0	180 0				1974

Materials and Methods

Samples of blood and milk were obtained at random from 29 women 2-4 days after normal delivery. These women had had no known exposure to organochlorine insecticides or PCB's.

Plasma was separated from whole blood and kept at −20° C until analysis. The determination of organochlorine residues in plasma is common among researchers performing routine biological sampling (*12, 30, 49, 51, 74*). The plasma was kept at −20° C until analyzed. Milk was obtained directly in graduated tubes (about 2.5 cc) and kept at −20° C until analyzed. The whole quantity of collected milk was used in the chemical analysis in order to maintain the natural concentration of milk constituents. PCB's and organochlorine insecticides, including DDT and metabolites, dieldrin, γ-BHC, and heptachlor epoxide, were determined in both plasma and milk.

The amounts of organochlorine insecticides and PCB's were expressed in ppm in extracted lipids of plasma and milk, and in whole plasma and whole milk.

Lipids were extracted by a modification of the method of Folch et al. (*17*): 1.5 ml plasma was homogenized with 10 ml of a mixture of 1:1 chloroform/methanol (v/v). For milk, about 2.5 ml was homogenized with 17 ml of the same solvent; the exact quantity of milk was noted in each case. Homogenates were filtered through fat-free paper into centrifuge tubes. For plasma, 1.5 ml water was added; for milk, 7 ml was added. The whole solution was mixed with a stirring rod and afterward centrifuged 2-3 minutes until two separate phases were obtained. The upper phase was removed as completely as possible. The lower phase was transferred into a weight tube and evaporated by a nitrogen flow until constant weight was reached. The figure obtained was a reference point for the calculation of the amount of organochlorine insecticides

and PCB's in the extracted lipids. Organochlorine insecticides were separated from PCB's using the Armour and Burke method of chromatography on silicic-acid/celite column (*5*). Extracted lipids were dissolved in 20 ml petroleum ether and allowed to pass through the column. PCB's were obtained in the eluate. Organochlorine insecticides were eluted afterward with 20 ml of a mixture of 1 percent acetonitrile, 19 percent hexane, and 80 percent methylene chloride. Each of the two eluates was concentrated to a volume of 0.5 ml. Organochlorine insecticide and PCB levels were determined by gas chromatography with an electron-capture detector and a spiral glass column, 6 feet by 4 mm, containing a mixture of equal parts of 15 percent QF-1 and 10 percent DC-200 on chromosorb WHP, 80-100 mesh for PCB's and 5 percent QF-1 on chromosorb WHP, 80-100 mesh for organochlorines.

Compounds used as standards were Aroclor 1254 and a mixture of pure organochlorine insecticides: *p,p'*-DDT, *p,p'*-TDE (DDD), *p,p'*-DDE, *o,p'*-DDT, *o,p'*-TDE, *o,p'*-DDE, γ-BHC, dieldrin, and heptachlor epoxide.

The plasma sample from one donor had a very high level of PCB's; this sample was not included in the statistical processing of PCB residues.

Results and Comments

Lipids extracted from plasma had a narrower range of values than had those extracted from milk.

Milk had a higher proportion of lipids than had plasma: 15.0 g/liter compared to 5.3 g/liter. For individual cases there was no correlation between the amount of lipids extracted from plasma and the amount from milk. Among women with low lipids in plasma the quantity of lipids in milk varied widely.

Ranges, mean values, standard deviations, and percentages of lipids extracted from plasma and milk appear in Table 7.

TABLE 7. *Lipids extracted from human plasma and milk for organochlorine insecticide and PCB analyses, Israel*

Samples	No. cases	Extracted Lipids		
		Range	g/liter Mean ± SD	%
Plasma	29	2.6- 8.4	5.28 ± 1.32	100
Milk	29	5.8-32.8	14.99 ± 7.78	284

The amount of fat in human milk is generally related to its proportions in the diet. The fat content of human milk has proved greater in women from nonfarming families than in those from farming families (*56*).

Tables 8-13 show mean levels of organochlorine insecticides (n:29) and PCB's (n:28) in whole plasma and milk, and in their extracted lipids.

The concentration of organochlorine insecticides was higher in extracted lipids of plasma than in those of milk: ΣDDT, 15.12 ppm versus 5.77 ppm; γ-BHC, 3.00 ppm versus 0.86 ppm; dieldrin, 2.01 ppm versus 0.58 ppm; heptachlor epoxide, 2.76 ppm versus 0.72 ppm ($p<0.01$) (Table 8). Concentrations of ΣDDT in whole plasma and milk were similar: 74 ppb versus 72 ppb. Gamma-BHC, dieldrin, and heptachlor epoxide had higher values in plasma: 15 ppb versus 10 ppb, 10 ppb versus 7 ppb, and 14 ppb versus 9 ppb, respectively ($p<0.01$) (Table 8).

The mean value of total PCB's was slightly higher in extracted lipids of plasma than in extracted lipids of milk; the difference was not statistically significant. Individual PCB compounds represented by peaks 11, 13, and 14 appeared in milk but there were no detectable amounts in plasma. The percentages of individual PCB compounds were similar for plasma and milk, with the exception of peak 6 which was higher in plasma ($p<0.01$), and peaks 2, 3, and 9 which were higher in milk (Table 9).

Whole plasma contained smaller quantities of total PCB's than did whole milk: 19.3 ppb versus 44.2 ppb ($p<0.01$). The statistical evaluation of individual PCB's showed

TABLE 8. *Organochlorines in human plasma and milk, Israel—1975*

Compound	Residues, ppm			
	Extracted Lipids		Whole Plasma and Milk	
	Plasma (Mean ± SD)	Milk (Mean ± SD)	Plasma (Mean ± SD)	Milk (Mean ± SD)
p,p'-DDT	2.6776 ± 1.5328	0.9724 ± 0.4893	0.0133 ± 0.0073	0.0122 ± 0.0056
p,p'-DDD	1.7788 ± 0.9220	0.8048 ± 0.4585	0.0087 ± 0.0037	0.0099 ± 0.0044
p,p'-DDE	3.9718 ± 1.8739	1.8139 ± 0.9026	0.0195 ± 0.0078	0.0217 ± 0.0073
o,p'-DDT	2.2319 ± 1.3544	0.6143 ± 0.3903	0.0107 ± 0.0058	0.0073 ± 0.0044
o,p'-TDE	1.5158 ± 1.3479	0.4818 ± 0.3613	0.0072 ± 0.0058	0.0060 ± 0.0048
o,p'-DDE	2.2327 ± 0.8842	0.7626 ± 0.4387	0.0112 ± 0.0040	0.0095 ± 0.0036
γ-BHC	3.0044 ± 1.3858	0.8607 ± 0.3713	0.0147 ± 0.0057	0.0101 ± 0.0035
Dieldrin	2.0104 ± 1.0886	0.5806 ± 0.3132	0.0099 ± 0.0051	0.0070 ± 0.0077
Heptachlor Epoxide	2.7601 ± 1.3366	0.7177 ± 0.4824	0.0136 ± 0.0057	0.0091 ± 0.0045
Total *p,p'*-DDT	8.8809 ± 4.1174	3.7881 ± 1.8980	0.0437 ± 0.0178	0.0467 ± 0.0165
Total *o,p'*-DDT	6.2349 ± 3.1287	1.9776 ± 1.0950	0.0304 ± 0.0127	0.0249 ± 0.0110
ΣDDT	15.1158 ± 7.2114	5.7738 ± 2.8220	0.0740 ± 0.0294	0.0717 ± 0.0250

TABLE 9 *PCB's in human plasma and milk, Israel—1975*

	Residues, ppm			
	Extracted Lipids		Whole Product	
Peaks	Plasma (Mean ± SD)	Milk (Mean ± SD)	Plasma (Mean ± SD)	Milk (Mean ± SD)
1	0.0609 ± 0.2149	0.0316 ± 0.0959	0.0003 ± 0.0010	0.0003 ± 0.0010
2	0.0809 ± 0.3167	0.1337 ± 0.6949	0.0004 ± 0.0016	0.0010 ± 0.0053
3	0.0499 ± 0.1414	0.0707 ± 0.3174	0.0002 ± 0.0006	0.0005 ± 0.0024
4	0.0822 ± 0.2412	0.0818 ± 0.2177	0.0005 ± 0.0045	0.0013 ± 0.0026
5	0.2469 ± 0.3691	0.1868 ± 0.3485	0.0013 ± 0.0020	0.0031 ± 0.0048
6	2.1224 ± 1.1710	0.9904 ± 1.1188	0.0103 ± 0.0050	0.0124 ± 0.0120
7	— —	0.0254 ± 0.1319	— —	0.0005 ± 0.0026
8	0.3146 ± 0.5616	0.3084 ± 0.5256	0.0016 ± 0.0028	0.0050 ± 0.0077
9	0.2627 ± 0.3130	0.4341 ± 0.7074	0.0013 ± 0.0014	0.0065 ± 0.0089
10	0.7321 ± 0.6899	0.4694 ± 0.5705	0.0033 ± 0.0026	0.0069 ± 0.0075
11	— —	0.0631 ± 0.1303	— —	0.0014 ± 0.0032
12	— —	— —	— —	— —
13	— —	0.1931 ± 0.1900	— —	0.0032 ± 0.0040
14	— —	0.1011 ± 0.1503	— —	0.0019 ± 0.0035
Total	3.9884 ± 2.4448	3.1008 ± 3.0502	0.0193 ± 0.0126[1]	0.0442 ± 0.0412[1]

[1] $p < 0.01$

TABLE 10. *Organochlorine levels in human whole plasma and milk by age, Israel—1975*

		Residues, ppb				
Sample	Age, yr	Σ DDT	γ-BHC	Dieldrin	Heptachlor Epoxide	PCB's
Plasma	20-29	63.6[1]	13.4	8.3[2]	12.2	21.1
	30-39	89.2[1]	16.3	12.4[2]	15.8	16.0
Milk	20-29	73.5	10.2	7.0	9.8	56.4[1]
	30-39	64.0	9.4	6.6	7.2	18.2[1]

[1] $p < 0.05$
[2] $p < 0.01$

TABLE 11. *Ratio of organochlorine residues in human whole milk : plasma by age, Israel—1975*

Age, yr	Σ DDT	γ-BHC	Dieldrin	Heptachlor Epoxide	PCB's
20-29	115.57	76.12	84.34	80.33	267.29
30-39	71.75	57.67	53.23	45.57	113.75

TABLE 12. *Organochlorine levels in human whole plasma and milk by weight, Israel, 1975*

		Residues, ppb				
Sample	Weight, kg	Σ DDT	γ-BHC	Dieldrin	Heptachlor Epoxide	PCB's
Plasma	Over 72	72.9	15.5	8.5	14.1	18.1
	Under 63	62.8	11.6	7.9	10.3	15.9
Milk	Over 72	67.8[1]	9.2[1]	6.0[2]	7.6	24.1
	Under 63	92.5[1]	12.6[1]	8.7[2]	12.0	66.1

[1] $p < 0.05$
[2] $p < 0.01$

TABLE 13. *Ratio of organochlorine residues in human whole milk : plasma by weight, Israel—1975*

Weight, kg	Σ DDT	γ-BHC	Dieldrin	Heptachlor Epoxide	PCB's
Over 72	93.0	59.3	70.6	53.9	133.14
Under 63	147.3	108.2	110.1	116.5	415.72

differences for the compound represented by peak 10 ($p < 0.05$) (Table 9). A larger proportion of organochlorine insecticides in milk than in plasma was also reported (75).

Average organochlorine levels reported here are rather low compared with those reported in studies from 10 other nations (Table 1).

Mean levels of organochlorines in whole plasma were lower in the younger age group of women sampled: Σ DDT, 63.6 ppb versus 89.2 ppb ($p < 0.05$); γ-BHC, 13.4 ppb versus 16.3 ppb, dieldrin, 8.3 ppb versus 12.4 ppb ($p < 0.01$), and heptachlor epoxide, 12.2 ppb versus 15.8 ppb (Table 10). All organochlorines were excreted in milk in a higher proportion among the younger women (Table 10). The ratios of organochlorine insecticides and PCB's in whole milk to those in plasma of the two age groups are presented in Table 11. Higher concentrations of organochlorine insecticides and PCB's are excreted in milk by the younger women, indicating that their offspring are exposed to greater danger than are those of the older mothers.

This finding contradicts that of Knoll and Jayarman (36) who maintain that organochlorines in milk increase with age of the donor.

Persons weighing over 72 kg had higher mean organochlorine insecticide and PCB levels in plasma than had those

under 63 kg. These differences are not statistically significant (Table 12).

Organochlorine insecticide and PCB concentrations in the milk of persons heavier than 72 kg were lower than in the group which weighed less than 63 kg: Σ DDT, 67.8 versus 92.5 ppb; ($p<0.05$); γ-BHC, 9.2 versus 12.6 ppb ($p<0.05$); dieldrin, 6.0 versus 8.7 ppb ($p<0.01$); heptachlor epoxide, 7.6 versus 12.0 ppb; and PCB's, 24.1 versus 66.1 ppb (Table 12). The ratios of organochlorine insecticides and PCB's in whole milk to those in plasma among the two weight groups are presented in Table 13. It is obvious that smaller concentrations of organochlorine insecticides and PCB's are excreted by women weighing over 72 kg than by those under 63 kg.

Such data call for suggestions of measures to prevent the occurrence of high levels of organochlorine insecticides and PCB's in human milk. Banning some organochlorine compounds in countries where residues in milk were high has proved effective.

Special care for the nutrition and environment of the mother during pregnancy and lactation may be beneficial. Mothers could avoid fat food, which contains larger quantities of organochlorine insecticides and PCB's and sea fish, which contain large quantities of PCB's. Heavily polluted work environments should be avoided. Abstention from the use of insecticides or other noxious compounds in households is advisable.

Although breast feeding is generally considered desirable, infants of mothers heavily exposed to chemical hazards should not be breast-fed.

Periodic surveys of organochlorine levels in mother's milk may provide a base for establishing preventive measures in the future.

LITERATURE CITED

(1) Acker, L., and E. Schulte. 1971. On the occurrence of BHC and PCB along with organochlorine insecticides in human adipose tissue and in human milk. Ernaehrungsforschung 16(4):559-567.

(2) *Adamovic, V. M., M. Hus, and V. Djukic. 1969.* Cumulation of organochlorine insecticides in the organism of the inhabitants of Serbia. Second Yugoslav Symp. on Pesticides, Zagreb.

(3) *Adamovic, V., B. Sokic, and O. Petrovic. 1971.* On factors influencing the occurrence of organochlorine insecticides in newborns. Ernaehrungsforschung 16(4):579-585

(4) *Allen J. R. 1975.* Response of Primates to PCB Exposures. Fed. Proc. 34(8):1675-1679.

(5) *Armour, J. A., and J. A. Burke. 1970.* Method for separating polychlorinated biphenyls from DDT and its analogs. J. Assoc. Off. Anal. Chem. 53(4):761-768.

(6) *1972.* BHC and DDT residues in human milk on the decline in Japan. Pestic. Business 56:458.

(7) *Bjerk, J. E. 1972.* DDT and polychlorinated biphenyl residues in human material in Norway. Tidsskr. Nor. Laegefor. 92(1):15-19.

(8) *Bogusz, M. 1972.* Organochlorine insecticides: the need for a realistic evaluation of risk. Pol. Tyg. Lek. 27(17):637-640.

(9) *Curley, A., and R. Kimbrough. 1969.* Chlorinated hydrocarbon insecticides in plasma and milk of pregnant and lactating women. Arch. Environ. Health 18(2):156-164.

(10) *Damaskin, V. I. 1965.* O stepeni kumuliatsii DDT v organizme cheloveka pri postuplenii s pishchevymi produktami i ego toksicheskom vozdeistvii [the extent of accumulation of DDT in the human body due to its presence in food and its toxic effect]. Gig Sanit. 30:109.

(11) *Denes, A., and R. Tarjan. 1969.* The effect of accumulation of DDT in the human body due to its presence in food and its toxic effects. Egeszsegtudomany 13(3):212-217.

(12) *Edmundson, W. F., J. E. Davies, and M. Cranmer. 1970.* DDT and DDE in blood and DDA in urine of men exposed to 3 percent DDT aerosol. U.S. Public Health Rep. 85(5):457-463.

(13) *Egan, H., R. Goulding, J. Roburn, and J. O'G. Tatton. 1965.* Organochlorine pesticide residues in human fat and human milk. Br. Med. J. 11(2):66-69.

(14) *Engst, R., and R. Knoll. 1971.* DDT and DDE residues in human milk. Ernaehrungsforschung 16(4):569-575.

(15) *Engst, R., and R. Knoll. 1972.* Organochlorine residues in human milk. Pharmazie 27(8):526-531.

(16) *Farvar, M. T. 1972.* Ecological implications of insect control in Central America: Agriculture, public health and development. Diss. Abstr. Int. 33(5):1939 B.

(17) *Folchi-Pi, J., M. Lees, and G. H. Sloane Stanley. 1957.* A simple method for isolation and purification of the total lipids from animal tissues. J. Biol. Chem. 226(1):497-509.

(18) *Gejvall, T., S. Jensen, and G. Lofroth. 1972.* Organochlorine Compounds in Some Ghanaian Human Milk samples. University of Stockholm, Sweden (preliminary draft).

(19) *Graca, J., S. Fernandes, and H. C. Mourao. 1974.* Organochlorine insecticide residues in human milk in Portugal. Pestic. Monit. J. 8(3):148-156.

(20) *Gracheva, G. V. 1969.* The possibility of DDT accumulation in the organism of persons not having occupational contact with it. Faktory Vneshn. Sredy Ikh. Znach. Zdorov'ya Naselenıya 1(1):125-129.

(21) *Gracheva, G. V. 1970.* Vydelenie DDT s grudnym molokom kormiashchikh zhenshchin, ne imevskikn professional'noge konakata s nim [DDT secretion in the breast milk of nursing women not having occupational contact with it]. Vopr. Pitan. 29(6):75-78.

(22) *Hagyard, S. B., W. H. Brown, J. W. Stull, F. M. Whiting, and S. R. Kemberling. 1973.* DDT and DDE content of human milk in Arizona. Bull. Environ. Contam. Toxicol. 9(3):169-172.

(23) *Hara, Y., H. Masago, K. Karino, I. Takiyima, I. Fukushima, S. Tuju, I. Tano, I. Kobayashi, O. Kurihara, K. Sudo, and I. Muto. 1972.* On pesticide residues in foods, first report. Organochlorine pesticide residues. Ann. Rep. Gumma Prefect. Inst. Public Health Cent. Study Environ. Pollut. 4:83-86.

(24) *Havashi, M. 1972.* Pesticide pollution of mother's milk. J. Jpn. Med. Assoc. 68(12):1281-1282.

(25) *Havashi, M. 1972.* Pollution of mother's milk by organochlorine insecticides. Jpn. J. Public Health 19(9):437-441.

(26) *Havashi, M. 1974.* Mother's milk and environmental pollution. J. Pediatr. Pract. 37(9):1113-1119.

(27) *Heyndrickx, A., and R. Maes. 1969.* The excretion of chlorinated hydrocarbon insecticides in human mother's milk. J. Pharm. Belg. 24(9-10):459-463.

(28) *Hidaka, K., T. Ohe, and K. Fujiwara. 1972.* PCB and organochlorine pesticides in mother's milk. Prog. Med. 82(8):519-520.

(29) *Hornabrook, R.W., P. G. Dyment, E. P. Gomes, and J. S. Wiseman. 1972.* DDT residues in human milk from New Guinea natives. Med. J. Aust. 25(1):1297-1300.

(30) *Inoue, Y., S. Abe, H. Esaki, and M. Takamatsu. 1973.* Polychlorinated biphenyls in human blood. Kurume Med. J. 29(2):83-86.

(31) *Inuyama, Y., and T. Takeshita. 1973.* Survey of pesticide residues and PCB's in mother's milk and human adipose tissue. Ann. Rep. Shimane Prefect. Inst. Pub. Health Environ. Pollut. 15:37-39.

(32) *Juszkiewicz, T., T. Szprengier, and T. Radomanski. 1975.* Mercury content of human milk. Pol. Tyg. Lek. 30(9):365-366.

(33) *Kamata, I. 1972.* Hygienic studies on pesticide residues, part 3. Determination of organochlorine pesticide residues in human tissues and other samples. Jpn. J. Hyg. 27(5):439-443.

(34) *Kato, K., I. Yamada, S. Watanabe, Y. Wado, et al. 1971.* Analyses of residual pesticides in vegetables, cow's milk and mother's milk. Annu. Rep. Kanagawa Prefect. Inst. Public Health 21:85-92.

(35) *Kawai, Y., Y. Hori, Y. Nigawa, I. Yamamoto, M. Kitayama, and K. Mori. 1973.* On the pollution of mother's milk by pesticides and PCB's in Hokkaido. J. Food Hyg. Soc. Jpn. 14(3):302-303.

(36) *Knoll, B., and S. Javaraman. 1973.* Organochlorine pesticide residues in human milk. Z. Gesamte Hyg. 19(1):43-45.

(37) *Knoll, B., and S. Javaraman. 1973.* On the contamination of human milk with chlorinated hydrocarbons. Nahrung 17(5):599-615.

(38) *Knoop, L. A. 1974.* Breast milk: a source of more than nutrition for the neonate. Clin. Toxicol. 7(1):69-82.

(39) *Kojima, S., M. Saito, H. Konno, and K. Ozowa. 1971.* Results of investigation of organochlorine pesticide residues in mother's milk and in blood of the mothers. Rep. Akita Prefect. Inst. Public Health 16:65-68.

(40) *Komarova, L. I. 1970.* DDT excretion with the breast milk and its effect on the body of the mother and child. Pediatr. Akush. Ginekol. 35(1):19-20.

(41) *Kontek, M., S. Kubacki, S. Paradowski, and B. Wierzchowiecka. 1971.* Determination of organic chlorine pesticides in human milk. Pediatr. Pol. 46(2):183-188.

(42) *Kroger, M. 1972.* Insecticide residues in human milk. J. Pediatr. 80(3):401-405.

(43) *Laug, E. P., F. M. Kunze, and C. S. Prickett. 1951.* Occurrence of DDT in human fat and milk. Arch. Ind. Hyg. 3(3):245-246.

(44) *Lofroth, G. 1971.* Who cares about DDT? Ecologist 1(17):8-9.

(45) *Luquet, F. M., J. Gours, J. Casalis. 1974.* Contamination of human milk by organochlorine pesticide residues in France. Aliment. Vie 62(1):40-69.

(46) *Mandroiu, V., and M. Jordachescu. 1971.* Determination of the BHC content in the human organism. Igiena 20(6):363-364.

(47) *Matsuda, H., T. Shimamoto, T. Ito, and K. Ogida. 1971.* On the analytical results of organochlorine pesticide residues in mother's milk. Rep. Ehime Prefect. Hyg. Lab. 33:43-48.

(48) *Matsushima, S. 1972.* Pollution of food by agricultural chemicals and the diet. J. Clin. Nutr. 40(5):555-563.

(49) *Mick, D. L., K. R. Long, and P. Bonderman. 1971.* Aldrin and dieldrin in the blood of pesticide formulators. Am. Ind. Hyg. Assoc. Sept. 72, pp. 94-99.

(50) *Miller, G. J., and J. A. Fox. 1973.* Chlorinated hydrocarbon pesticide residues in Queensland human milk. Med. J. Aust. 2(6):261-264.

(51) *Morgan, D. P., C. C. Roan, and E. H. Pischal. 1972.* Transport of DDT, DDE, and dieldrin in human blood. Bull. Environ. Contam. Toxicol. 8(6):321-326.

(52) *Mori, Y., K. Ito, K. Sakurai, M. Mori, and T. Sudo. 1971.* On the results of investigation of milk pollution by pesticide residues. Ann. Rep. Mie Prefect. Inst. Public Health 18:59-68.

(53) *Musial, C. J., O. Hutzinger, V. Zitko, and J. Crocker. 1974.* Presence of PCB, DDE and DDT in human milk in the provinces of New Brunswick and Nova Scotia, Canada. Bull. Environ. Contam. Toxicol. 12(3):258-267.

(54) *Nagai, I. 1972.* Residues of organochlorine pesticides in mother's milk in Yamaguchi Prefecture. Ann. Rep. Yamaguchi Prefect. Res. Inst. Public Health 14:93-94.

(55) *Narafu, T. 1971.* Pollution of cow's milk and human milk by BHC. J. Clin. Nutr. 39(1):26-34.

(56) *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.

(57) *Nishimoto, T., M. Uveta, S. Tane, and K. Okikazawa. 1972.* Organochlorine pesticide residues and PCB's in breast milk. Progr. Med. 82(9):974-975.

(58) *Nishimura, H. 1973.* Teratogenic substances. Int. Chem. Eng. 13(4):774-780.

(59) *Olszyna-Marzys, A. E., M. De Campos, M. Taghi Farvar, and M. Thomas. 1973.* Chlorinated pesticide residues in human milk in Guatemala. Bol. Sanit. Panamer. 74:93-107.

(60) *Osaka Prefect. 1973.* The countermeasures for damages due to agricultural pesticides. 2nd item of lst clause of Chapter XII. A draft of the plan of Environmental Administration, pp. 392-395.

(61) *Oura, H., H. Kobayashi, T. Oura, I. Senda, and K. Kubota. 1972.* On the pollution of human milk by PCB's and organochlorine pesticides. J. Jpn. Assoc. Rural Med. 21(2):300-301.

(62) *Quinby, G. E., J. F. Armstrong, and W. F. Durham. 1965.* DDT in human milk. Nature 207(4998):726-728.

(63) *Savage, E. P., J. D. Tessari, J. W. Malberg, H. W. Wheeler, and J. R. Bagby. 1973.* Organochlorine pesticide residues and polychlorinated biphenyls in human milk, Colorado—1971-72. Pestic. Monit. J. 7(1):1-5.

(64) *Shimamoto, T., H. Matsueda, M. Yoshinouchi, E. Okinaga, K. Mori, S. Yamatake, S. Nakajima, and K. Aihara. 1973.* Results of a survey on PCB and organochlorine pesticide residues in mother's milk. Ann. Rep. Ehime Prefect. Inst. Hyg. Sci. 35:71-73.

(65) *Shimizu, S. 1974.* Results of pursuing investigation on pesticide residues in Saga Prefecture. Jpn. J. Public Health 21(4):239-245.

(66) *Shirakawa, M. 1974.* On the results of investigation on the pesticide residues in the milk from lactating women of coastal areas in Wakayama Prefecture. Jpn. J. Hyg. 29(1):94.

(67) *Siyali, D. S. 1973.* Polychlorinated biphenyls, hexachlorobenzene and other organochlorine pesticides in human milk. Med. J. Aust. 2(17):815-818.

(68) *Stacey, C. I., and B. W. Thomas. 1975.* Organochlorine pesticide residues in human milk, Western Australia—1970-71. Pestic. Monit. J. 9(2):64-66.

(69) *1974.* The status quo of pollution by pesticides and its countermeasures. Status quo of environmental pollution and its countermeasures in Saga Prefecture. Saga Prefectural Office, pp 464-480.

(70) *Study Group: National Inst. of Hygienic Sci., Setayaga, Tokyo, Japan. 1972.* Studies on the analysis of pesticide residues in food (VII). Organochlorine pesticide residues in mother's milk. J. Food Hyg. Soc. Jpn. 13:422-437.

(71) *Suzuki, Y., H. Sugaya, and S. Sasaki. 1973.* Results of three years' tracing investigation of organochlorine pesticide residues in humans. J. Jpn. Assoc. Rural Med. 22(3):276-277.

(72) *Takano, H. 1972.* Results of inspection of pesticide residues in mother's milk and market milk. Annu. Rep. Iwate Inst. Public Health 15:81-91.

(73) *Takeshita, T., and Y. Inuyama. 1970.* Organochlorine residues in mother's milk and blood. Annu. Rep. Shimane Prefect. Inst. Public Health 12:27-28.

(74) *Tokutsu, K., T. Koyama, and T. Yokoyama. 1970.* Pesticide residue in mother's milk and plasma in Wakayama Prefecture. Annu. Rep. Wakayama Prefect. Inst. Public Health 19:59-62.

(75) *Tottori Prefectural Hygiene Research Institute, Tottori, Japan. 1971.* Tests and investigations on pesticide residues in mother's milk and blood. Rep. Tottori Prefect. Hyg. Res. Inst. 11:19.

(76) *Tottori Prefectural Hygiene Research Institute, Tottori, Japan. 1972.* Tests and investigations of pesticide residues in mother's milk. Rep. Tottori Prefect. Hyg. Res. Inst. 12:22.

(77) *Tuinstra, L. G. M. 1971.* Organochlorine insecticide residues in human milk in the Leiden region. Ned. Melk. Zuiveltijdschr. 25(1):24-32.

(78) *Unterman, W. M., and E. Sirghie. 1969.* Igiena Buc. 18(4):221. Ref. in Dairy Sci. Abstr. 32(3):192 (1970).

(79) *West, Irma. 1964.* Pesticides as contaminants. Arch. Environ. Health 9(5):626-633.

(80) *Westoo, G. 1974.* Changes in the levels of environmental pollutants (Hg, DDT, dieldrin, PCB) in some Swedish foods. Ambio 3(2):79-83.

(81) *Westoo, G., and K. Noren. 1968.* Nordforsk Biocid—Information 14(10):6-7.

(82) *Westoo, G., K. Noren, and M. Andersson. 1970.* The levels of organochlorine pesticides and polychlorinated biphenyls in margarine, vegetable oils and some foods of animal origin on the Swedish market in 1967-69. Var Foda 22(2-3):9-31.

(83) *Wilson, D. J., D. J. Locker, C. A. Kitzen, J. T. Watson, and W. Schaffner. 1973.* DDT concentrations in human milk. Am. J. Dis. Child. 125(6):814-817.

(84) *Yamada, T., and Y. Sakamoto. 1973.* Results of survey of pesticide residues in mother's milk and soil. Hiroshima Prefect. Inst. Prevent. Environ. Pollut. Annu. Rep. 3:57-58.

(85) *Yamagishi, T., K. Takeba, C. Fujimoto, K. Morimoto, and M. Haruta. 1972.* On the organochlorine pesticide residues in mother's body and her foetus' body. Rep. Tokyo Pub. 50:44-45.

(86) *Yamanashi Prefect. Inst. for Public Health, Yamanashi, Japan. 1972.* Results of investigation of mother's milk pollution by organochlorine pesticides. Annu. Rep. Yamanashi Prefect. Inst. Public Health 15:20.

Insecticide Residues in Human Milk from Arkansas and Mississippi, 1973-74 [1]

Sandra C. Strassman and Frederick W. Kutz

ABSTRACT

Between September 1973 and February 1974, 57 samples of human milk were collected from women residing in selected areas of Arkansas and Mississippi. Residues of p,p'-*DDT,* p,p'-*DDE,* p,p'-*TDE, β-BHC, dieldrin, heptachlor epoxide, oxychlordane, and* trans-*nonachlor were measured by electron-capture gas chromatography; trace amounts of* o,p'-*DDT and polychlorinated biphenyls were also detected. Additional analytical procedures were employed to confirm the presence of specific residues.*

Introduction

Residues of certain organochlorine insecticides and their transformation products have been found by many investigators in various human components such as adipose tissue, whole blood and blood serum, urine, feces, and milk. Demonstration of pesticide residues and their metabolites in human milk presents a critical health issue from at least two standpoints. First, the residues indicate total body burden of pesticides in the donor mother, providing some measure of lipophilic insecticides stored and accumulating in her body. Second, if the mother breastfeeds the newborn, her milk becomes a major vehicle for exposing the baby to insecticide residues.

Exposure to these chemicals begins in utero by transplacental passage (*1, 7*). After birth, exposure may continue through ingestion, respiration, and absorption through the skin and mucous membranes. Since babies are usually kept in protected environs, ingested food probably presents the major source of exposure to these pollutants.

This paper reports levels of organochlorine pesticide residues and the industrial pollutant, polychlorinated biphenyls (PCB's), detected in milk collected from women residing in selected counties of Arkansas and Mississippi. All information presented was developed by the National Human Monitoring Program for Pesticides of the U.S. Environmental Protection Agency. This program evaluates the exposure to pesticides experienced by the general population of the conterminous United States, and attempts to identify changes and trends when they occur. Details of the program have been reported by Yobs (*11*) and Kutz et al.(5).

Collection and Sampling

Between September 1973 and February 1974, milk was collected from donors residing in specified counties of Arkansas and Mississippi. All milk was analyzed in May 1975 for selected organochlorine insecticides, their transformation products, and PCB's.

Since the original intent of this study was to collect human milk for detection of chlorodioxins, possible contaminants of the herbicide 2,4,5-T (a 2,4,5-trichlorophenoxyacetic acid derivative), the survey design was limited to the collection of milk from women who probably had been exposed to this pesticide. Consequently, counties selected for the project (Figure 1) were those in which rice was grown or which exchanged public services with rice-growing areas of Arkansas and Mississippi where 2,4,5-T was being used or had been used recently.

Milk was collected from lactating mothers during their hospitalization after routine delivery or during postpartum examinations, and from members of cooperating LaLeche League chapters. Information received with each milk sample included the donor's age, race, county and State of residence, date of parturition, and any known pathological conditions. Since the object of the study was to reflect the pesticide burden in milk from the general population of the areas, samples were collected only from healthy women with no known occupational exposure to

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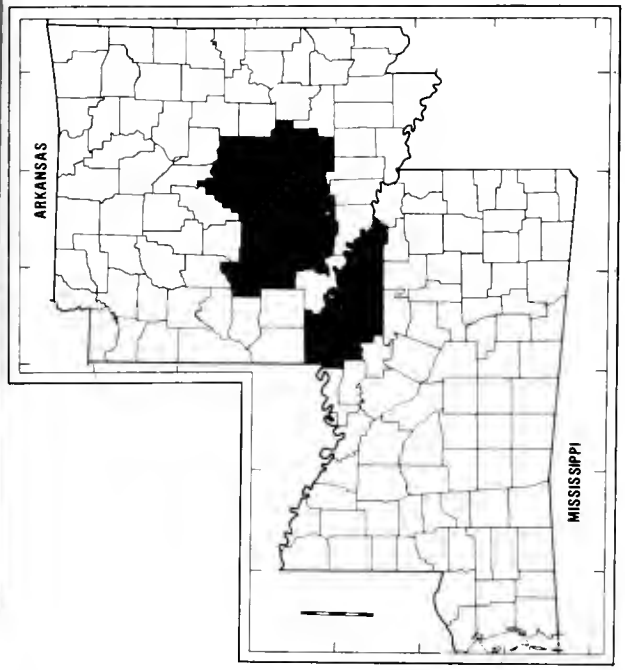

FIGURE 1. *Counties in Arkansas and Mississippi selected for sampling human milk for pesticide residue analysis, 1973-74*

pesticides. All individuals had established area residency; samples were not taken from transient or new residents.

Part of each milk sample was analyzed for organochlorine residues. The remainder is being retained for future chlorodioxin analysis.

Approximately one-half ounce of milk was manually expressed by each participant directly into a clean, pesticide-free glass bottle. Hind milk, which occurs after several minutes of nursing, was requested because of its high percentage of fat. Samples were immediately frozen and stored until analysis.

Chemical Analysis

All analyses were performed by a laboratory under contract to EPA following methods specified by the National Human Monitoring Program for Pesticides. The laboratory was required to maintain external quality-assurance standards.

Residues were extracted by a modification of the procedures described by Curley and Kimbrough (*2*) and Giuffrida et al. (*3*): the lipid was isolated from the milk, pesticides were extracted from the lipid, and the extract was cleaned up. Using the modified Mills-Olney-Gaither procedure (*10*), analysis was limited to determination of the chlorinated hydrocarbons presented in Table 1.

TABLE 1. *Chemicals detectable in human milk*[1]

CHEMICAL	LIMITS OF DETECTABILITY, PPB
o,p'-DDT	20
p,p'-DDT	20
o,p'-DDE	20
p,p'-DDE	10
o,p'-TDE	20
p,p'-TDE	20
α-BHC	10
β-BHC	20
γ-BHC (lindane)	10
δ-BHC	10
Endrin	20
Aldrin	10
Dieldrin	10
Heptachlor	10
Heptachlor epoxide	10
Oxychlordane	20
trans-Nonachlor	20
Hexachlorobenzene	10
Mirex	100
Polychlorinated biphenyls	1000

[1] Using the modified Mills-Olney-Gaither procedure (*10*).

After each sample was thawed and homogenized by a supersonic disintegrator, whole milk was weighed into a clean glass centrifuge bottle. Pre-cleaned glass wool was added to the centrifuge bottle to adhere to all the coarse precipitate of milk solids formed during the subsequent acetone extraction. Contents of the centrifuge bottle were extracted with acetone three times and pooled in a separatory funnel. Solids were separated from the acetone after each extraction by centrifugation. The remaining coarse milk solids were extracted twice with *n*-hexane, and these extracts were combined with acetone extracts in the separatory funnel. The combined *n*-hexane and acetone extracts were washed three times with 2 percent sodium sulfate, dried through an anhydrous sodium sulfate column, and concentrated in a Kuderna-Danish evaporator to approximately 5 ml. The concentrated extract was cleaned up by liquid-liquid acetonitrite partitioning and florisil procedures as described by Thomspon (*10*).

Residues were identified and quantified on a Micro-Tek 220 gas chromatograph equipped with tritium electron-capture detectors using two columns with different resolution characteristics. Column dimensions were 1.5 percent OV-17/1.95 percent QF-1 and 4 percent SE-30/6 percent OV-210. A Coulson electrolytic conductivity detector operated in the chloride mode was used to confirm *p,p'*-DDT and *p,p'*-DDE in every fifth sample (*9*). Results were reported on a whole-milk basis and the percent extractable lipid material was noted for each sample.

The 6 percent florisil fraction of each sample was composited for confirmation of selected pesticide residues by combined gas chromatography / mass spectrometry (GC-MS) and thin-layer chromatography.

Residue data, presented on a whole milk basis, were characterized by calculating the following statistical parameters:

Sample Size—total number of samples analyzed.

Percent Positive—percentage of the total number of samples in which a quantifiable residue of a given pesticide was detected.

Percent Trace—percentage of the total number of samples in which a residue of a given pesticide was reported but could not be quantified.

Extreme Values—highest and lowest values detected.

Arithmetic Mean—calculated using the standard formula.

Mean of Positives—arithmetic mean of residues found at quantifiable levels; reports of zero and trace amounts were excluded.

Residues present in trace amounts were identified on two columns; they could not, however, be quantified. In calculating the arithmetic means, only reports of quantifiable amounts of pesticide residues were considered; reports of trace amounts were treated as zero. Where a trace level represented the minimum value, this was indicated.

Results and Discussion

A demographic summary of the donors of the 57 human milk samples is presented in Table 2. The mean percent extractable lipid is included for each category.

The mean age of the 57 mothers was 27 years. Seventeen donors (29.8 percent) were Negroes; 40 (70.2 percent) were Caucasians. Sampling occurred from 1 to 448 days after delivery; the median postpartum time was 41 days. Lipid material extracted from each milk sample ranged from 0.6 to 8.8 percent, with a mean value of 3.0 percent.

Detected residues of the pesticides and their metabolites presented in Table 3 reflect donors' previous exposure to the chemicals; residues of PCB's represent exposure to these industrial chemicals. PCB's were present in trace amounts, below 1 ppm, in every sample. The presence of the compounds was confirmed in a composite of all extracts by combined GC-MS; hexachlorobiphenyls were the major components.

All milk samples showed evidence of prior exposure to DDT. The Σ DDT equivalent (o,p'-DDT + p,p'-DDT + 1.114 [o,p'-DDE + p,p'-DDE + o,p'-TDE + p,p'-TDE]) is calculated by adjusting the DDE and TDE transformation products of DDT by a molecular-weight-based constant to convert them to an equivalent weight of DDT. Thus the Σ DDT equivalent is a conglomerate figure ex-

TABLE 2. *Demographic summary of donors sampled for insecticide residues in human milk, Arkansas and Mississippi—1973-74*

Geographic Location	No. Samples	Percent Caucasians	Percent Negroes	Mean Age, Yr	Median No. Postpartum Days	Mean Extractable Lipid Material, %
Mississippi	8	12.5	87.5	29.5	4	2.7
Arkansas	49	79.6	20.4	26.6	110	3.0
Combined Survey	57	70.2	29.8	27.0	41	3.0

TABLE 3. *Organochlorine pesticide residues in 57 human whole milk samples, Arkansas and Mississippi—1973-74*

Pesticide	Samples with Residues, %		Residues, ppm			
	Positive	Trace	Arithmetic Mean	Mean of Positives	Extreme Values	
					Minimum	Maximum
Σ DDT equivalent[1]	100.0	0	0.344	0.344	0.02	2.76
p,p'-DDT[2,3]	100.0	0	0.092	0.092	0.01	0.84
p,p'-DDE[2,3]	100.0	0	0.227	0.227	0.01	1.72
β-BHC[4]	36.8	63.2	0.005	0.014	trace	0.01
Dieldrin[4]	28.1	73.9	0.004	0.012	trace	0.05
Heptachlor epoxide[4]	35.1	64.9	0.004	0.012	trace	0.03
Oxychlordane[2]	45.6	54.4	0.005	0.012	trace	0.02
trans-Nonachlor[4]	14.1	86.0	0.001	0.010	trace	0.01
PCB's[2,5]	100.0	100.0	trace	trace	trace	trace

[1] Σ DDT equivalent = o,p'-DDT + p,p'-DDT + 1.114 (o,p'-DDE + p,p'-DDE + o,p'-TDE + p,p'-TDE)
[2] Residues confirmed by combined gas chromatography—mass spectrometry
[3] Confirmation accomplished by Coulson conductivity conductor and thin-layer chromatography
[4] Residue levels were below instrument sensitivity and could not be confirmed
[5] Presence of PCB's represents exposure to these industrial chemicals

pressing total body burden of these chemicals as DDT. This equivalent, with a mean of 0.344 ppm, represents the insecticide found in the greatest concentration.

In the milk analyzed, 73.7 percent of the Σ DDT equivalent burden was found as DDE. Of the DDT transformation products found in the human milk, *p,p'*-DDT and *p,p'*-DDE were apparent at mean levels of 0.092 ppm and 0.227 ppm, respectively. The presence of these metabolites was confirmed by Coulson electrolytic conductivity detector, thin-layer chromatography, and combined GC-MS. There was a single observation of *p,p'*-TDE at 0.02 ppm. Trace quantities of *o,p'*-DDT were present in all 57 samples; *o,p'*-TDE and *o,p'*-DDE were not detected.

The presence of β-BHC residues indicate exposure to insecticides containing benzene hexachloride. This chemical appeared in at least trace amounts in all milk analyzed at a mean value of 0.005 ppm. The α, γ (lindane), and δ isomers of BHC were not detected.

Since aldrin is quickly epoxidized to dieldrin, dieldrin residues signify exposure to either or both of these pesticides. Quantifiable residues of dieldrin were detected in 28.1 percent of the samples at a mean concentration of 0.004 ppm.

Oxychlordane is a major mammalian metabolite of the insecticides chlordane and heptachlor. Along with heptachlor epoxide and *trans*-nonachlor, which also indicate exposure to heptachlor and chlordane, it was found in quantifiable or trace amounts in every milk sample analyzed. Oxychlordane and heptachlor epoxide were present at mean levels of 0.005 ppm and 0.004 ppm, respectively. The compound *trans*-nonachlor, one of several that comprise technical chlordane and technical heptachlor, was first reported in human adipose tissue in a recent study by Kutz et al. (*4*). This compound had a mean level of 0.001 ppm in the human milk sampled. Oxychlordane was qualitatively confirmed by combined GC-MS; levels of heptachlor epoxide and *trans*-nonachlor were below instrument sensitivity and, consequently, could not be confirmed.

To the authors' knowledge, this is the first report of the occurrence of oxychlordane and *trans*-nonachlor in human milk. Save et al. (*8*) and Curley and Kimbrough (*1,2*) have reported residue levels of heptachlor epoxide, dieldrin, BHC, DDT, and PCB's.

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LITERATURE CITED

(*1*) *Curley, A., M. F. Copeland, and R. D. Kimbrough. 1969.* Chlorinated hydrocarbon insecticides in organs of stillborn and blood of newborn babies. Arch. Environ. Health 19(5):628-632.

(*2*) *Curley, A., and R. Kimbrough. 1969.* Chlorinated hydrocarbon insecticides in plasma and milk of pregnant and lactating women. Arch. Environ. Health 18(2):156-164.

(*3*) *Giuffrida, L., D. C. Bostwick, and N. F. Ives. 1966.* Rapid cleanup techniques for chlorinated pesticide residues in milk, fats, and oils. J. Assoc. Off. Anal. Chem. 49(3):634-638.

(*4*) *Kutz, F. W., W. Sovocool, S. Strassman, and R. G. Lewis. 1977. trans*-Nonachlor residues in human adipose tissue. Bull. Environ. Contam. Toxicol. 16(1):9-14.

(*5*) Kutz, F. W., A. R. Yobs, W. G. Johnson, and G. B. Wiersma. 1974. Pesticide residues in adipose tissue of the general population of the United States, FY 1970 survey. Bull. Soc. Pharmacol. Environ. Pathol. 2(3):4-10.

(*6*) *Morgan, D. P., and C. D. Roan. 1971.* Absorption, storage, and metabolic conversion of ingested DDT and DDT metabolites in man. Arch. Environ. Health 22(3):309-315.

(*7*) *O'Leary, J. A., J. E. Davies, W. F. Edmundson, and G. A. Reich. 1970.* Transplacental passage of pesticides. Am. J. Obstet. Gynecol. 107(1):65-68.

(*8*) *Savage, E. P., J. D. Tessari, J. W. Malberg, W. H. Wheeler, and J. R. Bagby. 1973.* Organochlorine pesticide residues and polychlorinated biphenyls in human milk, Colorado—1971-72. Pestic. Monit. J. 7(1):1-5.

(*9*) *Su, G. C., and H. A. Price. 1973.* Element specific gas chromatographic analyses of organochlorine pesticides in the presence of PCB's by selective cancellation of interfering peaks. J. Agric. Food Chem. 21(6):1099-1102.

(*10*) *Thompson, J. F. (ed.). 1972.* Analysis of Pesticide Residues in Human and Environmental Samples. Prepared by EPA Environmental Toxicology Division, Research Triangle Park, N.C.

(*11*) *Yobs, A. R. 1971.* The National Human Monitoring Program for Pesticides. Pestic. Monit. J. 5(1):44-46.

RESIDUES IN FOOD AND FEED

Pesticide and Other Chemical Residues in Total Diet Samples (X)

D. D. Manske and R. D. Johnson[1]

ABSTRACT

Since 1964 the Food and Drug Administration Total Diet study has reported residues of pesticides and other chemicals ingested in the diet of a young adult male, statistically the Nation's largest eater. During the tenth year of the study, pesticide residues remained at the relatively low levels previously reported. Thirty market baskets were collected in 30 cities which ranged in population from less than 50,000 to 1,000,000 or more. Averages and ranges of residues are reported from August 1973 through July 1974 by food class. Individual items in the dairy and meat composites in four market baskets were analyzed for pesticides; results are included. Data for lead, cadmium, selenium, mercury, arsenic, and zinc are also included. Results of recovery studies within various classes of residues are also presented.

Introduction

The Food and Drug Administration Total Diet Program (*10*), sometimes called the Market Basket study, began with a program intended for surveillance of fission products from atmospheric tests of thermonuclear weapons in May 1961. The program was quickly extended to pesticides and certain nutrients (*10*). Although some changes have been made in sampling frequency, areas sampled, analytical methods used, and types of residues sought, the program has continued in essentially the same form to the present. A market basket of food representing the basic 2-week diet of a 16- to 19-year-old male, statistically the Nation's largest eater, is collected in each of several geographic areas. The various foods are prepared in the manner in which they would normally be served and eaten. Foods in each of 12 broad classes are composited into a slurry and analyzed for the presence of organochlorine pesticides, organophosphorous pesticides, carbaryl, herbicides, certain metals, and polychlorinated biphenyls (PCB's). Methodology includes atomic absorption spectroscopy, fluorometry, gas chromatography, thin-layer chromatography, and established extraction and cleanup techniques. Conditions, techniques, and limits of quantitation have been described in previous reports of the series (*1-6, 13-15, 19*. Also: H. K. Hundley and J. C. Underwood, Food and Drug Administration, 1970; personal communication). Amounts and types of residues found from June 1964 through July 1973 have also been described in earlier reports (*7-9, 11, 12, 15-18*). The present report presents results obtained from August 1973 through July 1974. Samples were collected in 30 different grocery markets in 30 different cities.

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Results

During this reporting period 1,613 residues of 42 different compounds were found in the 360 composites examined. In the previous reporting period, 1,729 residues of 40 different compounds had been found. The 42 different residues found are listed in decreasing order of frequency in Table 1. In Table 2, the frequency of occurrence of these residues is broken down according to food class. Table 3 gives the levels of the chemical residues by food class. The average stated in Table 3 is based on 30 composites examined; any trace residues have not been included in calculating the average. For this reason, an average value reported as "T" can be well below the detection limits of the method for that compound.

The most common residues and their maximum levels are disuessed below for each of the 12 classes of food composites. No findings have been corrected for recoveries obtained in recovery experiments. A summary of recovery studies appears in Table 4.

DAIRY PRODUCTS

Organochlorine compounds were the most frequently found residues in dairy products. The most common organochlorines were dieldrin, 0.0050 ppm; BHC, 0.0030 ppm; DDE, 0.010 ppm; and heptachlor epoxide, 0.0020 ppm. Other organochlorine residues present were DDT, lindane, TDE, methoxychlor, HCB, and PCP. Zinc,

ranging from 4.0 to 8.6 ppm, was found in all 30 composites. Selenium, cadmium, and lead were occasionally found in this food class. No organophosphorous residues were detected.

MEAT, FISH, AND POULTRY

Nine organochlorine compounds occurred in varying combinations in all 30 composites. The most common were DDE, 0.038 ppm; dieldrin, 0.033 ppm; DDT, 0.020 ppm; BHC, 0.0070 ppm; TDE, 0.005 ppm; and heptachlor epoxide, 0.0040 ppm. Other residues were lindane, PCB, HCB, ronnel, diazinon, and ethion. Mercury, selenium, and zinc, ranging from trace to 0.04 ppm, 0.1 to 0.4 ppm, and 21.0 to 35.5 ppm, respectively, were found in all 30 composites. Cadmium, arsenic, and lead were also found.

GRAIN AND CEREAL PRODUCTS

Malathion, ranging from 0.004 to 0.054 ppm, was found in all 30 composites. Selenium and zinc, ranging from 0.10 to 0.40 ppm and 5.9 to 10.1 ppm, respectively, were found in all 30 composites. Other residues included diazinon, BHC, DDT, PCP, chlordane, heptachlor, cadmium, and lead.

POTATOES

Zinc, ranging from 1.8 to 7.5 ppm, was found in all 30 composites. Of the ten organochlorine residues which appeared in this composite, the most common were CIPC, 0.467 ppm; dieldrin, 0.007 ppm; and DDE, 0.012 ppm. Other residues were endosulfan, DDT, TCNB, TDE, heptachlor epoxide, diazinon, HCB, PCNB, cadmium, lead, selenium, and mercury.

LEAFY VEGETABLES

Organophosphates were the most frequently detected pesticide residues in leafy vegetables. The most common were diazinon, 0.015 ppm; parathion, 0.022 ppm; and methyl parathion, 0.008 ppm. All 30 composites contained zinc ranging from 0.8 to 4.1 ppm. Cadmium, ranging from 0.01 to 0.14 ppm, was found in 28 composites, and lead, ranging from 0.03 to 0.40 ppm, was found in 20 composites. Less frequently occurring residues were endosulfan, DDE, malathion, selenium, dieldrin, perthane, DDT, DCPA, botran, nitrofen, lindane, and mercury.

LEGUME VEGETABLES

Zinc and lead, ranging from 5.0 to 14.5 ppm and 0.10 to 1.30 ppm, respectively, were found in all 30 composites. Other residues were cadmium, selenium, HCB, and carbaryl.

ROOT VEGETABLES

Zinc, ranging from 1.4 to 5.0 ppm, was found in all 30 composites. Twenty-four composites contained cadmium with a maximum level of 0.31 ppm, and 22 composites contained lead with a maximum level of 0.30 ppm. Other residues were selenium, arsenic, DDE, lindane, diazinon, TDE, HCB, parathion, and PCP.

GARDEN FRUITS

The most common pesticide residues in this composite were dieldrin, 0.015 ppm; lindane, 0.004 ppm; BHC, 0.005 ppm; diazinon, 0.003 ppm; and leptophos, 0.090 ppm. Thirty composites contained zinc ranging from 2.1 to 4.8 ppm. Other residues were cadmium, lead, selenium, DDE, DDT, arsenic, endosulfan, parathion, carbaryl, perthane, and toxaphene.

FRUITS

The nonmetallic residues most frequently encountered in fruits were carbaryl, 0.10 ppm; orthophenylphenol, 0.20 ppm; and ethion, 0.012 ppm. Zinc, ranging from 0.1 to 3.0 ppm, was found in all 30 composites. Other residues were lead, cadmium, selenium, dieldrin, diazinon, mercury, arsenic, parathion, botran, dicofol, aldrin, and phosalone.

OILS, FATS, AND SHORTENING

The most common residues were malathion, 0.115 ppm, and PCA, 0.050 ppm. Zinc, ranging from 3.6 to 8.4 ppm, was found in all 30 composites. Other residues were cadmium, lead, selenium, dieldrin, DDE, BHC, DDT, lindane, TDE, HCB, parathion, TCNB, PCNB, and captan

SUGARS AND ADJUNCTS

The most frequently found organochlorine residues were lindane, 0.008 ppm; BHC, 0.002 ppm; and PCP, 0.033 ppm. Thirty composites contained zinc ranging from 1.5 ppm to 6.4 ppm. Other residues included cadmium, lead, selenium, mercury, malathion, diazinon, PCB, and orthophenylphenol.

BEVERAGES

No organochlorine or organophosphates were found in any of the 30 beverage composites examined. Zinc, ranging from 0.3 to 1.3 ppm, was found in all 30 composites. Other metallic residues were cadmium, lead, and selenium.

Discussion

Of the 360 composites examined, organochlorine residues were found in 172, or 48 percent. Corresponding findings from previous years were 52 percent, 1972-73; 54 percent, 1971-72; and 61.4 percent, 1970-71. Organophosphorus residues in the current reporting period were found in 100 composites, or 28 percent. Corresponding findings in

previous years were 31, 27.8, and 21.4 percent, respectively.

Carbaryl occurred in eight composites during this reporting period; four of these findings were at trace levels. This is below the 12 findings in the previous reporting period. Orthophenylphenol, which is detected by the method used for carbaryl, was found in five composites; two of these findings represented trace levels. Only one composite revealed orthophenylphenol in the previous reporting period.

No chlorophenoxy acid herbicides appeared in this reporting period. Pentachlorophenol, which is detected by the method used for chlorophenoxy acids, was found 10 times. Seven of these findings occurred in Composite X1, sugars and adjuncts. Analysis of the individual commodities in this composite showed the source of the pentachlorophenols to be candy bars.

Zinc appeared in all composites ranging from 0.1 to 35.5 ppm. The second most commonly occurring metal, cadmium, was found in all 12 food classes. It occurred in 211 of the 360 composites examined at levels ranging from 0.01 to 0.31 ppm. Lead and selenium were also found in all 12 food classes. The highest of the 180 findings of lead was 1.30 ppm, and the highest of the 97 findings of selenium was 0.40 ppm. Mercury occurred in 34 composites; meat, fish, and poultry contributed 30 of those findings. The highest mercury residue was 0.04 ppm.

The individual commodity analysis for chlorinated, organophosphate, and PCP residues on food groups 1 (dairy) and 11 (meats) that began last reporting period was continued on four samples of this period's 30 Total Diet samples. Composites 1 and 11 were selected because they had had the most significant occurrence of chlorinated residues in previous analyses. Individual commodity analysis results are shown for dairy products in Table 5 and for meat, fish, and poultry in Table 6. Three items from the dairy group, namely, buttermilk, skim milk, and nonfat dry milk, and one item from the meat group, shrimp, are not shown because they contained no residues.

Recovery studies were conducted for all classes of chemicals sought throughout the entire year (Table 4). Each recovery experiment consisted of a single determination for the unfortified food composite and a single determination for the fortified sample. Because these were performed simultaneously, the fortification level occasionally was below the level present in the sample. In other cases, not enough recoveries were run to permit statistical evaluation. These data are not reported.

At very low fortification levels, recoveries may range from 0 to 200 percent. As the fortification level is raised, however, recovery improves. Recovery data indicate 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) *Association of Official Analytical Chemists. 1975.* Official Methods of Analysis, 12th ed. Washington, D.C. Sections 25.012-25.013.

(2) *Association of Official Analytical Chemists. 1975.* Official Methods of Analysis, 12th ed. Washington, D.C. Sections 25.026-25.030.

(3) *Association of Official Analytical Chemists. 1975.* Official Methods of Analysis, 12th ed. Washington, D.C. Sections 25.065-25.070.

(4) *Association of Official Analytical Chemists. 1975.* Official Methods of Analysis, 12th ed. Washington, D.C. Sections 25.103-25.105.

(5) *Association of Official Analytical Chemists. 1975.* Official Methods of Analysis, 12th ed. Washington, D.C. Sections 25.117-25.120.

(6) *Association of Official Analytical Chemists. 1975.* Official Methods of Analysis, 12th ed. Washington, D.C. Sections 25.143-25.147.

(7) *Corneliussen, P. E. 1969.* Pesticide residues in total diet samples (IV). Pestic. Monit. J. 2(4):140-152.

(8) *Corneliussen, P. E. 1970.* Pesticide residues in total diet samples (V). Pestic. Monit. J. 4(3):89-105.

(9) *Corneliussen, P.E. 1972.* Pesticide residues in total diet samples (VI). Pestic. Monit. J. 5(4):313-330.

(10) *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.

(11) *Duggan, R. E., H. C. Barry, and L. Y. Johnson. 1966.* Pesticide residues in total diet samples. Science 151 (3706):101-104.

(12) *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.

(13) *Finocchiaro, J.M., and W. R. Benson. 1965.* Thin-layer chromatographic determination of carbaryl (Sevin) in some foods. J. Assoc. Offic. Anal. Chem. 48(4):736-738.

(14) *Food and Drug Administration. 1971.* Pesticide Analytical Manual, Vol. I and II. U.S. Department of Health, Education, and Welfare.

(15) *Johnson, R D., and D. D. Manske. 1975.* Pesticide residues in total diet samples (IX). Pestic. Monit. J. 9(4):157-169.

(16) *Manske, D.D., and P. E. Corneliussen. 1974.* Pesticide residues in total diet samples (VII). Pestic. Monit. J. 8(2):110-124.

(17) *Manske, D. D., and R. D. Johnson. 1975.* Pesticide

residues in total diet samples (VIII). Pestic. Monit. J. 9(2):94-105.

(18) *Martin, R. J., and R. E. Duggan. 1968.* Pesticide residues in total diet samples (III). Pestic. Monit. J. 1(4):11-20.

(19) *Porter, M. L., R. J. Gajan, and J. A. Burke. 1969* Acetonitrile extraction and determination of carbaryl in fruits and vegetables. J. Assoc. Offic. Anal. Chem 52(1):177-181.

TABLE 1. *Chemical residues found in food composites, August 1973-July 1974*

Chemical	No. Composites With Residues	No. Positive Composites With Residues Reported As Trace [1]	Range, ppm
ZINC	360	0	0.1-35.5
CADMIUM	211	0	0.01-0.31
LEAD	180	0	0.02-1.30
SELENIUM	97	34	0.05-0.40
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-endo-exo-5,8-dimethanonaphthalene	93	17	0.0006-0.0330
DDE 1,1-dichloro-2,2-bis (p-chlorophenyl) ethylene (all isomers are included in reportings)	81	20	0.0006-0.0380
BHC 1,2,3,4,5,6-hexachlorocyclohexane, mixed isomers except gamma	76	12	0.0004-0.0070
DDT 1,1,1-trichloro-2,2-bis (p-chlorophenyl) ethane (isomers other than p,p' also included in reportings)	54	15	0.002-0.020
MALATHION diethylmercaptosuccinate, S-ester with 0,0-dimethyl phosphorodithioate	53	6	0.003-0.115
LINDANE 1,2,3,4,5,6-hexachlorocyclohexane, 99% or more gamma isomer	52	18	0.0003-0.0120
DIAZINON 0,0-diethyl o-(2-isopropyl-6-methyl-4-pyrimidyl) phosphorothioate	50	20	0.0007-0.0270
HEPTACHLOR EPOXIDE 1,4,5,6,7,8,8-heptachloro-2,3-epoxy-3a,4,7,7a-tetrahydro-4,7-endo-methanoindan	46	19	0.0005-0.0040
TDE 1,1-dichloro-2,2-bis (p-chlorophenyl) ethane (isomers other than p,p' also included in reportings)	3	23	0.001-0.005
MERCURY	34	17	0.01-0.04
ARSENIC (As_2O_3)	18	2	0.03-0.60
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)	17	10	0.003-0.012
HCB hexachlorobenzene	17	8	0.0003-0.0070
PARATHION O,O-diethyl O-p-nitrophenyl phosphorothioate	17	10	0.003-0.022
PCB (polychlorinated biphenyls) calculated as Aroclor with varied chlorine content	14	13	0.050
CIPC isopropyl n-(3-chlorophenyl) carbamate	12	0	0.005-0.467
PCA pentachloroaniline	10	1	0.004-0.050
PCP pentachlorophenol	10	0	0.010-0.033
CARBARYL 1-naphthyl methyl carbamate	8	4	0.05-0.50
TCNB 1,2,4,5-tetrachloro-3-nitrobenzene	8	2	0.001-0.284
METHOXYCHLOR 1,1,1-trichloro-2,2-bis (p-methoxyphenyl) ethane	7	2	0.004-0.009
METHYL PARATHION O,O-dimethyl O-p-nitrophenyl phosphorothioate	7	6	0.008
PCNB pentachloronitrobenzene	7	4	0.002-0.005
ETHION O,O,O',O'-tetraethyl S,S'-methylene bisphosphorodithioate	6	3	0.003-0.012
ORTHOPHENYLPHENOL 2-hydroxydiphenyl	5	2	0.05-0.20
LEPTOPHOS O-(2,5-dichloro-4-bromophenyl)-O-methylphenyl phosphorothioate	5	1	0.013-0.090

(Continued next page)

TABLE 1 (cont'd.). *Chemical residues found in food composites, August 1973—July 1974*

Chemical	No. Composites With Residues	No. Positive Composites With Residues Reported As Trace [1]	Range, ppm
PERTHANE 1,1-dichloro-2,2-bis (p-ethylphenyl) ethane	4	0	0.030-2.28
BOTRAN 2,6-dichloro-4-nitroaniline	3	0	0.006-0.067
TOXAPHENE chlorinated camphene containing 67 to 69% chlorine	3	2	0.163
DCPA (DACTHAL) 2,3,5,6-tetrachloroterephthalic acid dimethyl ester	2	0	0.003-0.013
DICOFOL (KELTHANE) 4,4'-dichloro-α-(trichloromethyl) benzhydrol	2	1	0.010
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	1	0	0.001
CAPTAN N-[(trichloromethyl)thio]-4-cyclohexene-1,2-dicarboximide	1	0	0.178
CHLORDANE (Technical) Cis and trans isomers of 1,2,4,5,6,7,8,8-octachloro-3a,4,7,7a-tetrahydro-4,7-methanoindane plus approximately 50% related compounds	1	1	T
HEPTACHLOR 1,4,5,6,7,8,8-heptachloro-3a,4,7,7a-tetrahydro-4,7-endo-methanoindene	1	0	0.004
PHOSALONE O,O-diethyl S-(6-chloro-2-oxobenzoxazolin-3-yl) methyl phosphorodithioate	1	0	0.171
RONNEL O,O-dimethyl O-(2,4,5-trichlorophenyl) phosphorothioate	1	0	0.001
NITROFEN 2,4-dichlorophenyl-p-nitrophenyl ether	1	0	0.039

[1] Chemicals detectable by the specific analytical methodology can be confirmed qualitatively but are not quantifiable in concentrations below the limit of quantitation. Limit of quantitation varies with residue and food class.

TABLE 2. *Occurrence frequency of chemical residues by food class, August 1973—July 1974*

Chemical	Food Class[1]											
	I	II	III	IV	V	VI	VII	VIII	IX	X	XI	XII
	Number of Occurrences											
Zinc	30	30	30	30	30	30	30	30	30	30	30	30
Cadmium	4	21	29	29	28	8	24	23	3	24	12	6
Lead	4	9	11	13	20	30	22	26	23	8	9	5
Selenium	10	30	30	5	3	5	3	2	1	3	3	2
Dieldrin	29	30		9	3			17	2	3		
DDE	27	30		9	4		7	2		2		
BHC	29	27	1					6		4	9	
DDT	10	29	1	8	1			1		4		
Malathion			30		4					16	3	
Lindane	10	19			1		3	6		2	11	
Diazinon		6	16	3	17		1	5	1		1	
Heptachlor Epoxide	22	22		2								
TDE	8	25		2			1			2		
Mercury		30		1	1				1		1	
Arsenic		10					2	1	5			
Endosulfan				6	8			3				
HCB	3	4		1		1	1			7		
Parathion					11		3	1	1	1		
PCB		13									1	
CIPC				12								
PCA										10		
PCP	1		1				1				7	
Carbaryl						1		1	6			
TCNB				6						2		
Methoxychlor	7											
Methyl Parathion					7							
PCNB				1						6		
Ethion		1							5			
Orthophenylphenol									4		1	
Leptophos								5				
Perthane					3			1				
Botran					1				2			
Toxaphene								3				
DCPA					2							

(Continued next page)

TABLE 2 (cont'd.). *Occurrence frequency of chemical residues by food class, August 1973—July 1974*

Chemical	Food Class[1]											
	I	II	III	IV	V	VI	VII	VIII	IX	X	XI	XII
	Number of Occurrences											
Dicofol									2			
Aldrin									1			
Captan										1		
Chlordane			1									
Heptachlor			1									
Phosalone									1			
Ronnel		1										
Nitrofen					1							

[1] See Table 3 for descriptions of food classes

Table 3. *Levels of chemical residues found—by food class in 30 composites, August 1973—July 1974*

	Residues, ppm
I Dairy Products	
ZINC	
Average	5 5
Positive Composites	
Total Number	30
Number Reported as Trace	0
Range	4 0–8 6
BHC	
Average	0 0008
Positive Composites	
Total Number	29
Number Reported as Trace	2
Range	0 0004–0 0030
DIELDRIN	
Average	0 0016
Positive Composites	
Total Number	29
Number Reported as Trace	3
Range	0 0006–0 0050
DDE	
Average	0 0015
Positive Composites	
Total Number	27
Number Reported as Trace	9
Range	0 0006–0 0100
HEPTACHLOR EPOXIDE	
Average	0 0004
Positive Composites	
Total Number	22
Number Reported as Trace	10
Range	0 0005–0 0020
DDT	
Average	0 0003
Positive Composites	
Total Number	10
Number Reported as Trace	8
Range	0 003–0 006
LINDANE	
Average	0 0002
Positive Composites	
Total Number	10
Number Reported as Trace	6
Range	0 0003–0 0028
SELENIUM	
Average	T
Positive Composites	
Total Number	10
Number Reported as Trace	9
Range	0 07
TDE	
Average	T
Positive Composites	
Total Number	8
Number Reported as Trace	8
Range	T
METHOXYCHLOR	
Average	0 001
Positive Composites	
Total Number	7
Number Reported as Trace	2
Range	0 004–0 03
CADMIUM	
Average	0 01
Positive Composites	
Total Number	4
Number Reported as Trace	0
Range	0 01–0 14
LEAD	
Average	0 01
Positive Composites	
Total Number	4
Number Reported as Trace	0
Range	0 04–0 08
HCB	
Average	T
Positive Composites	
Total Number	3
Number Reported as Trace	1
Range	0 0003–0 0006
PCP	
Average	T
Positive Composites	
Total Number	1
Number Reported as Trace	0
Range	0 010
II Meat, Fish, And Poultry	
DDE	
Average	0 0085
Positive Composites	
Total Number	30
Number Reported as Trace	0
Range	0 002–0 038
DIELDRIN	
Average	0 0056
Positive Composites	
Total Number	30
Number Reported as Trace	0
Range	0.002–0.033
TDE	
Average	0 002
Positive Composites	
Total Number	25
Number Reported as Trace	11
Range	0 001–0 005
HEPTACHLOR EPOXIDE	
Average	0 001
Positive Composites	
Total Number	22
Number Reported as Trace	8
Range	0 001–0 004

(Continued next page)

TABLE 3 (cont'd). *Levels of chemical residues found—by food class in 30 composites, August 1973—July 1974*

RESIDUES, PPM

II. MEAT, FISH, AND POULTRY

MERCURY		CADMIUM	
Average	0.01	Average	0.02
Positive Composites		Positive Composites	
Total Number	30	Total Number	21
Number Reported as Trace	13	Number Reported as Trace	0
Range	0.01–0.04	Range	0.01–0.06
SELENIUM		LINDANE	
Average	0.20	Average	0.0010
Positive Composites		Positive Composites	
Total Number	30	Total Number	19
Number Reported as Trace	0	Number Reported as Trace	3
Range	0.10–0.40	Range	0.0004–0.0120
ZINC		PCB	
Average	28.0	Average	0.002
Positive Composites		Positive Composites	
Total Number	30	Total Number	13
Number Reported as Trace	0	Number Reported as Trace	12
Range	21.0–35.5	Range	0.050
DDT		ARSENIC	
Average	0.006	Average	0.06
Positive Composites		Positive Composites	
Total Number	29	Total Number	10
Number Reported as Trace	0	Number Reported as Trace	1
Range	0.002–0.020	Range	0.03–0.6
BHC		LEAD	
Average	0.0011	Average	0.02
Positive Composites		Positive Composites	
Total Number	27	Total Number	9
Number Reported as Trace	1	Number Reported as Trace	0
Range	0.0004–0.0070	Range	0.03–0.10
DIAZINON		ETHION	
Average	0.0001	Average	T
Positive Composites		Positive Composites	
Total Number	6	Total Number	1
Number Reported as Trace	3	Number Reported as Trace	0
Range	0.0007–0.0010	Range	0.001
HCB		RONNEL	
Average	T	Average	T
Positive Composites		Positive Composites	
Total Number	4	Total Number	1
Number Reported as Trace	2	Number Reported as Trace	0
Range	0.0003–0.0006	Range	0.0010

III. GRAIN AND CEREAL PRODUCTS

MALATHION		DIAZINON	
Average	0.020	Average	0.002
Positive Composites		Positive Composites	
Total Number	30	Total Number	16
Number Reported as Trace	0	Number Reported as Trace	7
Range	0.004–0.054	Range	0.002–0.011
SELENIUM		LEAD	
Average	0.24	Average	0.03
Positive Composites		Positive Composites	
Total Number	30	Total Number	11
Number Reported as Trace	0	Number Reported as Trace	0
Range	0.10–0.40	Range	0.03–0.2
ZINC		BHC	
Average	8.1	Average	T
Positive Composites		Positive Composites	
Total Number	30	Total Number	1
Number Reported as Trace	0	Number Reported as Trace	0
Range	5.9–10.1	Range	0.006
CADMIUM		CHLORDANE	
Average	0.03	Average	T
Positive Composites		Positive Composites	
Total Number	29	Total Number	1
Number Reported as Trace	0	Number Reported as Trace	1
Range	0.02–0.05	Range	T
DDT		PCP	
Average	T	Average	T
Positive Composites		Positive Composites	
Total Number	1	Total Number	1
Number Reported as Trace	1	Number Reported as Trace	0
Range	T	Range	0.017

(Continued on

TABLE 3 (cont'd.). *Levels of chemical residues found—by food class in 30 composites, August 1973—July 1974*

	Residues, ppm
III Grain And Cereal Products	
HEPTACHLOR	
Average	T
Positive Composites	
Total Number	1
Number Reported as Trace	0
Range	0.004
IV Potatoes	
ZINC	
Average	4.5
Positive Composites	
Total Number	30
Number Reported as Trace	0
Range	1.8–7.5
CADMIUM	
Average	0.05
Positive Composites	
Total Number	29
Number Reported as Trace	0
Range	0.02–0.13
LEAD	
Average	0.03
Positive Composites	
Total Number	13
Number Reported as Trace	0
Range	0.02–0.10
CIPC	
Average	0.047
Positive Composites	
Total Number	12
Number Reported as Trace	0
Range	0.005–0.467
TCNB	
Average	0.010
Positive Composites	
Total Number	6
Number Reported as Trace	0
Range	0.001–0.284
SELENIUM	
Average	T
Positive Composites	
Total Number	5
Number Reported as Trace	5
Range	T
DIAZINON	
Average	0.001
Positive Composites	
Total Number	3
Number Reported as Trace	2
Range	0.027
HEPTACHLOR EPOXIDE	
Average	T
Positive Composites	
Total Number	2
Number Reported as Trace	1
Range	0.002
DDE	
Average	0.001
Positive Composites	
Total Number	9
Number Reported as Trace	3
Range	0.002–0.012
DIELDRIN	
Average	0.001
Positive Composites	
Total Number	9
Number Reported as Trace	3
Range	0.002–0.007
DDT	
Average	0.001
Positive Composites	
Total Number	8
Number Reported as Trace	4
Range	0.005–0.008
ENDOSULFAN	
Average	0.001
Positive Composites	
Total Number	6
Number Reported as Trace	3
Range	0.005–0.016
TDE	
Average	T
Positive Composites	
Total Number	2
Number Reported as Trace	2
Range	T
HCB	
Average	T
Positive Composites	
Total Number	1
Number Reported as Trace	0
Range	0.004
MERCURY	
Average	T
Positive Composites	
Total Number	1
Number Reported as Trace	1
Range	T
PCNB	
Average	T
Positive Composites	
Total Number	1
Number Reported as Trace	0
Range	0.005
V Leafy Vegetables	
ZINC	
Average	2.4
Positive Composites	
Total Number	30
Number Reported as Trace	0
Range	0.8–4.1
CADMIUM	
Average	0.04
Positive Composites	
Total Number	28
Number Reported as Trace	0
Range	0.01–0.14
PARATHION	
Average	0.002
Positive Composites	
Total Number	11
Number Reported as Trace	6
Range	0.004–0.022
LEAD	
Average	0.10
Positive Composites	
Total Number	20
Number Reported as Trace	0
Range	0.03–0.4
DIAZINON	
Average	0.002
Positive Composites	
Total Number	17
Number Reported as Trace	5
Range	0.001–.00
SELENIUM	
Average	1
Positive Composites	
Total Number	3
Number Reported as Trace	3
Range	T

(Continued next page)

TABLE 3 (cont'd.) *Levels of chemical residues found—by food class in 30 composites, August 1973—July 1974*

	Residues, ppm
V. Leafy Vegetables	
ENDOSULFAN	
Average	0.001
Positive Composites	
Total Number	8
Number Reported as Trace	4
Range	0.003–0.012
METHYL PARATHION	
Average	T
Positive Composites	
Total Number	7
Number Reported as Trace	6
Range	0.008
DDE	
Average	T
Positive Composites	
Total Number	4
Number Reported as Trace	1
Range	0.003–0.005
MALATHION	
Average	T
Positive Composites	
Total Number	4
Number Reported as Trace	2
Range	0.005–0.006
DIELDRIN	
Average	T
Positive Composites	
Total Number	3
Number Reported as Trace	3
Range	T
PERTHANE	
Average	0.13
Positive Composites	
Total Number	3
Number Reported as Trace	0
Range	0.03–2.28
DCPA	
Average	0.001
Positive Composites	
Total Number	2
Number Reported as Trace	0
Range	0.003–0.013
BOTRAN	
Average	T
Positive Composites	
Total Number	1
Number Reported as Trace	0
Range	0.008
DDT	
Average	T
Positive Composites	
Total Number	1
Number Reported as Trace	0
Range	0.015
LINDANE	
Average	T
Positive Composites	
Total Number	1
Number Reported as Trace	1
Range	T
MERCURY	
Average	T
Positive Composites	
Total Number	1
Number Reported as Trace	1
Range	T
NITROFEN	
Average	0.001
Positive Composites	
Total Number	1
Number Reported as Trace	0
Range	0.039
VI. Legume Vegetables	
LEAD	
Average	0.28
Positive Composites	
Total Number	30
Number Reported as Trace	0
Range	0.10–1.30
ZINC	
Average	8.5
Positive Composites	
Total Number	30
Number Reported as Trace	0
Range	5.0–14.5
CADMIUM	
Average	0.01
Positive Composites	
Total Number	8
Number Reported as Trace	0
Range	0.01–0.10
SELENIUM	
Average	T
Positive Composites	
Total Number	5
Number Reported as Trace	4
Range	0.05
CARBARYL	
Average	T
Positive Composites	
Total Number	1
Number Reported as Trace	0
Range	0.5
HCB	
Average	T
Positive Composites	
Total Number	1
Number Reported as Trace	1
Range	T
VII. Root Vegetables	
ZINC	
Average	2.8
Positive Composites	
Total Number	30
Number Reported as Trace	0
Range	1.4–5.0
CADMIUM	
Average	0.03
Positive Composites	
Total Number	24
Number Reported as Trace	0
Range	0.01–0.31
LEAD	
Average	0.09
Positive Composites	
Total Number	7
Number Reported as Trace	4
Range	0.03–0.30
DDE	
Average	T
Positive Composites	
Total Number	2
Number Reported as Trace	1
Range	0.003–0.00
LINDANE	
Average	T
Positive Composites	
Total Number	3
Number Reported as Trace	1
Range	0.003–0.00
PARATHION	
Average	T
Positive Composites	
Total Number	3
Number Reported as Trace	3
Range	T

(Continued next page)

TABLE 3 (cont'd.). *Levels of chemical residues found—by food class in 30 composites, August 1973—July 1974*

Residues, ppm	
VII Root Vegetables	
SELENIUM	
Average	T
Positive Composites	
Total Number	3
Number Reported as Trace	3
Range	T
ARSENIC	
Average	T
Positive Composites	
Total Number	2
Number Reported as Trace	0
Range	0.03–0.1
DIAZINON	
Average	T
Positive Composites	
Total Number	1
Number Reported as Trace	1
Range	T
HCB	
Average	T
Positive Composites	
Total Number	1
Number Reported as Trace	0
Range	0.002
PCP	
Average	T
Positive Composites	
Total Number	1
Number Reported as Trace	0
Range	0.01
TDE	
Average	T
Positive Composites	
Total Number	1
Number Reported as Trace	0
Range	0.004
VIII Garden Fruits	
ZINC	
Average	3.0
Positive Composites	
Total Number	30
Number Reported as Trace	0
Range	2.1–4.8
LEAD	
Average	0.14
Positive Composites	
Total Number	26
Number Reported as Trace	0
Range	0.06–0.60
CADMIUM	
Average	0.02
Positive Composites	
Total Number	23
Number Reported as Trace	0
Range	0.01–0.10
DIAZINON	
Average	T
Positive Composites	
Total Number	5
Number Reported as Trace	2
Range	0.002–0.003
LEPTOPHOS	
Average	0.005
Positive Composites	
Total Number	5
Number Reported as Trace	1
Range	0.013–0.090
ENDOSULFAN	
Average	T
Positive Composites	
Total Number	3
Number Reported as Trace	3
Range	T
TOXAPHENE	
Average	0.005
Positive Composites	
Total Number	3
Number Reported as Trace	2
Range	0.163
DDE	
Average	T
Positive Composites	
Total Number	2
Number Reported as Trace	2
Range	T
SELENIUM	
Average	T
Positive Composites	
Total Number	2
Number Reported as Trace	2
Range	T
DIELDRIN	
Average	0.002
Positive Composites	
Total Number	17
Number Reported as Trace	4
Range	0.002–0.01
BHC	
Average	0.0003
Positive Composites	
Total Number	6
Number Reported as Trace	3
Range	0.0009–0.00
LINDANE	
Average	T
Positive Composites	
Total Number	6
Number Reported as Trace	4
Range	0.002–0.004
ARSENIC	
Average	T
Positive Composites	
Total Number	1
Number Reported as Trace	0
Range	0.04
CARBARYL	
Average	T
Positive Composites	
Total Number	1
Number Reported as Trace	1
Range	T
DDT	
Average	T
Positive Composites	
Total Number	1
Number Reported as Trace	0
Range	0.011
PARATHION	
Average	T
Positive Composites	
Total Number	1
Number Reported as Trace	0
Range	0.006
PERTHANE	
Average	0.001
Positive Composites	
Total Number	1
Number Reported as Trace	0
Range	0.031

(Continued next page)

TABLE 3 (cont'd.) *Levels of chemical residues found—by food class in 30 composites, August 1973—July 1974*

	Residues, ppm
IX. Fruits	
ZINC	
Average	1.1
Positive Composites	
Total Number	30
Number Reported as Trace	0
Range	0.1–3.0
CARBARYL	
Average	0.01
Positive Composites	
Total Number	6
Number Reported as Trace	3
Range	0.05–0.10
ARSENIC	
Average	0.02
Positive Composites	
Total Number	5
Number Reported as Trace	1
Range	0.03–0.20
ETHION	
Average	0.001
Positive Composites	
Total Number	5
Number Reported as Trace	3
Range	0.005–0.012
ORTHOPHENYLPHENOL	
Average	0.02
Positive Composites	
Total Number	4
Number Reported as Trace	1
Range	0.05–0.20
CADMIUM	
Average	T
Positive Composites	
Total Number	3
Number Reported as Trace	0
Range	0.01–0.06
BOTRAN	
Average	0.002
Positive Composites	
Total Number	2
Number Reported as Trace	0
Range	0.006–0.067
DICOFOL	
Average	T
Positive Composites	
Total Number	2
Number Reported as Trace	1
Range	0.01
LEAD	
Average	0.10
Positive Composites	
Total Number	23
Number Reported as Trace	0
Range	0.04–0.44
DIELDRIN	
Average	T
Positive Composites	
Total Number	2
Number Reported as Trace	2
Range	T
ALDRIN	
Average	T
Positive Composites	
Total Number	1
Number Reported as Trace	0
Range	0.001
DIAZINON	
Average	T
Positive Composites	
Total Number	1
Number Reported as Trace	0
Range	0.003
MERCURY	
Average	T
Positive Composites	
Total Number	1
Number Reported as Trace	1
Range	T
PARATHION	
Average	T
Positive Composites	
Total Number	1
Number Reported as Trace	0
Range	0.003
PHOSALONE	
Average	0.006
Positive Composites	
Total Number	1
Number Reported as Trace	0
Range	0.171
SELENIUM	
Average	T
Positive Composites	
Total Number	1
Number Reported as Trace	1
Range	T
X. Oils, Fats and Shortening	
ZINC	
Average	5.1
Positive Composites	
Total Number	30
Number Reported as Trace	0
Range	3.6–8.4
CADMIUM	
Average	0.02
Positive Composites	
Total Number	24
Number Reported as Trace	0
Range	0.01–0.07
MALATHION	
Average	0.015
Positive Composites	
Total Number	16
Number Reported as Trace	4
Range	0.011–0.115
PCB	
Average	0.084
Positive Composites	
Total Number	10
Number Reported as Trace	
Range	0.04–0.150
BHC	
Average	T
Positive Composites	
Total Number	4
Number Reported as Trace	3
Range	0.003
DDT	
Average	0.001
Positive Composites	
Total Number	4
Number Reported as Trace	2
Range	0.009–0.011
DIELDRIN	
Average	T
Positive Composites	
Total Number	3
Number Reported as Trace	2
Range	0.004
SELENIUM	
Average	T
Positive Composites	
Total Number	3
Number Reported as Trace	2
Range	0.05

(Continued next page)

TABLE 3 (cont'd.). *Levels of chemical residues found—by food class in 30 composites, August 1973—July 1974*

Residues, ppm	
X Oils, Fats, And Shortening	
LEAD	
Average	0 03
Positive Composites	
Total Number	8
Number Reported as Trace	0
Range	0 03–0 40
HCB	
Average	T
Positive Composites	
Total Number	7
Number Reported as Trace	4
Range	0 001–0 007
PCNB	
Average	T
Positive Composites	
Total Number	6
Number Reported as Trace	4
Range	0 002–0 005
TDE	
Average	T
Positive Composites	
Total Number	2
Number Reported as Trace	2
Range	T
CAPTAN	
Average	0 006
Positive Composites	
Total Number	1
Number Reported as Trace	0
Range	0 178
DDE	
Average	T
Positive Composites	
Total Number	2
Number Reported as Trace	1
Range	0 004
LINDANE	
Average	T
Positive Composites	
Total Number	2
Number Reported as Trace	1
Range	0 002
TCNB	
Average	T
Positive Composites	
Total Number	2
Number Reported as Trace	2
Range	T
PARATHION	
Average	T
Positive Composites	
Total Number	1
Number Reported as Trace	1
Range	T
XI Sugars And Adjuncts	
ZINC	
Average	3 0
Positive Composites	
Total Number	30
Number Reported as Trace	0
Range	1 5–6 4
CADMIUM	
Average	0 01
Positive Composites	
Total Number	12
Number Reported as Trace	0
Range	0 01–0 09
LINDANE	
Average	T
Positive Composites	
Total Number	11
Number Reported as Trace	2
Range	0 001–0 003
BHC	
Average	0 0003
Positive Composites	
Total Number	9
Number Reported as Trace	3
Range	0 0008–0 0020
DIAZINON	
Average	T
Positive Composites	
Total Number	1
Number Reported as Trace	0
Range	0 002
MERCURY	
Average	T
Positive Composites	
Total Number	1
Number Reported as Trace	1
Range	T
LEAD	
Average	0 03
Positive Composites	
Total Number	9
Number Reported as Trace	0
Range	0 06–0 2
PCP	
Average	0 004
Positive Composites	
Total Number	7
Number Reported as Trace	0
Range	0 010–0 03
MALATHION	
Average	0 002
Positive Composites	
Total Number	3
Number Reported as Trace	0
Range	0 003–0 04
SELENIUM	
Average	T
Positive Composites	
Total Number	3
Number Reported as Trace	3
Range	T
ORTHOPHENYLPHENOL	
Average	T
Positive Composites	
Total Number	1
Number Reported as Trace	1
Range	T
PCB	
Average	T
Positive Composites	
Total Number	1
Number Reported as Trace	1
Range	T
XII Beverages	
ZINC	
Average	0 6
Positive Composites	
Total Number	30
Number Reported as Trace	0
Range	0 3–1 3
LEAD	
Average	0 01
Positive Composites	
Total Number	5
Number Reported as Trace	0
Range	0 03–0 1

(Continued next page)

TABLE 3 (cont'd.) *Levels of chemical residues found—by food class in 30 composites, August 1973—July 1974*

	Residues, ppm
	XII. Beverages
CADMIUM	
Average	T
Positive Composites	
Total Number	6
Number Reported as Trace	0
Range	0.01-0.03
SELENIUM	
Average	T
Positive Composites	
Total Number	2
Number Reported as Trace	2
Range	T

NOTE: T = trace; see Table 1, footnote 1.

TABLE 4. *Recovery data on residues found in total diet samples, August 1973—July 1974*

Residue	Type of Food Composites	Spike Level ppm	Range of Blank Level, ppm[1]	Range of Total Found, ppm[1]	No. of Recovery Studies
Cadmium	Fatty	0.10	0-0.042 (0.116)	0.075-0.160 (0.111)	30
	Nonfatty	0.10	0-0.139 (0.023)	0.031-0.236 (0.119)	60
Lead	Fatty	0.20	0-0.088 (0.035)	0.122-0.316 (0.219)	30
	Nonfatty	0.20	0-0.896 (0.200)	0.022-1.512 (0.287)	60
Selenium	Fatty	0.20	0-0.28 (0.0887)	0.10 -0.50 (0.243)	30
	Nonfatty	0.20	0-0.40 (0.040)	0.13 -0.58 (0.212)	60
Zinc	Fatty	5.0	3.78-10.72 (5.75)	8.22 -12.84 (10.6)	19
	Nonfatty	5.0	0.35-12.7 (3.67)	4.94 -16.5 (8.62)	60
	Fatty	25.0	24.0-35.5 (29.4)	45.1 -63.6 (52.9)	11
Mercury	Fatty	0.06	0-0.030 (0.007)	0.039-0.105 (0.067)	24
	Nonfatty	0.06	0-0.008 (0.003)	0.048-0.078 (0.062)	44
	Fatty	0.03	0-0.001 T	0.027-0.033 (0.030)	6
	Nonfatty	0.03	0-0.003 (0.001)	0.028-0.041 (0.035)	16
Carbaryl	Nonfatty	0.2 0	0-0.20 (0.18)	60	
Orthophenylphenol	Nonfatty	0.4	0	0-0.40 (0.29)	59
MCP	Fatty	0.02	0	0-0.019 (0.007)	7
	Nonfatty	0.02	0	0-0.023 (0.012)	14
2,4-DB	Fatty	0.02	0	0-0.026 (0.012)	6
	Nonfatty	0.02	0	0.004-0.032 (0.017)	12
2,4-D	Fatty	0.02	0	0-0.017 (0.011)	6
	Nonfatty	0.02	0	0-0.020 (0.016)	14
2,4,5-TP	Fatty	0.02	0	0.004-0.025 (0.013)	6
	Nonfatty	0.02	0	0-0.025 (0.015)	12
Methyl Parathion	Fatty	0.005	0	0-0.0034 (0.0025)	5
	Nonfatty	0.005	0-0.015 (0.0002)	0-0.0050 (0.0033)	10
CIPC	Fatty	0.05	0	0.027-0.046 (0.035)	5
	Nonfatty	0.05	0	0.033-0.059 (0.047)	10

(Continued next page)

TABLE 4 (cont'd.). *Recovery data on residues found in total diet samples, August 1973—July 1974*

Residue	Type of Food Composites	Spike Level, ppm	Range of Blank Level, ppm [1]	Range of Total Found, ppm [1]	No. of Recovery Studies
Dacthal	Fatty	0.005	0	0.0023-0.0050 (0.0036)	5
	Nonfatty	0.005	0	0.0033-0.0064 (0.0050)	10
Phosalone	Fatty	0.05	0	0.022-0.053 (0.038)	5
	Nonfatty	0.05	0-0.1706 (0.017)	0.030-0.212 (0.067)	10
PCNB	Fatty	0.003	0-0.0041 (0.0009)	0.0018-0.0056 (0.0028)	5
	Nonfatty	0.003	0	0.0022-0.0034 (0.0028)	9

[1] Numbers in parentheses represent average residue levels

TABLE 5. *Pesticide residues in individual commodities of dairy composite of four market basket samples, August 1973—July 1974* [1]

Residue Found	Commodity [2]							
	Whole Fluid Milk (4)	Evaporated milk (4)	Ice Cream (4)	Cottage Cheese (4)	Processed Cheese (4)	Natural Cheese (4)	Butter (4)	Ice Milk (3)
	Residues, ppm							
BHC								
Times Found	3	3	3	2	4	4	4	
ppm Range	T	T-0.002	T-0.001	T-0.002	0.003-0.008	0.004-0.016	0.009-0.021	
DDE								
Times Found	4	2	3	3	4	4	4	1
ppm Range	T-0.003	T	T-0.010	T-0.002	T-0.045	T-0.050	0.006-0.042	0.002
DIELDRIN								
Times Found	2	3	4	2	3	4	4	
ppm Range	T-0.002	0.002-0.003	T-0.004	T	0.003-0.018	0.005-0.009	0.016-0.050	
HEPTACHLOR EPOXIDE								
Times Found		2	2	1	3	4	3	
ppm Range		T	T-0.001	T	T-0.003	T-0.008	0.003-0.011	
TDE								
Times Found			1		1		2	
ppm Range			T		0.005		T	
DDT								
Times Found		1			2	3	2	
ppm Range		T			0.005-0.007	T-0.012	T-0.009	
METHOXYCHLOR								
Times Found			1	2	2	1	1	
ppm Range			0.027	T-0.015	0.005-0.038	0.076	0.154	
PCB								
Times Found	1							
ppm Range	T							
LINDANE								
Times Found	1				1		1	
ppm Range	0.001				0.003		0.002	

[1] Buttermilk, skim milk, and nonfat dry milk not shown because no residues were found

[2] Numbers in parentheses are numbers of replicates.

TABLE 6.—*Pesticide residues in individual commodities of meat composite of four market basket samples, August 1973—July 1974*[1]

Item	Commodity[2]														
	Roast Beef (4)	Ground Beef (4)	Pork Chops (4)	Bacon (4)	Chicken (4)	Fish Fillet (4)	Tuna or Salmon (4)	Lunch Meat (4)	Frankfurters (4)	Beef Liver (4)	Eggs (4)	Ham (4)	Round Steak (4)	Veal (4)	Lamb (4)
	Residues, ppm														
DIELDRIN															
Times Found	3	3	1	2	4	1	2	3	4	1					
ppm Range	0.005-0.52	T-0.004	0.002	0.003-0.004	0.004-0.007	0.004	T-0.001	0.002-0.006	0.002-0.009	T					
DDE															
Times Found	2	2	2	3	4	2	2	3	4	2	2	3	2	1	1
ppm Range	T-0.024	0.004-0.006	0.002-0.009	0.004-0.013	0.008-0.017	0.012-0.044	0.003-0.012	0.005-0.035	0.004-0.019	T-0.016	T-0.012	T-0.016	0.004-0.008	0.002	0.023
TDE															
Times Found	1		1	2	1		2	1	1						
ppm Range	T		0.006	0.004	0.004		0.008-0.010	0.008	0.003						
DDT															
Times Found		1	1	3	1	2		3	4		2	2			
ppm Range		T	0.010	0.008-0.013	0.005	0.021-0.045		0.006-0.029	0.008-0.018		T-0.016	0.011-0.016			
HCB															
Times Found						1									1
ppm Range						0.001									0.016
PCB															
Times Found		1				1									
ppm Range		T				T									
BHC															
Times Found	2	2	1	1			1	3	2			1			
ppm Range	T-0.002	T-0.005	0.001	0.001			0.010	0.001-0.002	0.002-0.003			0.001			
LINDANE															
Times Found		1	1	1				3	3						
ppm Range		0.002	0.001	0.002				0.001-0.009	0.002-0.004						
HEPTACHLOR EPOXIDE															
Times Found	1	1		1	1				2					1	1
ppm Range	0.002	0.005		0.001	T				0.002-0.004					0.002	0.006
METHOXYCHLOR															
Times Found														1	
ppm Range														0.026	
ETHION															
Times Found									1						
ppm Range									0.008						
RONNEL															
Times Found				1											
ppm Range				0.010											

[1] Shrimp not shown because no residues found

[2] Numbers in parentheses are number of replicates

RESIDUES IN FISH, WILDLIFE, AND ESTUARIES

Organochlorine Pesticide and Polychlorinated Biphenyl Residues in Selected Fauna from a New Jersey Salt Marsh—1967 vs. 1973[1]

Erwin E. Klaas[2] and Andre A. Belisle[1]

ABSTRACT

More than a half million pounds of DDT were applied to control mosquitoes in salt marsh estuaries of Cape May County, New Jersey, from 1946 to 1966. The use of DDT was discontinued in the County after 1966. In 1967, mean concentrations of DDT and metabolites ranged from 0.63 to 9.05 ppm in aquatic fauna, but by 1973 mean residue levels had decreased 84 to 99 percent among nine species. DDE was still present at reduced levels in nearly all samples in 1973, but other DDT isomers had mostly disappeared. Dieldrin was detected only in clapper rails, and residue levels decreased during the period. Mean concentrations of PCB's increased in the clapper rail, remained the same in the fiddler crab and mud snail, and decreased in the sheepshead minnow, mummichog, striped killifish, and salt marsh snail. Small amounts of mirex, toxaphene, cis-*chlordane (and/or* trans-*nonachlor), oxychlordane, and HCB were detected in a few specimens.*

Introduction

A narrow band of salt marshes with numerous estuaries and well-defined drainage systems extends along the eastern and southern coast of New Jersey. These marshes are important nursery areas for estuarine fauna, but because of their location near the large metropolitan areas of New York City, Philadelphia, and Baltimore, they are affected by real estate development and environmental pollution.

Cape May County, just southwest of Atlantic City, has over 50,000 acres of salt marsh bordering the Atlantic Ocean and Delaware Bay. This seashore County has been a popular summer resort for a century or more. After World War II, more people than ever before were attracted to the area and State and local governments tried to reduce the mosquito population to provide a more habitable environment for residents and vacationers, and to control the spread of mosquito-borne diseases.

DDT was first used in Cape May County in 1946 and was used for mosquito control until 1966, when it was replaced by organophosphates, chiefly malathion, fenthion (Baytex), and more recently, Abate.

In September 1967, Hurricane Doria hit the coast of New Jersey, causing high storm tides and killing clapper rails. Several hundred birds were found dead along causeways in Cape May County, and an estimated 2,000 or more died in the marshes. Biologists at the Patuxent Wildlife Research Center, U.S. Department of Interior—Fish and Wildlife Service, obtained 43 dead rails from six localities (Fig. 1). Concurrently, fish and invertebrates were collected from these locations and were frozen and stored. Sampling was repeated at the same localities in 1973. The two groups of samples collected 7 years apart, the first having been a year after use of DDT was discontinued in Cape May County, were then analyzed by the same procedures.

This paper reports residue levels of organochlorine pesticides and polychlorinated biphenyls (PCB's) detected in these samples and compares findings of 1967 and 1973. The history of pesticide spraying for mosquito control in Cape May County is reviewed as it pertains to residue levels.

History of Pesticide Use for Mosquito Control

The history of pesticide use on mosquitoes in Cape May County was obtained from the Proceedings of Annual Meetings of the New Jersey State Mosquito Extermination Association (*9, 13-15, 17, 18, 21*) and from unpublished daily work records in the files of the Cape May County Extermination Commission.

[1] Patuxent Wildlife Research Center, Fish and Wildlife Service, U.S. Department of Interior, Laurel, Md. 20811

[2] Iowa Cooperative Wildlife Research Unit, Iowa State University, Ames, Iowa

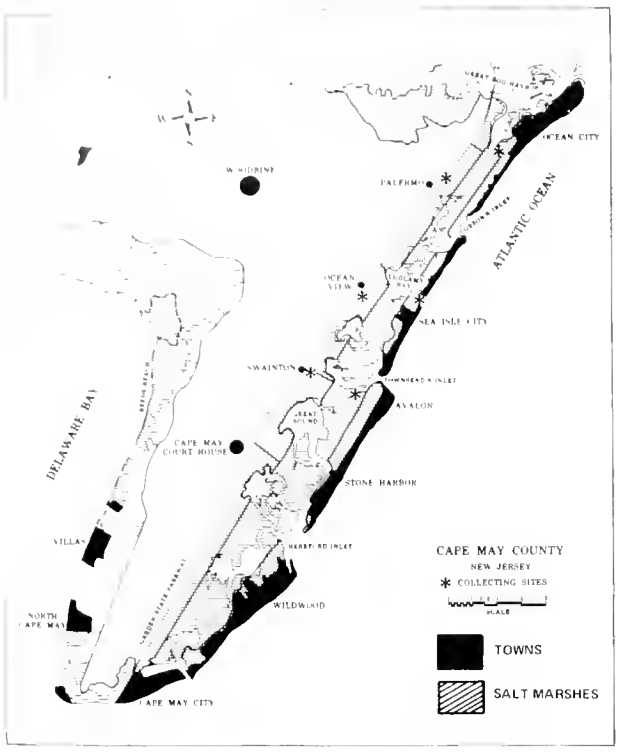

FIGURE 1. *Aerial spray zones and fauna collection sites in salt marshes of Cape May County, New Jersey*

Ditching, draining, and other methods of water control were the principal means of limiting mosquitoes in Cape May County before 1946. Small quantities of fuel oil and pyrethrum were applied as larvacides. In 1946, the County acquired an aerosol fog unit for control of adult mosquitoes. This machine was used to apply a 5 percent DDT emulsion in fuel oil along the streets of resort communities bordering the Atlantic Ocean in the summer of 1946 (*18*). The amounts of pesticide used in 1946-47 are unknown. In 1948 the mosquito control program included fog, mist, and spray work with DDT, TDE, and pyrethrum; total quantity used was 19,450 gallons. The marshes just west of Sea Isle City received an experimental aerial application June 15, 1948 (*21*).

By 1949, DDT was the principal chemical used for mosquito control in New Jersey (*9*). It was usually applied as a 5 percent emulsion in oil or as a wettable powder. For adult mosquito control, DDT was applied at 0.1 lb/acre; as a larvacide it was applied in early spring at 1-2 lb/acre in restricted areas. Statewide, oil was second in importance to DDT, and pyrethrum larvacide was third. The amount of DDT used in Cape May County in 1949 had risen to [illegible] gallons of emulsion applied from the ground, 1,05[illegible] gallons from the air, and 6,000 pounds of DDT dust applied from the ground (*17*). Neither oil nor pyrethrum was [illegible] after 1946.

Aerial spraying, supported by State funds, was begun on a wide scale in 1949. Areas to be sprayed included a band 2,000 feet wide which began at Cape May Point and continued west of the Atlantic seashore resort towns up to and including Ocean City. A similar band extended just east of the Garden State Parkway. Another band extended along the shore of Delaware Bay (Fig. 1). These bands were divided into 29 zones of known acreage to facilitate aerial application. A wide perimeter around the inland town of Woodbine was sprayed regularly from the air.

Aerial sprays were applied from heights of 50-75 feet at a rate of 0.1 lb of technical DDT in 1 quart of petroleum solvent per acre of ground surface (*13-15*). These formulation and application rates for aerial and most ground spraying of DDT were continued through 1966. DDT emulsion was sometimes applied as a larvacide in restricted areas at rates of 0.3 lb/acre (*13*). About half of all DDT applied between 1950 and 1966 was sprayed from the air; the remainder was dispersed from the ground through aerosol fog machines, truck- and tractor-mounted tank sprayers, and hand sprayers.

The total amount of active DDT applied in Cape May County from 1949 to 1966, assuming the formulation rate (0.4 lb/gal) remained the same for all years, was estimated to be 614,970 lb. Yearly amounts increased steadily from 1,926 lb in 1949 to a high of 58,515 lb in 1963 (Table 1). Malathion and fenthion began to replace DDT in 1964 and by 1966 DDT use had declined to 33,186 lb.

About 8-10 percent of all DDT applied after 1955 was in dust or pellet forms. Pellets contained either 5 or 10 percent active DDT and were usually applied at rates of 10 or 20 lb/acre (1.0 lb DDT). In the early 1960's pellets were used extensively as a larvacide.

After 1966, malathion became the principal chemical for mosquito control in Cape May County, although small amounts had been used earlier. Fenthion was also used in pellet form in some areas. Use of malathion and fenthion was essentially discontinued about 1971. Abate was first used in 1969, and by 1973 it was the only chemical in widespread use for mosquito control.

Table 2 summarizes the amount of DDT applied 1950-66 as emulsion to each of the six zones from which biotic samples were collected (Fig. 1). These zones, named after the largest nearby town, are Ocean City, Sea Isle City, Avalon, Palermo, Ocean View, and Swainton; they correspond to 6 of the 21 aerial spray zones designated on daily work records and maps of the County Mosquito Extermination Commission. The remaining 15 zones have been grouped into Atlantic Shore and Bay Shore areas for the purpose of this summary. The Atlantic Shore area includes five aerial spray zones along the Atlantic shore from Swainton and Stone Harbor to Cape May and one

TABLE 1. *Active DDT applied each year as emulsion, pellets, or dust in Cape May County, New Jersey, by County Mosquito Extermination Commission—1949-66*[1]

Year	Pounds	Year	Pounds
1949	1,926	1959	43,897
1950	8,861	1960	53,668
1951	18,189	1961	51,206
1952	19,587	1962	45,920
1953	22,853	1963	58,515
1954	26,117	1964	56,634
1955	24,267	1965	45,941
1956	29,018	1966	33,186
1957	37,531		
1958	37,654	TOTAL	614,970

[1] Total area sprayed was 46,638 acres

TABLE 2. *Active DDT applied as emulsion in different areas of Cape May County, New Jersey—1950-66*

Zone	Acres	Pounds	Pounds/Acre
Ocean City	3,000	57,103	19.0
Sea Isle City	1,500	34,486	23.0
Avalon	2,900	43,582	15.0
Palermo	2,100	14,510	6.9
Ocean View	1,180	7,961	6.8
Swainton	960	4,854	5.1
Atlantic Shore	13,631	192,676	14.1
Bay Shore	21,367	208,975	9.8
Total	46,638	564,147	12.1

zone northwest of Palermo. The Bay Shore area includes nine aerial spray zones on the Delaware Bay shore, Woodbine, and most of the rural areas, roads, and municipalities west of the Garden State Parkway. The Atlantic Shore and Bay Shore areas are included in this summary to complete the spraying data for the entire County. It is possible that residues were transported to the six sampling zones from the Atlantic Shore or Bay Shore areas by wind drift, tidal action, and water shed runoff.

Daily work records of aerial and ground applications included the spray site and the amount of emulsion dispersed at each location. Generally, each spraying location itemized on the work sheets could be assigned to one of the eight zones listed in Table 2 and shown in Figure 1. Quantity of DDT applied in pellet form is not included in Table 2 because exact locations where pellets were used could not always be determined.

Because most DDT used in both aerial and ground operations was dispersed in zones of known acreage, rough estimates of the total lb/acre applied in each zone in the 17-year period could be made (Table 2). The rates varied from 5.1 lb/acre in the Swainton zone to 23.0 lb/acre at Sea Isle City with a mean of 12.1 for all zones. Spraying was generally heavier in zones nearest the ocean. Annually, the rate of application for the entire County averaged 0.7 lb/acre and ranged from 0.2 lb/acre in 1950 to 1.1 lb/acre in 1963.

This brief history of pesticide use in Cape May County does not include pesticides applied on private lawns or gardens, agriculture lands, golf courses, or military bases. Truck crops are the chief agricultural products and most of the cropland is in the western part of the County. More extensive areas of cropland are found in counties to the west and north, and chemicals applied there may have eventually entered estuaries in Cape May County through runoff. Military bases cooperated with the County's mosquito program by furnishing some chemicals to be sprayed on military land, but it is not known how extensively these authorities may have sprayed on their own. Some larger communities along the Atlantic shore owned aerosol fog machines and applied limited amounts of chemicals. Undoubtedly, the County Mosquito Extermination Commission was the largest user of pesticides in Cape May County and dispersed the bulk of organochlorines entering the local environment during 1946-66.

Sample Collection and Preparation

Biotic samples were obtained at six of the spraying zones in Cape May County marshes in 1967 and 1973 (Fig. 1) during September 19-23. Collecting points were Ocean City: north side of New Jersey State Highway 23, and 0.5 mile west of State Highway 56; Sea Isle City: west of Highway 19 at the end of 30th Street; Avalon: south side of Highway 1, and 1 mile west of Highway 30; Palermo: east side of Garden State Parkway, 2 miles south of Highway 23; Ocean View: south side of Highway 25, 0.2 mile east of Garden State Parkway; Swainton: south side of Highway 1, 0.5 mile east of Garden State Parkway. Scientific and vernacular names of animal species in the study are listed in Table 3. Scientific and vernacular names of plants appear in the text.

Cape May County marshes are typical cordgrass (*Spartina alterniflora*) salt marshes. The taller (4-6 ft) dense saltmarsh cordgrass occurred as a narrow band along tidal creeks; the shorter (< 1 ft) sparse cordgrass covered the remainder of the marsh. The height of vegetation appeared to be correlated with the degree of tidal inundation; short grass was subject to less frequent inundation than was tall grass.

Marshes averaged about 3 miles wide in the area where samples were collected and were divided into an inland side and an ocean side by a meandering channel, the intercoastal waterway. Ocean City, Sea Isle City, and Avalon are on the ocean side of the marsh; Palermo, Ocean View, and Swainton are on the inland side.

In 1967, 40 dead clapper rails were picked up along highway causeways after the hurricane September 17. One rail was shot at the Palermo site September 2, one was found dead at Palermo August 15 immediately following an aerial application of malathion, and one was shot at the Sea Isle City site September 2. In 1973, all

TABLE 3—*Organisms analyzed for organochlorine residues in Cape May County, New Jersey—1967 vs. 1973*

Common and Scientific Names	
Clapper Rail	*Rallus longirostris*
Sheepshead Minnow	*Cyprinidon variegatus*
Mummichog	*Fundulus heteroclitus*
Striped Killifish	*Fundulus majalis*
Grass Shrimp	*Palaemonetes* sp.
Fiddler Crab	*Uca pugnax*
Blue Crab	*Callinectes sapidus*
Ribbed Mussel	*Geukensia demissa*
Periwinkle	*Littorina littorea*
Mud Snail	*Hyanassa obsoleta*
Salt Marsh Snail	*Melampus bidentatus*
Meadow Grasshopper	*Conocephalus fasciatus*

rails were shot. Carcasses were wrapped in aluminum foil, placed in plastic bags, and frozen until analysis.

Fish were seined from shallow pools and tidal creeks. Fiddler crabs and mussels were dug from their burrows and snails were picked from the mud or vegetation by hand. Samples were placed in acetone-rinsed glass bottles at the time of collection, and were frozen.

Before extraction and chemical analysis, clapper rails were skinned; as much subcutaneous fat as possible was retained with the carcass. Beaks, legs, and digestive tracts were removed and carcasses were homogenized. Stomachs were held for later identification of contents.

Fish and invertebrate samples were rinsed in distilled water to remove external soil and debris, and were drained briefly before homogenization. Total individuals of each species were pooled into a single sample for each sampling point. Fish and fiddler crabs were homogenized whole. Shells of periwinkles, mud snails, and ribbed mussels were removed and discarded. Only the salt marsh snail was homogenized with its shell because the animal is so small.

Because the samples of 1967 had been stored frozen for several years, authors compared moisture content with that of 1973 samples. Small aliquots of each invertebrate species from 1967 and 1973 were oven-dried at 100°C until weights remained constant for 2 days. No significant differences in moisture content between years were detected, hence residues expressed on a wet-weight basis are considered comparable for both groups.

Chemical Analysis

The biotic material was ground and a suitable aliquot, usually 10 g, was mixed with sodium sulphate to remove moisture. This mixture was transferred to a paper thimble and extracted with hexane for about 7 hours. Paper thimbles were pre-extracted for 7 hours in methylene chloride to remove background peaks. Cleanup was accomplished by column chromatography; the concentrated extract was placed on a florisil column and eluted with 200 ml 6 percent ethyl ether in hexane. The florisil eluate was concentrated and eluted from a silicic acid column to separate pesticides from PCB's. These procedures are described in detail by Cromartie et al. (*4*).

Samples were analyzed with an electron-capture gas chromatograph equipped with a 4 percent/6 percent SE-30/QF-1 column as 190°C. Pesticides were quantitated with a computing integrator; PCB's were estimated by comparing total area with Aroclor 1248 or 1254. Residues in about 10 percent of the samples were confirmed on a gas chromatograph/mass spectrometer.

Average percentage recoveries from spiked mallard carcass tissue were: DDE, 96; TDE, 103; DDT, 112; dieldrin, 101; heptachlor epoxide, 104; oxychlordane, 98; *cis*-chlordane, 100; *cis*-nonachlor, 98; HCB, 69; and Aroclor 1254, 101. Residue data were not corrected for percentage recoveries.

Limits of sensitivity were 0.01 ppm for pesticides and 0.02 ppm for PCB's in fish and invertebrate samples; corresponding limits in clapper rail samples were 0.1 ppm for pesticides and 0.5 ppm for PCB's.

For statistical analysis, residue values were converted to logarithms base 10 after adding 1.0 to all values to allow the use of zero values. Geometric means are the antilogs of log means minus one. For PCB residues that could only be quantified as < 0.5 ppm, an arbitrary value of 0.25 ppm was assumed in calculating means.

Results and Discussion

One-hundred-fifty-nine samples representing 12 species of vertebrates and invertebrates were analyzed for organochlorines and PCB's (Tables 4-6). The most frequently found chemical among all the samples was *p,p*-DDE; it occurred in 97 percent of the samples. Four other isomers of DDT also were found but their occurrence varied with the year of collection and the species of organism. For instance, *p,p'*-DDT was detected in 86 percent of the fish and invertebrate samples in 1967 but in only 6 percent in 1973. In clapper rails, the incidence of this chemical decreased from 37 percent in 1967 to 0 percent in 1973.

The isomer *p,p'*-TDE occurred in all fish samples from both 1967 and 1973, but among the invertebrates, its incidence decreased from 82 percent in 1967 to 42 percent in 1973. Among clapper rail samples the incidence decreased even more dramatically: from 63 percent to 4 percent. The lower incidence of *p,p'*-TDE and *p,p'*-DDT in rails was not unexpected because birds evidently metabolize *p,p'*-DDT readily into *p,p'*-DDE and *p,p'*-TDE, and there is a greater propensity for storage of DDE than TDE in bird tissue (*1,2*). Also, the rail samples

were analyzed as individuals whereas fish and invertebrates were analyzed as pooled samples in which each sample contained five or more individuals.

The isomers *o,p'*-DDT and *o,p'*-TDE were found in 71 percent of the invertebrate samples of mussels, mud snails, and salt marsh snails in 1967, but were not found in any samples in 1973. These isomers are not often detected in wildlife specimens although technical grade DDT contains up to 30 percent *o,p'*-DDT (*19, 26*). Lamont (*19*) found *o,p'* isomers in brown pelican (*Pelicanus occidentalis*) eggs collected in California in 1969, and in tissues of mallard ducks (*Anas platyrhynchos*) that had been fed *o,p'*-DDT for 10 weeks. An average ratio of 0.2 between *p,p'*-DDT and *o,p'*-DDT was reported for Lake Michigan fish in 1971 (*26*). However, *o,p'*-DDT was not detected in fish samples from New Jersey in 1967 or 1973.

Species differences in incidence of the various DDT isomers is probably the result of selective degradation in food and tissues caused by differences in metabolic pathways, storage, half-lives, and excretion rates in the various organisms (*16, 20*).

Changes in relative occurrence of DDE analogs between 1967 and 1973 were accompanied by changes in relative magnitude of residue levels in those years. Changes in magnitude and occurrence are obvious in Tables 4-6. Changes in magnitude of Σ DDT (Table 7) were tested by Wilcoxen's two-sample nonparametric test (*24*) for 9 of the 12 species sampled. Residue levels in all 9 species were significantly lower in 1973 ($p<0.05$). Decreases in Σ DDT varied from 84 to 99 percent of 1967 levels.

Mean residues of Σ DDT observed in 1967 ranged from 0.63 ppm in the periwinkle to 9.05 ppm in the mummichog. Each of the three species of fish contained higher mean residue levels than did any other species sampled.

Residues of Σ DDT averaged 3.36 ppm in clapper rails in 1967. Clapper rails feed principally on fiddler crabs in which DDT averaged 1.33 ppm in 1967. In 1973, DDT residues had dropped to 0.54 ppm in rails and 0.13 ppm in fiddler crabs. No significant differences ($p<0.05$) in residues were detected between male and female rails or between adults and immatures. In an acute toxicity study by Van Velzen and Kreitzer (25) clapper rails were highly tolerant of DDT, and the authors concluded that exposure to this pesticide in marshes probably does not cause death among adult rails. Ferrigno (7) observed production crashes in clapper rail populations in Cape May County in 1959 and 1965. Hatching success remained low from 1965 to 1969 but began to increase in 1970 (F. Ferrigno, Sr., State of New Jersey Department of Environmental Protection, 1973; personal communication). Peak years in hatching success were 1958, 1962, and 1972. Population studies were not conducted before the DDT era, so it would be interesting to document long-term rail population trends to see whether similar production crashes occur after the DDT era.

Mean and maximum residues of DDT in fish (Table 5)

TABLE 4. *Chlorinated hydrocarbon residues in carcasses of the clapper rail* (Rallus longirostris) *from six localities in Cape May County, New Jersey—1967 and 1973*

	Residues, ppm wet weight			
	1967		1973	
	Mean[1]	Range	Mean[1]	Range
Ocean City				
p,p'-DDE	1.8	0.55-5.3	0.49	0.20-1.2
p,p'-TDE	0.10	ND-0.28	ND	—
p,p'-DDT	ND	—	ND	—
Dieldrin	0.14	ND-0.23	0.04	ND-0.19
PCB's	<0.5	—	0.44	<0.5-1.1
Carcass wt, g	130.3	67.2-185.0	219.4	177.5-255.0
Percent lipid	4.1	2.4-7.1	8.1	2.1-17.1
No. samples	7		4	
Sea Isle City				
p,p'-DDE	2.7	1.1-7.0	0.60	0.31-0.77
p,p'-TDE	0.25	ND-1.9	ND	—
p,p'-DDT	0.14	ND-1.1	ND	—
Dieldrin	ND	—	ND	—
PCB's	<0.5	—	0.70	<0.5-2.0
Carcass wt, g	148.2	120.0-170.3	203.0	182.0-256.5
Percent lipid	3.5	1.9-6.5	8.7	5.1-12.9
No. samples	8		4	
Avalon				
p,p'-DDE	3.0	2.1-4.0	0.89	0.33-3.4
p,p'-TDE	0.10	ND-0.25	ND	—
p,p'-DDT	0.04	ND-0.17	ND	—
Dieldrin	0.04	ND-0.18	0.02	ND-0.11
PCB's	<0.5	—	0.83	<0.5-3.4
Carcass wt, g	127.6	94.3-149.0	206.7	164.0-254.0
Percent lipid	5.0	3.9-8.1	11.7	4.9-16.0
No. samples	7		6	
Palermo				
p,p'-DDE	6.3	2.5-15	0.78	0.33-1.9
p,p'-TDE	0.88	ND-2.3	ND	—
p,p'-DDT	0.81	ND-3.0	ND	—
Dieldrin	0.08	ND-0.22	0.02	ND-0.10
PCB's	<0.5	—	1.3	0.73-2.5
Carcass wt, g	144.4	77.4-214.2	202.8	177.5-243.5
Percent lipid	5.1	2.6-9.3	14.6	9.5-20.9
No. samples	7		6	
Ocean View				
p,p'-DDE	3.4	1.4-11.0	0.20	0.18-0.21
p,p'-TDE	0.26	ND-0.90	ND	—
p,p'-DDT	0.23	ND-0.48	ND	—
Dieldrin	0.08	ND-0.18	ND	—
PCB's	<0.5	—	0.55	<0.5-0.93
Carcass wt, g	151.8	74.9-184.3	181.5	167.0-196.0
Percent lipid	4.0	2.0-8.1	5.6	5.6-5.7
No. samples	7		2	
Swainton				
p,p'-DDE	3.4	0.78-8.8	0.54	0.31-1.6
p,p'-TDE	0.18	ND-0.68	0.03	ND-0.17
p,p'-DDT	0.15	ND-1.6	ND	—
Dieldrin	0.03	ND-0.11	ND	—
PCB's	<0.5	—	0.14	ND-0.5
Carcass wt, g	153.1	90.0-186.7	174.1	65.0-263.0
Percent lipid	5.0	2.5-7.1	8.2	2.8-14.2
No. samples	7		5	

Note: Three samples from 1973 contained mirex: Ocean City, 0.16 ppm; Sea Isle City, 0.39 ppm; Avalon, 0.15 ppm. The same sample from Avalon also contained 0.12 ppm oxychlordane.

ND = not detected

[1] Mean values for chemical residues are geometric means; mean values for carcass weight and percent lipid are arithmetic means.

TABLE 5. *Chlorinated hydrocarbon residues in pooled samples of fish from Cape May County, New Jersey—1967 and 1973*

Locality	Year	n[1]	Sample weight, g	Percent lipid	Residues, ppm wet weight			
					p,p'-DDE	*p,p'*-TDE	*p,p'*-DDT	PCB's
Sheepshead minnows (*Cyprinidon variegatus*)								
Ocean City	1967	56	23 8	3 8	1 5	4 0	2 0	0 60
	1973	168	200 3	4 3	0 12	0 55	ND	0 16
Sea Isle City	1967	88	86 0	4 8	1 7	15	4 2	1 1
	1973	121	160 8	5 4	0 38	0 53	ND	0 13
Avalon	1967	41	42 4	5 7	0 44	2 8	1 2	0 91
	1973	273	279 06	4 0	0 06	0 06	ND	0 18
Palermo	1967	46	30 9	4 2	3 5	12	5 5	1 5
Ocean View	1967	40	34 1	4 8	0 45	2 2	0 55	4 3
	1973	103	129 82	4 1	0 07	0 06	ND	0 18
Swainton	1973	88	100 56	4 3	0 10	0 18	ND	0 14
Striped killifish (*Fundulus majalis*)								
Ocean City	1973	28	29 9	2 2	0 14	0 52	ND	0 17
Sea Isle City	1967	3	3 6	3 9	2 3	9 2	9 5	2 8
	1973	8	9 4	2 8	0 15	0 15	ND	0 22
Avalon	1973	28	31 9	2 5	0 05	0 04	ND	0 17
Palermo	1973	30	35 0	3 0	0 19	0 07	ND	0 19
Ocean View	1967	19	31 3	2 0	0 55	1 8	0 55	2 3
	1973	17	18 3	3 1	0 06	0 04	ND	0 14
Swainton	1967	40	75 4	2 1	0 40	0 55	0 08	0 41
	1973	14	10 5	2 2	0 06	0 04	ND	0 20
Mummichogs (*Fundulus heteroclitus*)								
Ocean City	1967	20	6 9	4 2	2 0	3 6	4 8	0 83
	1973	73	73 2	2 2	0 10	0 33	ND	0 12
Sea Isle City	1967	30	38 0	4 6	10	9 9		
	1973[2]	3	18 5	3 5	0 22	0 09	12	0 02
				2 7				
				0 29				
Avalon	1967	40	80 2	4 9	1 3	3 2	1 6	1 5
	1973	21	48 7	2 6	0 06	0 05	ND	0 23
Palermo	1967	60	46 3	3 4	10	11	13	2 0
	1973	40	45 6	2 9	0 21	0 08	ND	0 18
Ocean View	1967	18	79 2	3 8	2 3	5 5	1 7	1 3
	1973	21	29 6	2 3	0 08	0 03	ND	0 19
Swainton	1967	64	88 9	3 2	0 45	0 39	ND	3 5
	1973[3]	22	15 71	3 0	0 09	0 04	ND	0 23
Mummichogs (*Fundulus heteroclitus*)								
Ocean City	1967	20	6 9	4 2	2 0	3 6	4 8	0 83
	1973	73	73 2	2 2	0 10	0 33	ND	0 12
Sea Isle City	1967	30	38 0	4 6	10	9 9	12	2 7
	1973[2]	3	18 5	3 5	0 22	0 09	0 02	0 29
Avalon	1967	40	80 2	4 9	1 3	3 2	1 6	1 5
	1973	21	48 7	2 6	0 06	0 05	ND	0 23
Palermo	1967	60	46 3	3 4	10	11	13	2 0
	1973	40	45 6	2 9	0 21	0 08	ND	0 18
Ocean View	1967	18	79 2	3 8	2 3	5 5	1 7	1 3
	1973	21	29 6	2 3	0 08	0 03	ND	0 19
Swainton	1967	64	88 9	3 2	0 45	0 39	ND	3 5
	1973[3]	22	15 71	3 0	0 09	0 04	ND	0 23

NOTE: ND = not detected
[1] n = number of individual fish in the pooled sample
[2] 0 02 ppm *cis*-chlordane or *trans*-nonachlor detected in sample
[3] 0 01 ppm *cis*-chlordane or *trans*-nonachlor detected in sample

collected in 1967 are high compared with residues reported in an extensive summary by Edwards (*6*) for marine and freshwater fish. A pooled sample of the sheepshead minnow and another of mummichog from Long Island in 1966 contained 0.94 ppm and 1.24 ppm ΣDDT, respectively (*27*). Veith reported mean DDT residues in 13 species of fish from Lake Michigan that ranged from 0.9 to 7.1 ppm (*26*). Fish from the Delaware River in New Jersey, analyzed as part of the National Pesticide Monitoring Program, had some of the highest mean residues of ΣDDT recorded on the Atlantic Coast; average levels [illegible] 45 ppm in 1968 (*10, 11*).

It is likely that [illegible] Jersey fish developed increased tolerance to DDT and its analogs after 20 years of continued DDT use in their habitat. Residues in 1967 samples, however, were much lower than those observed in genetically resistant mosquitofish (*Gambusia affinis*) in Texas which had average ΣDDT residues greater than 50 ppm on a whole-body basis (*5*).

Odum et al. (*22*) found that fiddler crabs that had fed on detritus containing approximately 10 ppm DDT residues developed poor coordination after 5 days, and residues in the claw muscles of these crabs averaged 0.885 ppm after 10 days. Residues in whole bodies of crabs from New Jersey in 1967 averaged 1.33 ppm, and ranged as high as 4.13 in one sample. The crabs were alive when collected

TABLE 6. *Chlorinated hydrocarbon residues in pooled samples of invertebrates from Cape May County, New Jersey —1967 and 1973*

Locality	Year	Sample weight, g	Percent lipid	Residues, ppm wet weight					
				p,p'-DDE	*p,p'*-TDE	*o,p'*-TDI	*p,p'*-DDT	*o,p'*-DDT	PCBs
Fiddler crab (*Uca pugnax*)									
Ocean City	1973[1]	33 78	0 9	0 12	0 09	ND	ND	ND	0 13
Sea Isle City	1967[2]	17 40	0 7	3 6	0 27	ND	0 32	ND	0 09
	1973	115 93	0 9	0 11	0 04	ND	ND	ND	0 11
Avalon	1967	41 13	1 4	0 41	0 19	ND	0 10	ND	0 17
	1973	70 37	1 1	0 06	0 05	ND	0 01	ND	0 10
Palermo	1967	26 47	0 8	1 3	0 14	ND	0 04	ND	0 23
	1973	40 57	0 5	0 76	ND	ND	ND	ND	0 27
Ocean View	1967	11 75	0 8	1 9	0 19	ND	0 29	ND	0 25
	1973	105 63	0 8	0 06	ND	ND	ND	ND	0 27
Swainton	1967	46 40	1 8	0 28	0 06	ND	0 07	ND	0 11
	1973	133 15	0 6	0 03	ND	ND	ND	ND	0 16
Ribbed Mussel (*Geukensia demissa*)									
Ocean City	1967	55 75	0 8	0 27	0 36	0 07	2 3	0 47	0 17
	1973	91 36	0 4	0 02	0 01	ND	ND	ND	ND
Sea Isle City	1967	62 64	0 3	0 37	0 51	0 09	3 6	0 73	0 05
	1973	107 97	0 2	0 01	0 01	ND	ND	ND	ND
Avalon	1973	101 59	0 2	0 02	ND	ND	ND	ND	0 10
Palermo	1967	25 19	0 7	0 94	1 5	0 23	9 0	1 2	0 36
	1973	83 98	0 2	0 06	0 03	ND	0 02	ND	0 22
Ocean View	1967	54 95	0 6	0 20	0 24	0 05	1 6	0 20	0 27
	1973	56 05	0 5	0 02	ND	ND	ND	ND	0 02
Swainton	1967	66 92	0 2	0 02	ND	ND	ND	ND	0 10
	1973	37 03	0 3	0 03	ND	ND	ND	ND	0 24
Periwinkle (*Littorina littorea*)									
Ocean City	1973	2 76	1 1	ND	ND	ND	ND	ND	ND
Sea Isle City	1973	55 33	1 4	0 04	ND	ND	ND	ND	ND
Avalon	1967	1 34	1 5	0 14	0 31	ND	0 18	ND	0 72
	1973	64 89	2 6	0 02	ND	ND	ND	ND	0 14
Palermo	1973	25 47	0 9	0 02	ND	ND	ND	ND	0 15
Ocean View	1973	8 87	2 2	0 04	ND	ND	ND	ND	0 29
Swainton	1973	4 08	4 2	0 04	ND	ND	ND	ND	0 30
Mud snail (*Ilyanassa obsoleta*)									
Ocean City	1967[3]	4 69	0 2	0 30	0 77	0 13	0 47	0 07	0 07
	1973[3]	30 51	0 2	0 05	0 02	ND	ND	ND	0 06
Sea Isle City	1967	10 68	2 1	1 6	4 3	0 82	0 85	0 02	0 13
	1973	66 91	0 8	0 14	0 07	ND	ND	ND	0 06
Avalon	1967	5 51	0 4	0 05	ND	ND	ND	ND	0 12
	1973	53 20	1 3	0 03	0 03	ND	ND	ND	0 14
Palermo	1973	39 15	0 9	0 04	0 02	ND	ND	ND	0 16
Ocean View	1973	59 38	0 9	0 04	ND	ND	ND	ND	0 34
Swainton	1973	35 72	1 0	0 03	ND	ND	ND	ND	0 02
Salt marsh snail (*Melampus bidentatus*)									
Ocean City	1967	6 79	1 3	0 46	1 2	0 10	2 4	0 16	0 07
	1973	29 16	0 7	0 06	0 04	ND	ND	ND	ND
Sea Isle City	1967	17 19	1 1	1 0	2 5	0 21	2 9	0 28	0 08
	1973	43 23	0 6	0 01	0 01	ND	ND	ND	0 06
Avalon	1967	16 85	1 3	0 06	0 20	ND	0 30	ND	0 07
	1973	29 73	0 4	ND	ND	ND	ND	ND	0 06
Palermo	1967	27 25	1 8	2 0	5 0	0 45	6 0	0 41	1 4
	1973	25 89	0 8	0 02	0 02	ND	ND	ND	0 06
Ocean View	1967	12 42	1 7	0 76	1 1	0 08	3 5	0 14	0 34
	1973	37 99	0 6	0 01	ND	ND	ND	ND	0 13
Swainton	1967	28 30	1 0	0 05	0 06	ND	0 13	ND	0 06
	1973	37 71	0 4	< 0 01	ND	ND	ND	ND	0 06
Grass Shrimp (*Palaemonetes* sp.)									
Ocean City	1973	39 47	1 0	0 02	0 01	ND	ND	ND	0 05
Sea Isle City	1973	180 30	0 5	0 02	ND	ND	ND	ND	ND
Avalon	1967	3 97	0 5	ND	ND	ND	ND	ND	< 0 02
Swainton	1973	7 81	0 5	ND	ND	ND	ND	ND	ND
Blue crab (*Callinectes sapidus*)									
Ocean City	1973	6 95	4 8	0 03	0 09	ND	ND	ND	ND
Avalon	1967	41 28	2 9	0 87	ND	ND	ND	ND	0 11
Avalon	1973	6 50	1 0	0 02	ND	ND	ND	ND	0 28
Meadow Grasshopper (*Conocephalus fasciatus*)									
Palermo	1973[4]	6 32	4 0	ND	ND	ND	ND	ND	ND

NOTE: ND = not detected

[1] 0 13 ppm oxychlordane present in sample

[2] 0 04 ppm toxaphene present in sample

[3] 0 02 ppm HCB detected in samples

[4] 0 02 ppm *cis*-chlordane and/or *trans*-nonachlor detected in sample

TABLE 7 *Comparison of ΣDDT residues in selected biota from salt marshes, Cape May County, New Jersey—1967 vs. 1973*

Species	Residues, ppm wet weight						Percent change[2]
	1967			1973			
	n[1]	Geometric mean	Range	n[1]	Geometric mean	Range	
Clapper Rail	43	3.36	0.55-18.70	27	0.54	0.18-3.4	−84
Sheepshead Minnow	5	8.59	3.20-21.00	5	0.31	0.12-0.91	−96
Mummichog	6	9.05	0.84-34.00	6	0.20	0.11-0.43	−98
Striped Killifish	3	3.97	1.03-21.00	6	0.19	0.09-0.66	−95
Fiddler Crab	5	1.33	0.41-4.19	6	0.13	0.03-0.76	−90
Ribbed Mussel	5	1.61	0.02-12.87	6	0.03	0.02-0.11	−98
Periwinkle	1	0.63	—	6	0.03	0.00-0.04	−95
Mud Snail	3	0.87	0.05-7.59	6	0.06	0.03-0.21	−93
Salt Marsh Snail	6	2.60	0.24-13.86	6	0.03	0.00-0.10	−99

[1] For clapper rail, n = number of individuals; for all others, n = number of pooled samples
[2] Changes are all significant at probability levels of 0.05 or less (two-tailed, Wilcoxen two-sample test)

but behavior was not recorded. Crabs collected in 1973 behaved normally and were not sluggish or awkward when DDT residues ranged from 0.03 to 0.76 ppm.

Residue levels in the mollusks collected in 1967 were generally higher than levels reported by Edwards (*6*) for a wide variety of related species except oysters. The maximum ΣDDT residues reported in eastern oysters (*Crassostrea virginica*) collected in the New Jersey waters of Delaware Bay June 1966—June 1972 was 0.272 ppm, and most residues in these extensive samples were less than half this amount (*3*). Concentrations in the oysters decreased during the 1966-72 collection period. Woodwell et al. (*27*) reported 0.26 ppm ΣDDT in mud snails and 0.44 ppm ΣDDT in the hard clam (*Mercenaria mercenaria*) from Long Island, New York, in 1966 when DDT use was curtailed there. Concentrations of DDT and its metabolites were low in six species of shellfish collected in Long Island waters during 1968-1970; only a few values were greater than 0.22 ppm (*8*).

Although residue levels varied at the six localities in New Jersey, simple correlation coefficients between ΣDDT residues and amounts of DDT sprayed for mosquito control at these localities were low and statistically nonsignificant ($p > 0.05$). However, residue levels of ΣDDT were consistently higher in all species at Palermo and Sea Isle City. The Sea Isle City zone was sprayed more than the other localities during the 17 years of recorded DDT usage (Table 2), but Palermo was sprayed less than either Ocean City or Avalon. Foehrenbach (*8*) was able to correlate pesticide concentrations in shellfish with land use in the watersheds surrounding his collecting stations. It is possible that other pesticide use in the Palermo watershed contributed to concentrations in the biota there. Another explanation is that DDT sprayed from the air drifted with prevailing offshore breezes toward Palermo from Sea Isle City and Ocean City. Because of the widespread coverage of DDT spraying in Cape May County and the short distances involved, further interpretation of observed differences in residue levels between localities is pointless.

PCB's were the second most common residue found. They occurred in 93 percent of all samples. Significant changes in concentrations occurred between 1967 and 1973 (Table 8), but the pattern was not so consistent in all species as it was for ΣDDT. Residues decreased in all three species of fish and in the salt marsh snail. A large increase in residues occurred in clapper rails but mean levels remained low. Changes in other species were not significant.

Dieldrin was not found in fish and invertebrates but did occur in 37 percent of the rail carcasses in 1967. Only 11 percent of the rails collected in 1973 contained dieldrin. Dieldrin apparently was never used for mosquito control in Cape May County but, until banned in 1974, it had been used widely in the United States as an insecticide. Clapper rails feed primarily on fiddler crabs but occasionally take small fish and snails. The absence of dieldrin in any of these species may mean that rails obtained the chemical from salt marsh organisms not included in this study, or that rails can concentrate dieldrin in their tissues from residue levels in their food supply that are below detection limits of the present study.

All other organochlorines were either absent or occurred in small quantities in only a few samples (see footnotes, Tables 4-6). The infrequent occurrence and low concentration of other organochlorines indicate that the use of these persistent insecticides has not increased appreciably as a result of the cessation of DDT use.

The lull which followed 20 years of intensive spraying of DDT for mosquito control in Cape May County has been marked by rather rapid decreases in occurrence and concentration of ΣDDT in aquatic fauna. More information is needed for species in higher trophic levels such as fish-eating birds and carnivorous fish, but these forms should also begin to show decreased residue levels. Reproduction in the osprey (*Pandion haliaetus*) in Cape May County had been seriously depressed for several years, but it began to improve slightly in 1974 (*12*). However, heron eggs col-

lected in Cape May County in 1972 still contained rather high residue levels (*23*).

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LITERATURE CITED

(1) *Bailey, S., P. J. Bunyan, B. D. Rennison, and A. Taylor. 1969.* The metabolism of 1,1-Di(p-chlorophenyl-2,2,2-trichloroethane and 1,1-Di(p-chlorophenyl)-2,2-dichloroethane in the pigeon. Toxicol. Appl. Pharmacol. 14(*1*):13-22.

(2) *Bailey, S., P. J. Bunyan, B. D. Rennison, and A. Taylor. 1969.* The metabolism of 1,1-Di(p-chlorophenyl)-2,2-dichloroethylene and 1,1-Di(p-chlorophenyl)-2-chloroethylene in the pigeon. Toxicol. Appl. Pharmacol. 14(1):23-32.

(3) *Butler, P. A. 1973.* Organochlorine residues in estuarine mollusks, 1965-72—National Pesticide Monitoring Program. Pestic. Monit. J. 6(4):238–362.

(4) *Cromartie, E., W. L. Reichel, L. N. Locke, A. A. Belisle, T. E. Kaiser, T. G. Lamont, B. M. Mulhern, R. M. Prouty, and D. M. Swineford. 1975.* Residues of organochlorine pesticides and polychlorinated biphenyls and autopsy data for bald eagles, 1971-72. Pestic. Monit. J. 9(1):11-14.

(5) *Dziuk, L. J., and F. W. Plapp. 1973.* Insecticide resistance in mosquitofish from Texas. Bull. Environ. Contam. Toxicol. 9(1):15-19.

(6) *Edwards, C. A.* 1973. Persistent Pesticides in the Environment. CRC Press, Cleveland, Ohio. 170 pp.

(7) *Ferrigno, F., Sr. 1966.* They go up and down: population dynamics of the clapper rail. N. J. Outdoors 16(8):3-9.

(8) *Fochrenbach, J. 1972.* Chlorinated pesticides in estuarine organisms. J. Water Pollut. Control Fed. 44(4):619-624.

(9) *Ginsburg, J. M. 1950.* Chemicals used for mosquito control in New Jersey in 1949. Proc. 37th Annu. Meet. N. J. Mosq. Exterm. Assoc.: 69–75.

(10) *Henderson, C., A. Inglis, and W. L. Johnson. 1971.* Organochlorine insecticide residues in fish—fall 1969 (National Pesticide Monitoring Program). Pestic. Monit. J. 5(1):1-11.

(11) *Henderson, C., W. L. Johnson, and A. Inglis. 1969.* Organochlorine insecticide residues in fish (National Pesticide Monitoring Program). Pestic. Monit. J. 3(3):145-171.

(12) *Henny, C. J. 1976.* Research, management, and status of the osprey in North America. Paper presented at World Conference on Birds of Prey, Vienna, Austria, October 1-3, 1975. (Proceed., in press).

(13) *Jobbins, D. M. 1951.* Aerial spraying for mosquito control in New Jersey seashore counties. Proc. 38th Annu. Meet. N. J. Mosq. Exterm. Assoc.: 5-10.

(14) *Jobbins, D. M. 1953.* Airplane spraying for mosquito control along the Jersey shore, 1950-1952. Proc. 40th Annu. Meet. N. J. Mosq. Exterm. Assoc.: 197-201.

(15) *Jobbins, D. M. 1955.* Aircraft spraying for mosquito control—five years' operation in seashore counties. Proc. 42nd Annu. Meet. N. J. Mosq. Exterm. Assoc. 147-150.

(16) *Khan, M. A. Q., R. H. Stanton, and G. Reddy. 1973.* Detoxification of foreign chemicals by invertebrates. Pages 177-201 *in* M. A. Q. Khan and J. P. Bederka, Jr., eds. Survival in Toxic Environments. Academic Press, Inc., New York.

(17) *Lafferty, B. 1950.* The six-year supplemental program for mosquito control in Cape May County. Proc. 37th Annu. Meet. N. J. Mosq. Exterm. Assoc.: 184-187.

(18) *Lafferty, O. W. 1947.* An aerosol fog unit used for control of adult mosquitos in seashore communities. Proc. 34th Annu. Meet. N. J. Mosq. Exterm. Assoc.: 182-184.

TABLE 8. *Comparison of polychlorinated biphenyl residues in selected biota from salt marshes, Cape May County, New Jersey—1967 vs. 1973*

	Residues, ppm wet weight						
	1967			1973			
Species	n[1]	Geometric mean	Range	n[1]	Geometric mean	Range	Percent change
Clapper Rail	43	0.25[2]	—	27	0.65[2]	0.08-3.40	+160[3]
Sheepshead Minnow	5	1.31	0.60-4.30	5	0.16	0.13-0.18	−88[3]
Mummichog	6	1.77	0.83-3.50	6	0.20	0.12-0.29	−89[3]
Striped Killifish	3	1.38	0.41-2.80	6	0.18	0.14-0.22	−87[3]
Fiddler Crab	5	0.16	0.09-0.25	6	0.16	0.10-0.27	0
Ribbed Mussel	5	0.15	0.05-0.36	6	0.09	0.0 -0.24	−40
Periwinkle	1	0.72	—	6	0.14	0.14-0.30	−81
Mud Snail	3	0.11	0.07-0.13	6	0.12	0.06-0.34	+9
Salt Marsh Snail	6	0.27	0.06-1.40	6	0.06	0.0 -0.13	−78[3]

[1] For clapper rail, n = number of individuals, for all others, n = number of pooled samples

[2] Geometric means were calculated by assuming an arbitrary value of 0.25 ppm for residues that could only be quantified as <0.5 ppm

[3] Changes are significant at probability levels of 0.05 or less (two-tailed, Wilcoxen two-sample test)

(19) *Lamont, I. G., G. J. Bagley, and W. L. Reichel 1970.* Residues of *o,p'*-DDD and *o,p'*-DDT in brown pelican eggs and mallard ducks. Bull. Environ. Contam. Toxicol. 5(3): 231-236.

(20) *Matsumura, F. 1973.* Microbial degradation of pesticides. Pages 129-154 *in* M. A. Q. Khan and J. P. Bederka, Jr., eds. Survival in Toxic Environments. Academic Press, Inc., New York.

(21) *Malhern, I. D. 1949.* A review for New Jersey for 1948. Proc. 36th Annu. Meet. N. J. Mosq. Exterm. Assoc. 187–194.

(22) *Odum, W. E., G. M. Woodwell, and C. F. Wurster 1969.* DDT residues absorbed from organic detritus by fiddler crabs. Science 164: 576-577.

(23) *Ohlendorf, H. M., J. F. Klaas, and T. E. Kaiser 1973.* Environmental pollution in relation to estuarine birds. Pages 53-81 *in* M. A. Q. Khan and J. P. Bederka, Jr., eds. Survival in Toxic Environments. Academic Press, Inc., New York.

(24) *Sokal, R. R., and F. J. Rohlf 1969.* Biometry. W. H. Freeman and Co., San Francisco. 776 pp.

(25) *Van Velzen, A., and J. F. Kreitzer. 1975.* The toxicity of *p,p'*-DDT to the clapper rail. J. Wildl. Manage. 39(2):305-309.

(26) *Veith, G. D. 1975.* Baseline concentrations of polychlorinated biphenyls and DDT in Lake Michigan fish, 1971. Pestic. Monit. J. 9(1):21-29.

(27) *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(3776):821-824.

GENERAL

Monitoring Agricultural Insecticides in the Cooperative Cotton Pest Management Program in Arizona, 1971—First-Year Study [1]

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ABSTRACT

A county-wide pest management program was initiated in Pinal County, Ariz., in 1971 to improve ecologically, economically, and socially the system for protecting cotton from insect pests. Included in this program was a plan to determine the environmental impact of any resulting pesticide load in the environment. Monitoring studies were developed for the assay of insecticide residues in soil, sediment, water, and biological materials. This report presents results of the first year's study and analytical methodology used to achieve those results.

Introduction

A county-wide cotton pest management program was initiated in Pinal County, Ariz., in 1971 as a cooperative endeavor of the U.S. Department of Agriculture—Animal and Plant Health Inspection Service (USDA-APHIS), Cooperative Extension Service and the University of Arizona Department of Entomology. The main objective of this pilot study was to establish a more ecologically, economically, and socially acceptable system for protecting cotton from insect pests.

During the first year of the study various aspects of this pest management program were organized and executed, including an environmental impact analysis program. This report concerns results obtained from that program.

Both biotic (birds, snakes, lizards, frogs, fish) and abiotic (soil, sediment, water) samples were collected and analyzed for pesticide residues to determine what impact, if any, the application of currently used pesticides has on the environment.

Sampling Procedures

The sample collection and analysis programs were designed to obtain comparisons of residues within and outside the project areas before treatment and after harvest. The effects of pesticide treatments on pond water and aquatic life were also determined by collecting samples of water, sediment, and aquatic organisms from ponds near the cotton sites.

Biotic samples included birds, toads and frogs, snakes, lizards, aquatic and terrestrial insects, and fish, i.e., minnows. Abiotic samples were pond water, pond sediment, and soil from cottonfields.

Cottonfields in the Pest Management Program were selected to provide at least one site in each cotton-growing area of Pinal County, further restricted to areas near or adjacent to permanent or semipermanent water supplies. Sites outside the program were chosen for their locations near selected cotton sites. Insecticide treatment information was obtained from each sampling site when available (Table 1).

Random soil samples were collected within and outside program areas utilizing a core sampling device described previously by Woodham et al. (5). All soil was composited, screened, weighed, stored, and shipped according to those procedures.

Sediment samples were collected randomly with an Eckman dredge, composited, subsampled, stored, and shipped according to Woodham (5). Approximately 10 drags of the dredge were required for each sample; great care was taken to collect all possible fine and coarse sediment and silt material.

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TABLE 1 *Pesticide treatment information, Pinal County, Arizona—1971*

Site	Application Date	Pesticide	Actual amount/acre
1A	3 25	Strobane methyl parathion	1 3 gal
2A	7 14	Ethyl parathion methyl parathion	1 3 gal
	7 24	Ethyl parathion methyl parathion	1 pt
	7 30	Ethyl parathion methyl parathion	1-1 2 pt
	8 05	Ethyl parathion methyl parathion	1-1 2 pt
	8 12	Ethyl parathion methyl parathion	1 pt
	8 20	Ethyl parathion methyl parathion	1-1 2 pt
3A	—	NA	—
4A	—	NA	—
5A	7 23	Dimethoate	NA
	8 06	Malathion	NA
	8 15	Ethyl parathion	NA
	8 22	Methyl parathion toxaphene	NA
6A	7 23	Sevin-molasses	2 lb
	7 30	Sevin-molasses	2 lb
	8 04	Sevin-molasses	2 lb
	8 11	Sevin-molasses	2 lb
	8 21	Methyl parathion toxaphene	1 qt
	8 27	Methyl parathion	3-1 4 qt
		Toxaphene	1-1 2 qt
7A	7 16	Methyl parathion toxaphene	1-1 2 pt
	7 25	Methyl parathion toxaphene	1-1 2 pt
	8 02	Methyl parathion toxaphene	1 2 gal
	8 09	Methyl parathion toxaphene	1 3 gal
	8 12	Ethyl-methyl parathion	1 pt
		Endrin	1 pt
	8 16	Methyl parathion toxaphene	1 3 gal
	8 27	Methyl parathion toxaphene	1 3 gal
	9 11	Ethyl-methyl parathion	1 pt
		Ethyl parathion toxaphene	1 3 gal
	9 14	Ethyl-methyl parathion	1 6 gal
		Endrin	1 qt
	8 23	Ethyl-methyl parathion	1 6 gal
8A	7 17	Ethyl parathion	1 qt
		Toxaphene	1 qt
	7 28	Ethyl-methyl parathion	1 pt
	8 22	Ethyl-methyl parathion-toxaphene	1 3 gal
	9 01	Ethyl parathion-toxaphene	1 3 gal
9A	7 26	Ethyl parathion-methyl parathion	1 3 gal
	7 30	Ethyl parathion-methyl parathion	1 3 gal
	8 07	Methyl parathion toxaphene	1 3 gal
	8 10	Methyl parathion toxaphene	1 3 gal
	8 15	Methyl parathion toxaphene	1 3 gal
	8 25	Methyl parathion toxaphene	1 qt
	8 29	Methyl parathion toxaphene	1 qt
10A	—	NA	—

NA not available

Random water samples were collected from tailwater ponds, irrigation ditches, or canals as near as possible to the corresponding sediment sampling sites. By varying the depth of the dredge except for bottom samples, a representative gallon of pond water was collected and stored in sealed gallon glass bottles.

Birds, mammals, lizards, frogs, toads and snakes were collected by shooting with either a .22 caliber rifle with birdshot or a 12-gauge shotgun, within the various sampling sites. Minnows and other fish were caught in a small-mesh minnow seine. Water beetles were collected from sediment samples and grasshoppers were caught in the fields with hand nets. Crickets and some ants were gathered by hand; the remaining ants were collected with an aspirator sampling device.

Soil, sediment and water samples were stored at approximately 40 F in a refrigerator pending shipment to the USDA Environmental Quality Laboratory, Brownsville, Tex. Biological samples were stored at 0° F pending airmail shipment in styrofoam biomailers with dry ice. Once samples were received in the laboratory, they were immediately unpacked; biological samples were stored again in a 0° F freezer, and soil, sediment, and water were stored at 40°C pending residue analysis.

Preparation of Samples

EXTRACTION

Representative 300-g soil samples were extracted with 600 ml of a 3:1 (v/v) hexane-isopropyl alcohol solvent mixture in half-gallon Mason jars on a concentric rotator for 4 hours as described previously by Stevens et al. (*4*). After rotation, 300 ml of the extract was filtered into 1000-ml separatory funnels where the alchohol was removed by washing three times with equal volumes of distilled water. The hexane extract was dried by filtering through a layer of anhydrous granular sodium sulfate into amber sample bottles. The bottles were sealed and refrigerated pending gas-chromatographic (GC) analysis. Soil extracts did not normally require cleanup before analysis.

Sediment samples were prepared and stored as soil samples had been, except that 250 g anhydrous granular sodium sulfate was added to absorb excess water. As usual, sediment samples contained excessive amounts of sulfur which interfere with analyses for organophosphate and chlorinated hydrocarbon residues. These samples were treated utilizing the sulfur removal procedure of Schultzmann et al. (*3*).

Water samples were extracted by shaking representative 500-g subsamples in 1000-ml separatory funnels three times with fresh 100-ml portions of nanograde (Mallinckrodt, Inc.) dichloromethane. The organic layers were filtered through a layer of granular anhydrous sodium sulfate to remove entrained water into 500-ml Erlenmeyer flasks. One ml of a 0.01 percent Nujol in hexane solution and glass beads were added and the solvent was evaporated through Snyder columns to approximately 5 ml on a warm water bath: 40°-50° C. One hundred ml nanograde hexane was added through the Snyder columns and the solvent was again evaporated to approximately 5 ml. The concentrated extracts were transferred to 15-ml graduated centrifuge tubes which were stoppered; the volume was adjusted to 12.5 ml with nanograde hexane. Samples were refrigerated pending GC analysis. Water samples did not normally require cleanup before residue analysis.

Larger biological samples such as rabbits, birds, lizards, snakes, and fish were prepared according to the procedure used by Woodham et al. (*7*). Samples were thoroughly ground in a Hobart food grinder; then representative 25-g subsamples were weighed into 1000-ml Waring blendor jars with 150 ml of a 3:1 mixture of nanograde hexane: isopropyl alcohol and blended at low speed for 2 minutes. The macerated materials were transferred into half-gallon Mason jars with 250 ml of the hexane: isopro-

pyl alchohol mixture and the jars were sealed and rotated concentrically 4 hours. Extracts were filtered through glass wool into 1000-ml separatory funnels where the alchohol was removed with three successive washings of equal volumes of distilled water; the aqueous layers were discarded. Hexane extracts were filtered through layers of anhydrous granular sodium sulfate into graduated cylinders where 100-ml aliquots were collected. The aliquots were transferred into amber sample bottles, sealed, and refrigerated pending cleanup.

Smaller biological samples, mainly insects, weighing 25 g or less were weighed and transferred into micro-blendor cups with 50-ml nanograde isopropyl alchohol and blended for 2 minutes at high speed. The macerates were sealed into quart Mason jars with 150 ml nanograde hexane and rotated concentrically 4 hours at 30 rpm. Extracts were filtered into 500-ml separatory funnels where all alcohol and water were removed by three successive washings with equal portions of distilled water. Extracts were dried and refrigerated.

CLEANUP

Biological sample extracts were cleaned by liquid:liquid partitioning between two immiscible organic solvents, hexane:acetonitrile, to remove fats and oils. The procedure, described previously by Woodham et al. (5), involved transfer of 10-g aliquots of the extracts into 125-ml Erlenmeyer flasks and concentrating to approximately 25 ml on a warm water bath using a gentle stream of dry air to facilitate evaporation of the solvent. The concentrated extracts were diluted to exactly 50 ml with nanograde hexane and transferred into 250-ml separatory funnels and partitioned three times with 100-ml portions of nanograde acetonitrile saturated with hexane. The hexane layers were discarded and the combined acetonitrile layers were collected in 500-ml separatory funnels and washed once with 20 ml nanograde hexane saturated with acetonitrile to remove any trace of fats or oils. The acetonitrile fraction was divided into equal portions for further processing.

For organophosphates, one portion of the acetonitrile fraction was transferred to 250-ml Erlenmeyer flasks, 1 ml of 0.01 percent solution of Nujol in hexane and glass beads were added, and the solvent was evaporated to approximately 5 ml on hotplates through Snyder columns. The concentrated extracts were transferred to 15-ml graduated centrifuge tubes where the volume was adjusted to exactly 12.5 ml with nanograde acetonitrile. The stoppered tubes were refrigerated pending GC analysis.

For chlorinated hydrocarbons, the remaining portion was transferred into 250-ml Erlenmeyer flasks, glass beads and 1 ml of a 0.01 percent Nujol in hexane solution were added, and the solvent was evaporated to approximately 10 ml on hotplates through Snyder columns. The flasks were cooled and 100 ml hexane was added through the Snyder columns and the evaporation procedure described previously was repeated on a hot water bath. This step was repeated two additional times, and the flasks were sealed and refrigerated pending florisil cleanup.

FLORISIL CLEANUP

Florisil chromatographic cleanup columns have been described previously (5). Only two fractions were collected from the columns in the present study because organophosphate residue analyses were conducted on the partitioned samples. Aliquots from the extraction procedure were transferred into the hexane prewashed columns and eluted with 100 ml nanograde hexane, then with 100 ml 15 percent diethyl ether in hexane; each eluate was collected in separate 250-ml Erlenmeyer flasks. The solvent was evaporated and stored as described previously (5). The less polar pesticide residues such as lindane, heptachlor, aldrin, DDE, TDE, DDT, and toxaphene were contained in the first fraction; the second fraction contained the more polar residues such as dieldrin, endrin, and heptachlor epoxide.

Gas-Chromatographic Analysis

Analysts used MT-220 gas chromatographs equipped with Ni-63 high-temperature electron-capture detectors and a Melpar Flame Photometric Detector (FPD). The FPD detector was designed to operate simultaneously in the sulfur (394 mu) and the phosphorous (526 mu) modes.

Operating parameters were:

Columns: 6-ft-by-1/4-in.-glass packed with 3 percent DC-200 on 100/200-mesh Gas-Chrom Q; 3 percent OV-1 on 80/100-mesh Chromosorb-W; 5 percent QF-1 on 100/120-mesh Gas-Chrom Q; and 11 percent mixture of 1.95 percent QF-1 : 1.5 percent OV-17 on 80/100-mesh Gas-Chrom Q. A 3 percent DC-200 column as described in (*1*) was also used for the FPD analysis of organophosphate residues.

Temperatures (isothermal): Columns: 200° C
Injector: 250° C
Detectors EC 300° C
FPD 200° C

Gas flow rates: Nitrogen (carrier) 80 ml/min
Air 40 ml/min
Hydrogen 75 ml/min
Oxygen 20 ml/min

Recorder chart speed was 30 in./hr; sensitivity was adjusted to obtain approximately half full-scale deflection of the recorder pen with a 0.05-ng injection of aldrin on the electron-capture detectors and 1.50 ng of ethyl parathion

on the FPD detector. Calculations were based on peak heights obtained from analytical standards compared with identical peaks in the samples. Lower limit of sensitivity was 0.01 ppm for organophosphates and chlorinated hydrocarbon pesticides except in water, whose lower limit was 0.01 ppb.

Toxaphene was analyzed using the GC method of Hawthorne and Dawsey (USDA Environmental Monitoring Laboratory, Gulfport, Miss., 1972: personal communication). Extraction, cleanup, and other processing steps were identical to those used for the organochlorine and organophosphate pesticide residues. The quantitation procedure involved comparing heights of the four major peaks in a toxaphene standard with heights of those peaks in the environmental samples. Gas-chromatographic operating parameters were identical to those described previously for organochlorine and organophosphate pesticides on the 3 percent DC-200 column. When minor peaks interfered with the four major peaks of toxaphene, as few as two such peaks could be used for accurate quantitation. The lower limit of sensitivity of toxaphene was 0.05 ppm except for water, whose limit was 0.05 ppb.

Doubtful pesticide peaks were confirmed by several methods described in previous publications: thin-layer chromatography, Schutzmann et al. (*2*); partitioning coefficients (*p*-values), Bowman and Beroza (*1*); chemical means, Woodham, et al. (*4*); and multiple column methods. Peaks which were not at least twice the interference level were rejected.

Recovery

A series of control samples extracted, purified, and analyzed in identical manner as the unknowns, was included with each group of samples. These controls included a solvent check, nonfortified sample and a sample fortified with known amounts of the suspected pesticides. These controls were necessary in order to monitor possible contamination of solvents, determine residues in nonfortified sample material, and determine extraction and analytical efficiency of the entire procedure. No interfering peaks were detected in the solvents; pesticide peaks detected in unfortified samples were deducted from those in fortified samples to obtain recovery percentages. Average recovery values are listed in Table 2.

Results and Discussion

Table 3 presents residue data for the soil samples collected within and outside the program areas, before pesticide treatments began and after harvest. The organophosphate, ethyl parathion, was detected in trace amounts, 0.13 ppm and 0.03 ppm, in soil from sites 2A and 3A, respectively, within the program area after harvest. No organophosphate residues were detected in soil collected before the pesticide treatments or in soil outside the program area. Residues of ethyl parathion were detected in soil from sites 1B, 2B, 3B, 5B, 7B, and 8B at harvest outside program areas. Residues in soil from these sites apparently resulted from direct pesticide application to cotton crops.

Organochlorine pesticides were detected in all soils before pesticide treatments and after harvest, within and outside program areas. Before pesticide application, residues ranged from 0.29 to 1.43 ppm *p,p'*-DDE, 0.11 to 1.49 ppm *p,p'*-DDT, and <0.05 to 3.94 ppm toxaphene in soil from sites within the program area. After harvest, residues ranged from 0.21 to 0.76 ppm *p,p'*-DDE, 0.11 to 1.33 ppm *p,p'*-DDT, and 1.18 to 5.18 ppm toxaphene in the soil. Outside the program area, the same organochlorine pesticide residues were detected, ranging from 0.50 to 1.82 ppm *p,p'*-DDE, 0.25 to 1.53 ppm *p,p'*-DDT, and <0.05 to 2.68 ppm toxaphene in pretreatment soil. At harvest, organochlorine pesticide residues ranged from 0.33 to 1.24 ppm *p,p'*-DDE, 0.31 to 0.86 ppm *p,p'*-DDT, and 2.41 to 4.04 ppm toxaphene in soil collected outside the program area. The decline in *p,p'*-DDE residues was apparently due to cultivation practices on the various sites.

Residue data for pesticides in biological samples are given in Table 4. Ethyl parathion residues ranged from 0.03 ppm in a frog sample collected before treatment within the program area and a rabbit sample collected before treatment outside the treatment area to 1.24 ppm in a sample of minnows collected before treatment within the program area.

Organochlorine pesticide residues were detected in all biological samples, predominantly *p,p'*-DDT and other isomers of DDE, DDT, and TDE. Residue patterns were similar among samples from inside and outside program areas although concentrations were generally lower in samples from outside the program.

Various pretreatment samples collected inside program areas had residues of heptachlor epoxide, <0.01-0.06 ppm; β-BHC, <0.01-0.05 ppm; dieldrin, <0.01-0.55 ppm; *o,p'*-DDE, <0.01-1.52 ppm; *p,p'*-DDE, 0.03-45.52 ppm; *o,p'*-TDE, <0.01-0.60 ppm; *p,p'*TDE, <0.01-1.73 ppm; *o,p'*-DDT, <0.01-0.17 ppm; and *p,p'*-DDT, <0.01-2.36 ppm. Residues in post-treatment samples produced generally the same pattern of pesticides, but at generally lower levels.

Pretreatment samples collected outside program areas showed residues of β-BHC, <0.01-0.47 ppm; heptachlor epoxide, <0.01-0.07 ppm; dieldrin, <0.01-4.68 ppm; *o,p'*-DDE, <0.01-0.31 ppm; *p,p'*-DDE, 0.02-57.62 ppm; *o,p'*-TDE, <0.01-0.16 ppm; *p,p'*-TDE, <0.01-1.36 ppm; *o,p'*-DDT, <0.01-0.31 ppm; and *p,p'*-DDT, <0.01-2.12 ppm, in such varied samples as frogs, toads, lizards, birds, and fish. Post-treatment samples from outside program areas generally produced similar residue patterns with lower concentrations; some exceptions occurred, how-

ever, such as an increase in *p,p'*-DDE residues to a range of 0.04-76.30 ppm in post-treatment bird samples.

Residues of pesticides used during the 1971 growing season in the Arizona Cotton Pest Management Program did not accumulate, except for toxaphene in soil samples. An increase of toxaphene residues was noted in harvest soil inside and outside program areas. The increase in residues outside program areas was apparently due to pesticide treatments during 1971. No toxaphene residue were detected in sediment, water, or biological samples inside or outside the program areas, which indicates that this chlorinated camphene is not transferred to the biological food chain.

TABLE 2. *Average pesticide recoveries from fortified environmental sample materials, Pinal County, Arizona—1971*

Sample Material	Recovery, %: Ethyl Parathion	Methyl Parathion	Malathion	Methyl Trithion	Ethion	β-BHC	γ-BHC	Heptachlor	Aldrin	Heptachlor Epoxide	*o,p'*-DDE	*p,p'*-DDE	Dieldrin	Endrin	*o,p'*-TDE	*p,p'*-TDE	*o,p'*-DDT	*p,p'*-DDT	Toxaphene
Soil	102.2	96.4	101.5	100.6	107.3	91.0	89.0	84.1	89.4	94.8	79.7	91.0	91.0	91.0	91.0	91.0	91.0	91.0	91.0
Sediment	93.0	80.0	86.0	90.0	89.0	85.5	94.2	86.1	80.8	91.1	85.5	85.5	85.5	79.4	77.0	85.5	87.7	88.6	85.5
Water	89.8	91.3	89.2	78.9	99.6	93.6	92.4	93.0	89.9	94.6	95.6	93.5	93.1	95.9	95.0	93.4	92.9	93.5	93.6
Lizards and Snakes	88.4	85.4	82.6	82.6	74.1	100.0	97.0	100.9	103.5	82.9	71.5	82.9	82.9	96.8	86.0	80.5	83.3	80.8	82.9
Frogs, Toads and Polliwogs	95.8	88.4	83.4	97.8	96.3	100.0	97.0	101.2	95.1	101.2	76.0	76.0	96.8	96.8	76.0	76.0	76.0	76.0	98.0
Birds, Nestlings and Eggs	93.5	94.8	97.0	93.6	95.2	100.0	75.6	86.4	69.0	85.8	93.2	89.0	85.8	91.9	82.3	92.3	88.7	92.9	85.8
Fish and Freshwater Clams	86.4	96.0	84.6	60.8	72.6	100.0	78.9	72.7	58.4	81.4	100.2	100.2	78.9	76.3	104.8	109.1	91.5	95.5	100.2
Insects	95.7	103.3	106.3	101.8	99.8	100.0	100.5	88.6	76.2	100.5	93.6	88.9	96.5	102.7	104.0	98.7	101.0	97.0	95.7

TABLE 3. *Pesticide residues in soil from pest management area, Pinal County, Arizona—1971*

Site	Sampling Date[1]	Residues, ppm: Ethyl Parathion[2]	Dieldrin	*o,p'*-DDE	*p,p'*-DDE	*o,p'*-TDE	*p,p'*-TDE	*o,p'*-DDT	p,p'-DDT	Toxaphene
Program Sites										
1A	7/13	<0.01	<0.01	<0.01	1.42	<0.01	<0.01	<0.01	1.00	2.31
	11/24	<0.01	<0.01	<0.01	0.53	<0.01	<0.01	<0.01	0.60	3.61
2A	6/25	<0.01	<0.01	<0.01	1.33	<0.01	<0.01	<0.01	1.33	1.90
	11/24	0.13	<0.01	<0.01	0.67	<0.01	<0.01	<0.01	0.67	2.06
3A	7/13	<0.01	<0.01	<0.01	0.65	<0.01	<0.01	<0.01	1.06	1.97
	11/29	0.03	<0.01	<0.01	0.68	<0.01	<0.01	<0.01	0.68	2.52
4A	7/06	<0.01	<0.01	<0.01	1.43	<0.01	<0.01	<0.01	1.49	3.94
	11/23	<0.01	<0.01	<0.01	0.72	<0.01	<0.01	<0.01	0.92	4.71
5A	7/06	<0.01	<0.01	<0.01	0.61	<0.01	<0.01	<0.01	0.61	2.51
	11/23	<0.01	<0.01	<0.01	0.38	<0.01	<0.01	<0.01	0.38	2.57
6A	7/13	<0.01	<0.01	<0.01	0.29	<0.01	<0.01	<0.01	0.11	0.85
	11/30	<0.01	<0.01	<0.01	0.21	<0.01	<0.01	<0.01	0.11	1.18
7A	7/09	<0.01	<0.01	<0.01	1.00	<0.01	<0.01	<0.01	1.08	3.20
	11/22	<0.01	<0.01	<0.01	0.76	<0.01	<0.01	<0.01	1.07	5.18
8A	7/12	<0.01	<0.01	<0.01	0.58	<0.01	<0.01	<0.01	1.39	0.05
	12/02	<0.01	<0.01	<0.01	0.39	<0.01	<0.01	<0.01	0.99	1.39
9A	7/13	<0.01	<0.01	<0.01	0.59	<0.01	<0.01	<0.01	0.45	0.86
	12/01	<0.01	<0.01	<0.01	0.33	<0.01	<0.01	<0.01	0.35	2.21
10A	7/02	<0.01	<0.01	<0.01	0.70	<0.01	<0.01	<0.01	0.77	2.48
Nonprogram Sites										
1B	7/17	<0.01	<0.01	<0.01	1.29	<0.01	<0.01	<0.01	0.36	1.83
	11/29	0.10	<0.01	<0.01	1.24	<0.01	<0.01	<0.01	0.33	2.41
2B	7/16	<0.01	<0.01	<0.01	1.64	<0.01	<0.01	<0.01	0.32	0.05
	11/24	0.02	<0.01	<0.01	0.79	<0.01	<0.01	<0.01	0.54	2.75
3B	7/23	<0.01	<0.01	<0.01	0.85	<0.01	<0.01	<0.01	0.27	1.61
	11/29	0.05	<0.01	<0.01	0.58	<0.01	<0.01	<0.01	0.43	3.52
4B	7/16	<0.01	<0.01	<0.01	0.50	<0.01	<0.01	<0.01	0.29	1.45
5B	7/15	<0.01	<0.01	<0.01	0.66	<0.01	<0.01	<0.01	0.25	1.09
	11/23	0.06	<0.01	<0.01	0.33	<0.01	<0.01	<0.01	0.31	3.52
6B	7/16	<0.01	<0.01	<0.01	1.82	<0.01	<0.01	<0.01	0.72	1.93
	11/30	<0.01	<0.01	<0.01	0.86	<0.01	<0.01	<0.01	0.76	3.02
7B	7/22	<0.01	<0.01	<0.01	1.73	<0.01	<0.01	<0.01	0.33	2.11
	11/22	<0.01	<0.01	<0.01	0.67	<0.01	<0.01	<0.01	0.39	4.04
8B	7/21	<0.01	<0.01	<0.01	1.10	<0.01	<0.01	<0.01	0.37	1.57
	11/23	0.02	<0.01	<0.01	0.54	<0.01	<0.01	<0.01	0.46	2.46
9B	7/14	<0.01	<0.01	<0.01	1.53	<0.01	<0.01	<0.01	1.53	2.68
	12/01	<0.01	<0.01	<0.01	0.65	<0.01	<0.01	<0.01	0.65	3.64
10B	7/21	<0.01	<0.01	<0.01	1.65	<0.01	<0.01	<0.01	0.87	1.82
	12/02	<0.01	<0.01	<0.01	0.65	<0.01	<0.01	<0.01	0.86	3.43

NOTE: Residue data corrected for pesticide recovery from fortified samples and for moisture content of oven-dried samples. Lower limits of sensitivity = 0.01 ppm, except for toxaphene, which was 0.05 ppm.

[1] Postharvest samples were not collected from sites listed.

[2] No residues of methyl parathion, malathion, methyl trithion, ethion, or other organophosphates exceeding the lower limits of sensitivity (0.01 ppm) were detected.

Conversely, residues of dieldrin, b-BHC, and heptachlor epoxide which did not appear in soil, sediment, or water were found in all biological materials sampled except for rats and rabbits. These residues may have resulted from pesticide treatments in previous years.

Residues of DDT, DDE, and TDE which appeared in soil and biological samples but not in sediment and water, decreased between the spring and fall samplings. The passage of an Arizona State ordinance in 1969 banning the use of DDT apparently contributed to this decline.

In order to determine the trend of accumulation or decline of pesticide residues, a longer study must be conducted. The present study will be continued for a minimum of 3 years before any baseline may be established; a more likely estimate is 5 years. Such a long-term study must be conducted to obtain residue data which can be used to project trends and draw conclusions pertaining to the impact of the Pinal County pest management system and its reduced pesticide load.

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LITERATURE CITED

(1) *Bowman, M.C., and M. Beroza. 1965.* Extraction p-values of pesticides and related compounds in six binary solvent systems. J. Assoc. Offic. Agric. Chem. 48(2):943-952.

(2) *Schutzmann, R. L., W. F. Barthel, and J. A. Warrington. 1966.* Cleanup and confirmation of identity of pesticide residues by thin-layer chromatography. Part I: Soil, Water, and Sediment. USDA-ARS, 81-12. 13 pp.

(3) *Schutzmann, R. L., D. W. Woodham, and C. W. Collier. 1971.* Removal of sulfur in environmental samples prior to gas chromatographic analysis for pesticide residues. J. Assoc. Offic. Agric. Chem. 54(5):1117-1119.

(4) *Stevens, L. J., C.W. Collier, and D. W. Woodham. 1970.* Monitoring pesticides in soils from areas of regular, limited, and no pesticide use. Pestic. Monit. J. 4(3):145-164.

(5) *Woodham, D.W., R. R. Edwards, R. G. Reeves, and R. L. Schutzmann. 1973.* Total toxic aldicarb residues in soil, cottonseed and cotton lint following a soil treatment with the insecticide on the Texas high plains. J. Agr. Food Chem. 21(2):303-307.

(6) *Woodham, D. W., C. D. Loftis, and C. W. Collier. 1972.* Identification of the gas chromatographic dieldrin and endrin peaks by chemical conversion. J. Agr. Food Chem. 20(1):163-165.

TABLE 4. *Pesticide residues in biological samples from Cotton Pest Management Project, Pinal County, Arizona—1971*

Site	Sampling Date	Sample Material	Residues, ppm									
			Ethyl Parathion[1]	β-BHC	Heptachlor Epoxide	Dieldrin	*o,p'*-DDE	*p,p'*-DDE	*o,p'*-TDE	*p,p'*-TDE	*o,p'*-DDT	*p,p'*-DDT
			Program Samples									
Frogs and Toads												
1A	7-13	Frogs	0.03	0.01	< 0.01	0.02	0.02	7.01	0.01	0.04	0.01	0.05
	10-14	Frogs	<0.01	<0.01	< 0.01	0.02	< 0.01	9.15	< 0.01	< 0.01	<0.01	0.30
	10-14	Toads	<0.01	< 0.01	< 0.01	< 0.01	< 0.01	1.93	< 0.01	< 0.01	<0.01	0.10
2A	10-12	Toads	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	1.43	< 0.01	< 0.01	<0.01	0.20
4A	7-20	Frogs	< 0.01	<0.01	0.01	0.01	0.04	6.76	0.02	0.21	0.07	0.39
	10-12	Frogs	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	17.60	< 0.01	< 0.01	<0.01	1.47
	7-20	Toads	< 0.01	0.02	0.06	0.10	0.12	45.52	0.60	1.01	0.32	2.50
	10-12	Toads	<0.01	<0.01	< 0.01	< 0.01	< 0.01	12.39	< 0.01	< 0.01	<0.01	1.46
5A	7-13	Frogs	< 0.01	< 0.01	< 0.01	< 0.01	0.01	4.19	0.01	0.02	<0.01	0.02
	10-18	Frogs	<0.01	< 0.01	< 0.01	< 0.01	< 0.01	24.84	< 0.01	< 0.01	<0.01	0.99
6A	10-19	Toads	< 0.01	<0.01	< 0.01	< 0.01	< 0.01	4.59	0.01	< 0.01	< 0.01	0.51
7A	7-12	Toads	< 0.01	0.01	0.02	0.01	0.09	8.34	0.10	0.22	0.17	0.53
	10-15	Toads	< 0.01	<0.01	< 0.01	< 0.01	< 0.01	3.05	0.01	< 0.01	< 0.01	0.63
	10-15	Frogs	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	27.01	0.01	< 0.01	< 0.01	0.26
8A	7-20	Frogs	< 0.01	< 0.01	< 0.01	0.03	0.03	4.61	0.03	0.06	0.05	0.38
	10-20	Toads	< 0.01	<0.01	< 0.01	< 0.01	0.01	0.29	0.01	< 0.01	< 0.01	0.03
9A	10-20	Toads	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	0.98	0.01	< 0.01	< 0.01	0.32
10A	7-18	Toads	< 0.01	0.05	0.03	0.55	0.12	37.62	0.24	0.84	0.36	2.36
	10-21	Toads	0.01	< 0.01	< 0.01	< 0.01	< 0.01	11.12	0.01	< 0.01	< 0.01	4.44
	10-21	Frogs	0.01	< 0.01	< 0.01	< 0.01	0.01	2.95	0.01	0.01	< 0.01	0.57
Fish												
1A	7-13	Minnows	1.24	0.04	0.06	0.06	1.19	13.07	0.01	1.73	0.12	0.64
	10-14	Minnows	0.01	< 0.01	< 0.01	< 0.01	< 0.01	17.42	0.01	< 0.01	< 0.01	< 0.01
3A	10-15	Minnows	0.01	< 0.01	< 0.01	< 0.01	0.01	3.58	0.01	0.01	< 0.01	< 0.01
5A	7-13	Minnows	0.01	0.01	0.02	0.04	1.24	8.71	0.01	0.02	0.02	0.10
6A	7-18	Minnows	0.08	0.03	0.06	0.07	1.52	24.22	0.01	2.30	0.07	1.48
	10-19	Minnows	0.01	0.01	< 0.01	< 0.01	0.01	0.60	0.01	< 0.01	< 0.01	< 0.01

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TABLE 4 (cont'd.). *Pesticide residues in biological samples from Cotton Pest Management Project, Pinal County, Arizona—1971*

Site	Sampling Date	Sample Material	Residues, ppm									
			Ethyl Parathion[1]	β-BHC	Heptachlor Epoxide	Dieldrin	o,p'-DDE	p,p'-DDE	o,p'-TDE	p,p'-TDE	o,p'-DDT	p,p'-DDT
			Program Samples									
Birds												
1A	7/13	Mourning Dove	<0.01	<0.01	<0.01	<0.01	<0.01	0.35	<0.01	0.01	<0.01	0.01
	10/14	Mourning Dove	<0.01	<0.01	<0.01	<0.01	<0.01	0.65	<0.01	<0.01	<0.01	<0.01
2A	7/19	Mourning Dove	<0.01	<0.01	<0.01	0.01	0.01	0.75	0.01	0.01	0.01	0.02
	10/12	Mourning Dove	<0.01	<0.01	<0.01	<0.01	<0.01	0.20	<0.01	<0.01	<0.01	<0.01
	7/19	Nestlings	<0.01	<0.01	<0.01	<0.01	0.01	0.50	0.01	0.01	0.01	0.01
3A	7/17	Whitewing Dove	<0.01	<0.01	<0.01	<0.01	<0.01	0.03	<0.01	<0.01	<0.01	<0.01
	10/14	Dove	<0.01	<0.01	<0.01	<0.01	<0.01	0.81	<0.01	<0.01	<0.01	<0.01
	10/14	Sparrow	<0.01	<0.01	<0.01	<0.01	<0.01	0.34	<0.01	<0.01	<0.01	<0.01
	7/17	Mourning Dove	<0.01	0.01	<0.01	0.09	0.02	2.87	<0.01	0.04	0.01	0.11
5A	7/18	Wren	<0.01	0.01	<0.01	0.02	0.02	6.59	<0.01	0.05	<0.01	0.11
	10/18	Woodpecker	<0.01	<0.01	<0.01	<0.01	<0.01	0.70	<0.01	<0.01	<0.01	<0.01
	10/18	Sparrows	<0.01	<0.01	<0.01	<0.01	<0.01	1.94	<0.01	<0.01	<0.01	<0.01
	10/18	Mourning Dove	<0.01	<0.01	<0.01	<0.01	<0.01	2.16	<0.01	<0.01	<0.01	<0.01
6A	10/19	Owl	<0.01	<0.01	<0.01	<0.01	<0.01	8.13	<0.01	<0.01	<0.01	<0.01
	10/19	Mourning Dove	<0.01	<0.01	<0.01	<0.01	<0.01	0.15	<0.01	<0.01	<0.01	<0.01
	10/19	Sparrows	<0.01	<0.01	<0.01	<0.01	<0.01	0.45	<0.01	<0.01	<0.01	<0.01
7A	7/12	Dove	<0.01	<0.01	<0.01	<0.01	0.01	1.01	0.01	<0.01	<0.01	0.02
	10/15	Mourning Dove	<0.01	<0.01	<0.01	<0.01	<0.01	1.58	<0.01	<0.01	<0.01	<0.01
	7/12	Wren	<0.01	<0.01	<0.01	<0.01	0.07	3.04	<0.01	0.02	0.01	0.02
	10/15	Mexican Dove	<0.01	<0.01	<0.01	<0.01	<0.01	0.01	<0.01	<0.01	<0.01	<0.01
	10/15	Finch	<0.01	<0.01	<0.01	<0.01	<0.01	5.78	<0.01	<0.01	<0.01	<0.01
8A	7/20	Wren	<0.01	<0.01	<0.01	<0.01	0.01	0.96	<0.01	<0.01	0.01	<0.01
	7/20	Sparrow	<0.01	0.01	<0.01	<0.01	0.02	8.38	<0.01	0.02	<0.01	0.02
	12/02	Inca Doves	<0.01	<0.01	<0.01	<0.01	<0.01	0.47	<0.01	<0.01	<0.01	<0.01
	10/20	Woodpeckers	<0.01	<0.01	<0.01	<0.01	<0.01	0.22	<0.01	<0.01	<0.01	<0.01
	10/20	Redheaded Woodpecker	<0.01	<0.01	<0.01	<0.01	<0.01	0.01	<0.01	<0.01	<0.01	<0.01
10A	7/18	Mourning Dove	<0.01	<0.01	<0.01	<0.01	<0.01	0.63	<0.01	0.01	<0.01	0.06
	10/21	Mourning Dove	<0.01	<0.01	<0.01	<0.01	<0.01	0.55	<0.01	<0.01	<0.01	<0.01
Snakes and Lizards												
1A	7/13	Lizards	<0.01	0.02	<0.01	0.04	0.03	37.15	<0.01	0.04	0.01	0.06
	10/14	Lizards	<0.01	<0.01	<0.01	<0.01	<0.01	7.57	<0.01	<0.01	<0.01	<0.01
2A	7/19	Lizards	<0.01	<0.01	<0.01	0.01	0.01	4.97	<0.01	0.01	<0.01	0.01
	10/12	Lizards	<0.01	<0.01	<0.01	<0.01	<0.01	0.19	<0.01	<0.01	<0.01	<0.01
	10/12	Lizards	<0.01	<0.01	<0.01	<0.01	<0.01	11.31	<0.01	<0.01	<0.01	<0.01
	10/12	Lizards	<0.01	<0.01	<0.01	<0.01	<0.01	1.66	<0.01	<0.01	<0.01	<0.01
3A	7/17	Lizards	<0.01	<0.01	<0.01	<0.01	<0.01	2.38	<0.01	0.01	<0.01	0.01
	10/14	Lizards	<0.01	<0.01	<0.01	<0.01	<0.01	0.42	<0.01	<0.01	<0.01	<0.01
	10/14	Lizards	<0.01	<0.01	<0.01	<0.01	<0.01	7.54	<0.01	<0.01	<0.01	<0.01
	10/14	Rattlesnake	<0.01	<0.01	0.01	<0.01	<0.01	1.89	<0.01	<0.01	<0.01	0.04
7A	7/12	Lizards	<0.01	0.01	0.01	0.01	0.09	12.08	<0.01	0.08	0.02	0.09
	10/15	Lizards	<0.01	<0.01	<0.01	<0.01	<0.01	0.16	<0.01	<0.01	0.01	0.23
	10/15	Lizards	<0.01	<0.01	<0.01	<0.01	<0.01	18.05	<0.01	<0.01	0.01	0.29
9A[2]	7/13	Lizards	<0.01	0.01	0.01	0.01	0.01	2.71	0.01	0.01	<0.01	<0.01
	10/20	Lizards	<0.01	0.01	0.01	0.01	<0.01	9.70	0.01	<0.01	<0.01	0.21
	12/01	Snake Skin	<0.01	0.01	0.01	0.01	<0.01	0.90	0.01	<0.01	<0.01	0.27
10A	7/18	Lizards	<0.01	0.01	0.01	<0.01	0.04	29.38	<0.01	0.07	0.03	0.02
	10/21	Lizards	<0.01	<0.01	<0.01	<0.01	<0.01	5.59	<0.01	<0.01	<0.01	0.40
Insects												
4A	10/21	Hydrophilid Beetles	<0.01	<0.01	<0.01	<0.01	<0.01	0.84	<0.01	<0.01	<0.01	<0.01
5A	7/13	Toebiters	<0.01	<0.01	0.01	0.02	0.19	8.12	0.03	0.02	0.06	0.02
	11/23	Grasshoppers	<0.01	<0.01	<0.01	<0.01	<0.01	0.02	<0.01	<0.01	<0.01	<0.01
	11/23	Grasshoppers	<0.01	<0.01	<0.01	<0.01	<0.01	0.03	<0.01	<0.01	<0.01	<0.01
	10/18	Hydrophilid Beetles	<0.01	<0.01	<0.01	<0.01	<0.01	3.24	<0.01	<0.01	<0.01	<0.01
6A	10/19	Fire Ants	<0.01	<0.01	<0.01	<0.01	<0.01	0.05	<0.01	<0.01	<0.01	<0.01
	11/30	Earwigs	<0.01	<0.01	<0.01	<0.01	<0.01	0.17	<0.01	<0.01	<0.01	<0.01
	11/30	Harvester Ants	<0.01	<0.01	<0.01	<0.01	<0.01	0.02	<0.01	<0.01	<0.01	<0.01
	11/30	Darkling Ground Beetles	<0.01	<0.01	<0.01	<0.01	<0.01	0.06	<0.01	<0.01	<0.01	<0.01
8A	12/02	Grasshoppers	<0.01	<0.01	<0.01	<0.01	<0.01	0.01	<0.01	<0.01	<0.01	<0.01
	12/02	Grasshoppers	<0.01	<0.01	<0.01	<0.01	<0.01	0.01	<0.01	<0.01	<0.01	<0.01
	10/20	Ground Beetles	<0.01	<0.01	<0.01	<0.01	<0.01	0.77	<0.01	<0.01	<0.01	<0.01
9A	7/13	Grasshoppers	<0.01	0.01	<0.01	0.01	0.01	0.04	<0.01	0.01	<0.01	<0.01
	12/01	Grasshoppers	<0.01	<0.01	<0.01	<0.01	<0.01	0.04	<0.01	<0.01	<0.01	<0.01
	12/01	Crickets	<0.01	<0.01	<0.01	<0.01	<0.01	0.05	<0.01	<0.01	<0.01	<0.01
	10/20	Red Harvester Ants	<0.01	<0.01	<0.01	<0.01	<0.01	0.06	<0.01	<0.01	<0.01	<0.01
	12/01	Grasshoppers	<0.01	<0.01	<0.01	<0.01	<0.01	0.02	<0.01	<0.01	<0.01	<0.01
10A	7/18	Fire Ants	0.01	0.01	<0.01	<0.01	0.02	0.75	<0.01	0.01	<0.01	<0.01
	7/13	Crickets	<0.01	<0.01	<0.01	<0.01	0.08	1.93	0.01	0.03	0.07	0.02
	10/21	Field Crickets	<0.01	<0.01	<0.01	<0.01	<0.01	0.04	<0.01	<0.01	<0.01	<0.01
	10/21	Black Harvester Ants	<0.01	<0.01	<0.01	<0.01	<0.01	0.18	<0.01	<0.01	<0.01	<0.01
	10/21	Hydrophilid Beetles	<0.01	<0.01	<0.01	<0.01	<0.01	0.12	<0.01	<0.01	<0.01	<0.01
Rabbits												
2A	7/19	Rabbits	<0.01	<0.01	<0.01	<0.01	<0.01	0.04	<0.01	<0.01	<0.01	<0.01

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TABLE 4 (cont'd.) *Pesticide residues in biological samples from Cotton Pest Management Project, Pinal County, Arizona—1971*

Sample No.	Sample Date	Sample Material	Residues—ppm									
			Ethyl Parathion	α-BHC	Heptachlor Epoxide	Dieldrin	*o,p'*-DDE	*p,p'*-DDE	*o,p'*-TDE	*p,p'*-TDE	*o,p'*-DDT	*p,p'*-DDT
			Nonprogram Samples									
Frogs and Toads												
1B	13	Toads	< 0.01	0.02	0.01	4.68	0.02	27.20	0.02	0.25	0.04	1.12
	10-13	Toads	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	3.66	< 0.01	< 0.01	< 0.01	1.15
	10-13	Frogs	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	5.35	< 0.01	< 0.01	< 0.01	0.32
2B	10-13	Frogs	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	7.93	< 0.01	< 0.01	< 0.01	0.29
	10-13	Toads	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	3.83	< 0.01	< 0.01	< 0.01	0.34
3B	7-23	Frogs	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	0.87	< 0.01	0.01	< 0.01	< 0.01
	10-14	Frogs	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	2.76	< 0.01	< 0.01	< 0.01	0.22
	7-23	Toads	< 0.01	< 0.01	0.01	0.07	0.03	7.32	0.02	0.17	0.06	0.32
	10-14	Toads	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	1.76	< 0.01	< 0.01	< 0.01	0.55
4B	7-20	Frogs	< 0.01	< 0.01	< 0.01	< 0.01	0.01	1.60	< 0.01	0.09	< 0.01	0.13
	10-12	Toads	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	1.80	< 0.01	< 0.01	< 0.01	0.28
	10-12	Pollywogs	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	24.84	< 0.01	< 0.01	< 0.01	0.99
5B	10-18	Toads	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	3.03	< 0.01	< 0.01	< 0.01	0.73
	10-18	Frogs	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	8.69	< 0.01	< 0.01	< 0.01	0.27
6B	7-23	Toads	< 0.01	0.02	0.03	0.01	0.17	12.02	0.04	1.36	0.09	2.12
	10-19	Toads	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	0.73	< 0.01	< 0.01	< 0.01	0.06
	10-19	Frogs	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	0.97	< 0.01	< 0.01	< 0.01	0.11
7B	7-22	Toads	< 0.01	0.02	0.03	0.18	0.26	19.22	0.16	0.46	0.31	0.65
	10-15	Toads	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	2.13	< 0.01	< 0.01	< 0.01	2.13
8B	10-20	Toads	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	0.99	< 0.01	< 0.01	< 0.01	0.22
9B	12-01	Toads	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	1.79	< 0.01	< 0.01	< 0.01	0.43
	—	Toads	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	8.90	< 0.01	< 0.01	< 0.01	1.03
10B	7-14	Toads	< 0.01	< 0.01	0.01	0.01	0.02	15.67	0.01	0.41	0.01	0.38
	10-21	Toads	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	5.71	< 0.01	< 0.01	< 0.01	0.69
	7-14	Frogs	< 0.01	< 0.01	< 0.01	< 0.01	0.04	9.72	0.01	0.82	0.02	0.31
Fish												
1B	7-13	Minnows	< 0.01	0.04	0.04	< 0.01	0.14	4.39	< 0.01	0.19	< 0.01	0.08
	10-13	Minnows	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	9.92	< 0.01	< 0.01	< 0.01	< 0.01
3B	7-23	Minnows	< 0.01	< 0.01	< 0.01	< 0.01	0.04	0.28	< 0.01	0.04	0.01	0.01
	10-14	Minnows	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	0.63	< 0.01	< 0.01	< 0.01	< 0.01
7B	10-15	Minnows	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	18.86	< 0.01	< 0.01	< 0.01	< 0.01
8B	7-16	Minnows	< 0.01	0.01	0.01	0.01	0.21	8.64	< 0.01	0.14	0.01	0.09
	10-20	Minnows	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	1.63	< 0.01	< 0.01	< 0.01	< 0.01
	10-20	Sunfish	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	0.14	< 0.01	< 0.01	< 0.01	< 0.01
	10-20	Freshwater Clams	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	0.34	< 0.01	< 0.01	< 0.01	< 0.01
Birds												
1B	7-13	Mourning Dove (Eggs)	< 0.01	0.01	< 0.01	< 0.01	0.01	0.85	< 0.01	0.01	< 0.01	0.01
	11-29	Gambel's White Crowned Sparrow	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	2.84	< 0.01	< 0.01	< 0.01	< 0.01
2B	10-13	Mourning Dove	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	1.07	< 0.01	< 0.01	< 0.01	< 0.01
	10-13	Sparrow	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	0.64	< 0.01	< 0.01	< 0.01	< 0.01
3B	10-14	Mallard Duck	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	0.09	< 0.01	< 0.01	< 0.01	< 0.01
5B	7-15	Wren	< 0.01	< 0.01	< 0.01	< 0.01	0.01	0.81	< 0.01	0.01	< 0.01	< 0.01
	10-18	Mourning Dove	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	0.28	< 0.01	< 0.01	< 0.01	< 0.01
	12-14	Fox Sparrow	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	0.44	< 0.01	< 0.01	< 0.01	< 0.01
6B	10-19	Mourning Doves	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	1.33	< 0.01	< 0.01	< 0.01	< 0.01
	10-19	Sparrows	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	0.04	< 0.01	< 0.01	< 0.01	< 0.01
	11-30	House Finch	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	0.96	< 0.01	< 0.01	< 0.01	< 0.01
	11-30	Cassin's Sparrow	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	1.17	< 0.01	< 0.01	< 0.01	< 0.01
	11-30	Savanna Sparrow	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	3.96	< 0.01	< 0.01	< 0.01	< 0.01
7B	7-22	Mourning Doves	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	0.10	< 0.01	0.01	< 0.01	0.01
	7-20	Wren	< 0.01	0.02	0.01	0.02	0.08	2.22	0.04	0.02	0.04	0.01
	10-15	Mourning Doves	0.01	< 0.01	< 0.01	< 0.01	< 0.01	0.98	< 0.01	< 0.01	< 0.01	< 0.01
	10-15	Sparrows	< 0.01	< 0.01	0.01	< 0.01	< 0.01	0.57	< 0.01	< 0.01	< 0.01	< 0.01
9B	7-20	Mourning Doves	0.01	< 0.01	< 0.01	< 0.01	< 0.01	0.32	< 0.01	< 0.01	< 0.01	0.01
	7-20	Wren	< 0.01	< 0.01	< 0.01	0.02	< 0.01	0.58	< 0.01	0.02	< 0.01	0.02
	10-21	Mourning Doves	< 0.01	0.01	< 0.01	< 0.01	< 0.01	0.56	< 0.01	< 0.01	< 0.01	< 0.01
	10-21	Wren	0.01	< 0.01	< 0.01	< 0.01	< 0.01	0.99	< 0.01	< 0.01	< 0.01	< 0.01
	12-01	Mourning Doves	0.01	0.01	< 0.01	< 0.01	< 0.01	0.80	< 0.01	< 0.01	< 0.01	< 0.01
10B	10-02	Loggerhead Shrike	0.01	0.01	< 0.01	< 0.01	< 0.01	76.30	< 0.01	< 0.01	< 0.01	< 0.01
Snakes and Lizards												
1B	[illegible]	Lizards	0.01	0.01	0.01	0.01	0.01	12.70	< 0.01	0.01	< 0.01	0.01
	10-1	Lizards	0.01	0.01	0.01	< 0.01	< 0.01	8.12	< 0.01	< 0.01	< 0.01	< 0.01
	9-1	Snake	0.01	0.01	0.01	< 0.01	< 0.01	44.26	< 0.01	< 0.01	< 0.01	0.88
2B	7-6	Lizard	0.01	0.02	0.01	0.01	0.03	48.92	< 0.01	0.03	< 0.01	0.06
	9-8	Lizards	0.01	0.01	0.01	< 0.01	< 0.01	18.17	< 0.01	< 0.01	< 0.01	< 0.01
	9-8	Lizards	0.01	0.01	0.01	0.01	< 0.01	0.86	< 0.01	< 0.01	< 0.01	< 0.01
9B	[illegible]	Lizard	0.01	0.01	0.01	0.01	< 0.01	0.12	< 0.01	< 0.01	< 0.01	< 0.01
	[illegible]	[illegible]	0.01	0.01	0.01	0.01	< 0.01	0.02	< 0.01	< 0.01	< 0.01	< 0.01
	[illegible]	[illegible]	0.01	0.01	0.01	0.01	0.02	9.30	< 0.01	0.05	0.01	0.05
			0.01	0.01	0.01	0.01	< 0.01	3.16	0.01	0.01	0.01	0.01

(Continued next page)

TABLE 4 (cont'd.). *Pesticide residues in biological samples from Cotton Pest Management Project, Pinal County, Arizona—1971*

Site	Sampling Date	Sample Material	Residues, ppm									
			Ethyl Parathion[1]	β-BHC	Heptachlor Epoxide	Dieldrin	*o,p'*-DDE	*p,p'*-DDE	*o,p'*-TDE	*p,p'*-TDE	*o,p'*-DDT	*p,p'*-DDT
Nonprogram Samples												
	10/14	Lizards	<0.01	<0.01	<0.01	<0.01	<0.01	3.56	<0.01	<0.01	<0.01	<0.01
	10/14	Lizards	<0.01	<0.01	<0.01	<0.01	<0.01	0.21	<0.01	<0.01	<0.01	<0.01
5B	7/15	Lizards	<0.01	0.47	0.01	0.02	0.07	8.68	<0.01	0.10	0.04	0.03
6B	7/23	Lizards	<0.01	0.01	<0.01	0.04	0.04	57.62	<0.01	0.05	0.01	0.08
7B	7/22	Lizards	<0.01	0.01	0.01	0.01	0.01	6.84	<0.01	0.01	<0.01	0.01
	7/22	Lizards	<0.01	0.01	<0.01	0.01	<0.01	0.11	<0.01	<0.01	<0.01	0.01
	10/15	Lizards	<0.01	<0.01	<0.01	<0.01	<0.01	0.85	<0.01	<0.01	<0.01	0.01
	10/15	Lizards	<0.01	<0.01	<0.01	<0.01	<0.01	25.61	<0.01	<0.01	<0.01	1.34
7B	10/15	Lizards	<0.01	<0.01	<0.01	<0.01	<0.01	0.94	<0.01	<0.01	<0.01	0.01
9B	7/20	Lizards	<0.01	0.03	0.01	0.04	0.04	16.05	<0.01	0.08	0.02	0.02
10B	7/21	Lizards	<0.01	0.03	0.01	0.01	0.07	20.29	<0.01	0.19	0.01	0.34
	7/14	Lizards	<0.01	0.01	<0.01	<0.01	0.01	10.62	<0.01	<0.01	<0.01	0.02
	10/20	Lizards	<0.01	<0.01	<0.01	<0.01	<0.01	21.21	<0.01	<0.01	<0.01	1.06
Insects												
1B	7/17	Crickets	<0.01	<0.01	<0.01	<0.01	0.05	1.20	0.01	0.02	0.02	0.01
	10/13	Hydrophilid Beetles	<0.01	<0.01	<0.01	<0.01	<0.01	1.22	<0.01	<0.01	<0.01	<0.01
2B	10/13	Ground Beetles	<0.01	<0.01	<0.01	<0.01	<0.01	0.34	<0.01	<0.01	<0.01	<0.01
3B	7/23	Backswimmers	<0.01	0.08	0.07	0.19	0.31	0.58	<0.01	0.04	0.04	0.07
	7/23	Grasshoppers	<0.01	0.01	<0.01	0.02	<0.01	0.82	<0.01	0.01	<0.01	0.01
	7/23	Crickets	<0.01	<0.01	<0.01	<0.01	0.02	0.10	<0.01	0.02	0.01	0.01
	7/16	Harvester Ants	<0.01	0.01	<0.01	0.01	0.01	0.54	0.01	<0.01	<0.01	0.01
4B	7/20	Toebiters	<0.01	0.06	0.01	0.02	0.24	0.88	<0.01	0.02	0.01	<0.01
	—	Toebiters	<0.01	<0.01	<0.01	<0.01	<0.01	0.40	<0.01	<0.01	<0.01	<0.01
	10/12	Grasshoppers	<0.01	<0.01	<0.01	<0.01	<0.01	0.13	<0.01	<0.01	<0.01	<0.01
5B	7/15	Crickets	<0.01	0.02	0.01	0.02	0.02	0.20	0.02	0.02	0.06	0.05
	12/14	Grasshoppers	<0.01	<0.01	0.01	<0.01	<0.01	0.02	<0.01	<0.01	<0.01	<0.01
6B	7/16	Crickets	<0.01	0.01	0.01	0.20	0.09	1.70	0.03	0.11	0.02	<0.01
7B	7/22	Crickets	<0.01	<0.01	<0.01	<0.01	0.02	0.23	<0.01	0.02	0.02	0.02
	7/22	Grasshoppers	<0.01	<0.01	<0.01	<0.01	0.02	0.23	0.01	0.02	0.02	0.02
	10/15	Toebiters	<0.01	<0.01	<0.01	<0.01	0.01	0.01	<0.01	<0.01	<0.01	<0.01
	10/15	Hydrophilid Beetles	<0.01	<0.01	<0.01	<0.01	<0.01	0.02	<0.01	<0.01	<0.01	<0.01
	10/15	Ground Beetles	<0.01	<0.01	<0.01	<0.01	<0.01	0.03	<0.01	<0.01	<0.01	<0.01
8B	7/21	Grasshoppers	<0.01	<0.01	<0.01	0.01	0.01	0.23	<0.01	0.01	<0.01	0.01
	10/20	Red Harvester Ants	<0.01	<0.01	<0.01	<0.01	<0.01	0.03	<0.01	<0.01	<0.01	<0.01
9B	12/01	Darkling Ground Beetles	<0.01	<0.01	<0.01	<0.01	<0.01	0.16	<0.01	<0.01	<0.01	<0.01
	10/21	Hydrophilid Beetles	<0.01	<0.01	<0.01	<0.01	<0.01	0.09	<0.01	<0.01	<0.01	<0.01
	10/21	Toebiters	<0.01	<0.01	<0.01	<0.01	<0.01	0.41	<0.01	<0.01	<0.01	<0.01
	10/21	Ground Beetles	<0.01	<0.01	<0.01	<0.01	<0.01	0.11	<0.01	<0.01	<0.01	<0.01
	10/21	Grasshopper	<0.01	<0.01	<0.01	<0.01	<0.01	0.07	<0.01	<0.01	<0.01	<0.01
10B	7/21	Grasshoppers	<0.01	0.03	0.01	0.01	0.02	0.02	<0.01	0.01	<0.01	0.02
	7/21	Grasshoppers	<0.01	0.01	<0.01	<0.01	0.01	0.17	0.01	0.02	<0.01	0.02
	10/02	Bandwing Grasshoppers	<0.01	<0.01	<0.01	<0.01	<0.01	0.02	<0.01	<0.01	<0.01	<0.01
	10/21	Hydrophilid Beetles	<0.01	<0.01	<0.01	<0.01	<0.01	1.12	<0.01	<0.01	<0.01	<0.01
	10/21	Backswimmers	<0.01	<0.01	<0.01	<0.01	<0.01	6.24	<0.01	<0.01	<0.01	<0.01
Rabbits and Rats												
1B	11/29	Cotton Rat	<0.01	<0.01	<0.01	<0.01	<0.01	0.01	<0.01	<0.01	<0.01	0.01
9B	7/20	Rabbit	<0.01	<0.01	<0.01	<0.01	<0.01	0.02	<0.01	<0.01	<0.01	<0.01
10B	7/21	Rabbit	0.03	<0.01	<0.01	<0.01	0.01	0.18	<0.01	0.01	<0.01	<0.01

NOTE: Data corrected for pesticide recovery from fortified samples.
Lower limits of sensitivity = 0.01 ppm, except for toxaphene, which was 0.05 ppm

[1] Methyl parathion, malathion, methyl trithion, and ethion residues did not exceed the lower limits of detectability of 0.01 ppm.

[2] γ-BHC = 0.01 ppm

BRIEF

DDT Residues in Air in the Mississippi Delta, 1975[1]

Robert D. Arthur, Jimmie D. Cain, and Ben F. Barrentine[2]

ABSTRACT

In a previous publication the authors reported an 88 percent decrease in ΣDDT (DDT plus metabolites) in air between 1972 and 1974 in the Mississippi Delta. This period was the first two years after the use of DDT was banned in the United States. The present report shows an additional 36 percent decrease in ΣDDT levels in air between 1974 and 1975. Thus in the past three years ΣDDT in air has decreased by 92 percent, a much more rapid decrease than had been expected.

Introduction

For the past several years, pesticide levels in air in the Mississippi Delta have been measured to determine seasonal and yearly trends. Arthur et al. (*1*) reported pesticide levels in the Delta for 1972-74. The authors observed an 84 percent decrease in Σ DDT (DDT plus metabolites) residues between 1972 and 1973, the first year after the ban on DDT use in the United States. A 26 percent decrease in Σ DDT in air was reported between 1973 and 1974.

Sampling and Analysis

Air samples were taken weekly in Stoneville, Miss., located in the middle of the most intensive cotton-growing area of the State. A Misco Model 88 air pesticide sampler was used with ethylene glycol as the trapping agent. A timer was set so that the sampler would operate 4.29 minutes every hour for seven days, making a total collecting time of 12 hours a week. Approximately 7m^3 air was sampled each week.

Analytical procedures and instrument parameters were described previously (*1*).

Results and Discussion

Monthly arithmetic and geometric means of Σ DDT in air from 1972 through 1975 are presented in Table 1. The arithmetic mean in 1975 was 7.6 ng/m^3 compared to 11.9 ng/m^3 in 1974, and the geometric mean in 1975 was 5.1 ng/m^3 compared to 8.1 ng/m^3 in 1974. This represents a 36 percent decrease in the arithmetic mean of DDT and a 37 percent decrease in the geometric mean of Σ DDT during the year. Since January 1, 1973, the date on which DDT was banned, arithmetic and geometric means of ΣDDT in air have decreased 92 percent and 85 percent, respectively.

So far some DDT has been found each month in the air from the Delta. The lowest monthly value was 1.3 ng/m^3 in December 1975. Since ΣDDT has decreased so rapidly, it is extremely important to continue monitoring air in the Mississippi Delta in order to determine at what point DDT will no longer be detected.

In light of these findings, and as more data on the disappearance of DDT from the environment are obtained, authors believe that certain reported characteristics of DDT should be re-evaluated, particularly its extreme stability and or lack of biodegradability in the environment.

Paper No. 3296, Mississippi Agricultural and Forestry Experiment Station, Mississippi State, Miss. Study financed by U. S. Environmental Protection Agency Contract 68-02-0699, Epidemiologic Studies Program, Technical Services Division, Office of Pesticide Programs.

Department of Biochemistry, Mississippi State University, Mississippi State, Miss. 39762. Reprints available from this address.

LITERATURE CITED

(*1*) *Arthur, R. D., J. D. Cain, and B. F. Barrentine, 1976.* Atmospheric levels of pesticides in the Mississippi Delta. Bull. Environ. Contam. Toxicol. 15(2):129-134.

APPENDIX

Chemical Names of Compounds Discussed in This Issue[1]

ABATE	See temefos
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
AROCLOR	A mixture of chlorinated terphenyls
BHC (BENZENE HEXACHLORIDE)	1,2,3,4,5,6-Hexachlorocyclohexane (mixture of isomers). Commercial product contains several isomers of which *gamma* is most active as an insecticide
CARBARYL	1-Naphthyl N-methylcarbamate
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
DDD	See TDE
DDE	Dichlorodiphenyl dichloro-ethylene (degradation product of DDT) *p,p'*-DDE: 1,1-Dichloro-2,2-bis(*p*-chlorophenyl) ethylene *o,p'*-DDE: 1,1-Dichloro-2-(*o*-chlorophenyl)-2-(*p*-chlorophenyl)ethylene
DDT	Main component (*p,p'*-DDT): α-Bis(*p*-chlorophenyl) β,β,β-trichloroethane Other isomers are possible and some are present in the commercial product *o,p'*-DDT [1,1,1-Trichloro-2-(*o*-chlorophenyl)-2-(*p*-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-*endo-exo*-5,8-dimethanonaphthalene
DIMETHOATE	O,O-Dimethyl S-(N-methylcarbamoylmethyl) phosphorodithioate
ENDRIN	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
ETHION	O,O,O',O'-Tetraethyl S,S'-methylene bisphosphorodithioate
FENTHION	*O,O*-Dimethyl *O*-[3-methyl-4-(methylthio) phenyl]phosphorothioate
HEPTACHLOR	1,4,5,6,7,8,8-Heptachlor-3a,4,7,7a-tetrahydro-4,7-*endo*-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
MALATHION	S-[1,2-Bis(ethoxycarbonyl)ethyl] O,O-dimethyl phosphorodithioate
MIREX	Dodecachlorooctahydro-1,3,4-metheno-2H-cyclobuta[cd]pentalene
NONACHLOR	1,2,3,4,5,6,7,8,8-Nonachloro-3a,4,7,7a-tetrahydro-4,7-methanoindan
OXYCHLORDANE	2,3,4,5,6,6a,7,7-Octachloro-1a,1b,5,5a,6,6a hexahydro-2,5-methano-2H-indeno(1,2-β)oxirene
PARATHION	O,O-Diethyl O-*p*-nitrophenyl phosphorothioate
PCB'S (POLYCHLORINATED BIPHENYLS)	Mixtures of chlorinated biphenyl compounds having various percentages of chlorine
SEVIN	See carbaryl
STROBANE	Polychlorinates of camphene, pinene, and related terpenes
2,4,5-T	(2,4,5-Trichlorophenoxy) acetic acid
TDE	2,2-Bis(*p*-chlorophenyl)-1,1-dichloroethane
TOXAPHENE	Chlorinated camphene (67-69% chlorine). Product is a mixture of polychlor bicyclic terpenes with chlorinated camphenes predominating.
TRITHION	S-((*p*-Chlorophenylthio)methyl)*O,O*-diethyl phosphorodithioate

[1] Does not include chemicals listed only in tables of paper by Manske/Johnson

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SUBJECT AND AUTHOR INDEXES

Volume 10, June 1976—March 1977

Preface

Primary headings in the subject index include pesticide compounds, media in which pesticide residues are monitored, and major concepts related to the monitoring of pesticides in the environment. Pesticide compounds are listed by common names; trade names are used for those which have no common names.

Secondary headings cross-reference the primary headings. For a paper which discusses five or more organochlorines the compounds are grouped by class under media and concept headings but each compound appears individually under the primary headings for pesticide compounds.

In the author index all information on a paper appears in the senior author's citations: associate authors, title of the paper, and volume, issue, and pages where the article was published. Names of associate authors are cross-referenced as minor headings, but the reader is referred to the senior author's entry for the paper's complete citation.

SUBJECT INDEX

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The *Pesticides Monitoring Journal* welcomes from all sources qualified data and interpretative information on pesticide monitoring. The publication is distributed principally to scientists, technicians, and administrators associated with pesticide monitoring, research, and other programs concerned with pesticides in the environment. Other subscribers work in agriculture, chemical manufacturing, food processing, medicine, public health, and conservation.

Articles are grouped under seven headings. Five follow the basic environmental components of the National Pesticide Monitoring Program: Pesticide Residues in People; Pesticide Residues in Water; Pesticide Residues in Soil; Pesticide Residues in Food and Feed; and Pesticide Residues in Fish, Wildlife, and Estuaries. The sixth is a general heading; the seventh encompasses briefs.

Monitoring is defined here as the repeated sampling and analysis of environmental components to obtain reliable estimates of levels of pesticide residues and related compounds in these components and the changes in these levels with time. It can include the recording of residues at a given time and place, or the comparison of residues in different geographic areas. The Journal will publish results of such investigations and data on levels of pesticide residues in all portions of the environment in sufficient detail to permit interpretations and conclusions by author and reader alike. Such investigations should be specifically designed and planned for monitoring purposes. The Journal does not generally publish original research investigations on subjects such as pesticide analytical methods, pesticide metabolism, or field trials (studies in which pesticides are experimentally applied to a plot or field and pesticide residue depletion rates and movement within the treated plot or field are observed).

Authors are responsible for the accuracy and validity of their data and interpretations, including tables, charts, and references. Pesticides ordinarily should be identified by common or generic names approved by national or international scientific societies. Trade names are acceptable for compounds which have no common names. Structural chemical formulas should be used when appropriate. Accuracy, reliability, and limitations of sampling and analytical methods employed must be described thoroughly, indicating procedures and controls used, such as recovery experiments at appropriate levels, confirmatory tests, and application of internal standards and interlaboratory checks. The procedure employed should be described in detail. If reference is made to procedures in another paper, crucial points or modifications should be noted. Sensitivity of the method and limits of detection should be given, particularly when very low levels of pesticide residues are being reported. Specific note should be made regarding correction of data for percent recoveries. Numerical data, plot dimensions, and instrument measurements should be reported in metric units.

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CONTENTS

Volume 11 June 1977 Number 1

PESTICIDES IN PEOPLE

DDT and DDE in the Blood and Diet of Eskimo Children from Hooper Bay, Alaska[1]

William F. Serat, Min K. Lee, Albert J. Van Loon, Donald C. Mengle, James Ferguson,[2] John M. Burks,[3] and Thomas R. Bender[4]

ABSTRACT

An analysis of the levels of DDT and DDE in the blood of some Alaskan Eskimo children and in the fat of some local marine mammals taken for food suggests that the children's pesticide burden is only modestly lower than that of other American children. Authors suggest that some other food source, perhaps packaged food, supplies a portion of the dietary chlorohydrocarbon pesticide.

Introduction

Marine mammals from virtually all waters contain chlorinated hydrocarbon contaminants in their tissues, reflecting the ubiquitous distribution of agricultural and industrial chemicals (*2,3,7,8,15*). Highest levels of DDT have been reported in migratory seals from Canadian waters of the North Atlantic, from the North Sea, and from the Baltic Sea (*8*). Except for nonmigratory harbor seals (*1*), the pesticide and its metabolites are generally less prominent in the tissues of mammals from Antarctic and Pacific waters.

Although perhaps less dependent on aquatic food sources now than in the past, native populations of western coastal Alaska still derive a substantial portion of their diet from the sea. Thus in the absence of any other substantial contact with DDT, levels of the pesticide and its metabolites in tissues of Alaskan Natives likely reflect the marine component of their diet.

Children and adolescents in these Eskimo populations have lived in the era of worldwide contamination by chlorohydrocarbons. Although a portion of any body burden of DDT-type materials may well have been received through the placenta or from breast milk (*4,5,10*), such sources would be difficult to evaluate in the presence of a contaminated marine diet for all but the very young. This paper reports results of a study undertaken to determine whether blood levels of DDT and DDE in Eskimo children of western Alaska are near those of children from other segments of the American population. Alaskan seals and waterfowl which are used as food were also examined for chlorohydrocarbons.

Methods

BLOOD SAMPLES

In May 1972, serum and heparinized whole blood were collected from 40 Eskimo children in Hooper Bay. Thirty-eight sera with 25 matching whole blood samples, and two single whole blood samples were available. They were selected from a listing of 204 specimens which had been collected for other purposes. This list representing nearly every school child in the village, kindergarten through ninth grade, was stratified by grade level and sex. A technique of substitution was used so that no specimens finally selected were from children in the same household. The donors' ages ranged from 6 to 17 years; there were 20 males and 20 females.

Aliquots of 2.0 ml whole blood or sera were extracted with 6.0 ml hexane on a slow rotary mixer. Nanograde (Mallinkrodt) hexane was used in the extraction and as a rinse for all glassware.

Pesticide residues in the extracts were quantitated by gas chromatography using electron-capture detectors. Two 6-ft-by-1/4-in. pyrex glass columns allowed separation of residues. One contained 1.5 percent OV-17/1.95 percent QF-1 on 100/120 mesh Chromosorb WHP, and the other

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contained 5 percent OV-210 on 80/100 mesh Supelcoport. Columns were maintained at 190° C, inlets at 215° C, and detectors at 210° C. Detectors were operated in the pulsed mode, with 10 percent methane in argon carrier gas at 80 ml/min.

Pesticide residue standards were more than 99 percent pure. Recoveries of residues undergoing the analytical regimen were greater than 90 percent and the reliable sensitivity of detection was 0.001 ppm for *p,p'*-DDE and 0.002 ppm for *p,p'*-DDT. Measured residue levels in blood and food source samples were not corrected for recovery values.

FOOD SOURCE SAMPLES

In May 1974, animals which residents had hunted and killed for food near Hooper Bay were tested. Single samples of seal meat, seal fat, and sea duck meat, all components of the native diet, were cleaned by a modification of the procedure of Stanley and Le Favoure (*12*). Following digestion in a mixture of perchloric-acetic acids and extraction with hexane, fats in the extracts were destroyed in large part by treatment with 0.5 ml concentrated H_2SO_4 in a graduated centrifuge tube. After centrifugation, the DDT-DDE residues were quantified by procedures described above. The limit of sensitivity was 0.001 ppm DDE and 0.002 ppm DDT. Neither the digestion mixture nor the H_2SO_4 contained extractable interfering material.

In April 1975, five additional samples of seal oil from hunted species were obtained from food caches in villages 150 miles south of Hooper Bay. Following three extractions with 20 volumes of acetonitrile the extracts were chromatographed. Interfering peaks appeared, so the acetonitrile extracts were mixed with six volumes of water and then extracted with hexane. Acceptable quantitation of chlorohydrocarbons could be made from the hexane solution with minimal interference after reacting with concentrated H_2SO_4. Chromatographic columns were similar to those used to quantitate residues extracted from blood. One column was prepared with 5 percent OV-210 on 100/120 mesh Gas-Chrom Q and the other with 1.5 percent OV-17/1.95 percent QF-1 on 80/100 mesh Gas-Chrom Q. The former column operated at 183° C with the carrier gas at 95 ml/min and the latter operated at 200° C under a gas flow of 80 ml/min. Reliable sensitivities were 0.001 ppm for DDE and 0.002 ppm for DDT.

Polychlorinated biphenyl compounds (PCB's) are reported to be as ubiquitous as DDT-type materials. For this reason extraneous gas chromatographic peaks in the extract of seal fat were compared with peaks obtained in chromatographing the PCB compound, Aroclor 1242. No correlation could be made between unidentified peaks from the seal fat extract and six prominent peaks from a chromatogram of the PCB. Therefore, authors cannot report the presence of any such contaminant in the fat sample at the sensitivity level of 0.2 ppm for nonmetabolized material by the methods used.

Aroclor 1254 chromatographed on 1.5 percent OV-17/1.95 percent QF-1 on Gas-Chrom Q presented one major peak, from a total of ten, which had a retention time of 6.4 minutes in contrast to 5.0 minutes for *p,p'*-DDE. Thus there is no discernible nonmetabolized PCB (Aroclor 1254) in lipids from the seals indigenous to the coast of western Alaska, determined at a sensitivity of 0.2 ppm.

Results

DDT-DDE

Table 1 summarizes results of analyses of DDE in serum. Pesticide levels in the whole blood samples were, in every case where matching serum levels were available for comparison, lower than serum levels by a factor which would relate to the dilution of serum by red blood cells. DDT levels in serum were beneath the limits of reliable detection (0.002 ppm) in 29 of the 38 samples and ranged from 0.002 to 0.003 ppm in the remaining nine sera.

TABLE 1. *Serum levels of* p,p'*-DDE in children of Hooper Bay, Alaska—1972*

Donor	Number	*p,p'*-DDE Levels, ppm	
		Mean	Range
Total	38	0.011	0.005-0.022
Male	19	0.011	0.005-0.022
Female	19	0.011	0.007-0.016
Ages 6-11 yr	18	0.011	0.005-0.018
Male	9	0.010	0.005-0.018
Female	9	0.012	0.009-0.016
Ages 12-17 yr	20	0.011	0.007-0.022
Male	10	0.012	0.008-0.022
Female	10	0.010	0.007-0.014

DDT-DDE IN FOOD SOURCE SAMPLES

Pesticide levels in the single samples of seal fat, seal meat, and sea duck meat ranged from undetectable levels in seal meat to 0.110 ppm DDE and 0.020 ppm DDT in seal fat (Table 2). The highest residue in samples of seal oil was 0.80+0.01 ppm DDE (Table 3).

Discussion

A study reported in 1961 (*6*), preceding the present study by at least 11 years, indicated that DDT-related compounds were virtually absent in the natural dietary com-

TABLE 2. *Levels of* p,p'*-DDE and* p,p'*-DDT in three food source samples, Hooper Bay, Alaska—1974*

Sample	Pesticide Level, ppm				Percent Fat
	Wet Weight Basis		Fat Basis		
	p,p'-DDE	*p,p'*-DDT	*p,p'*-DDE	*p,p'*-DDT	
Seal fat	0.105	0.019	0.110	0.020	95.5
Seal meat	ND	ND	ND	ND	0.4
Sea duck meat	0.004	ND	0.17	ND	2.4

NOTE: ND = no residues could be detected within limits of reliable sensitivity.

TABLE 3. *Levels of chlorohydrocarbon residues in seal oil, western Alaska—1975*

Collection Location	Residues, ppm		
	p,p'-DOE	*o,p'*-DDT	*p,p'*-DDT
Kuskokwim Bay near Kwigillingok			
(Spotted seal)	0.80±0.01	0.02±0.02	0.29±0.02
(Bearded seal, baby mukluk)	0.32±0.01	0.02±0.02	0.23±0.02
Kuskokwim Bay near Kongiganok	0.19±0.01	0.02±0.02	0.02±0.02
Kipnuk	0.36±0.01	0.02±0.02	0.13±0.02
Newtok	0.51±0.01	0.02±0.02	0.28±0.02

ponents of Alaska Natives. In addition the body fat levels of chlorohydrocarbons described for Natives were substantially lower than those of the general population. It might be assumed, on the basis of average values from a number of measurements, that *p,p'*-DDT levels in fat were some 450 times higher than in serum and that *p,p'*-DDE levels were some 400 times higher. Therefore, with reported mean levels of 0.8±0.10 ppm DDT and 2.0±0.41 ppm DDE in fat tissue, an approximate serum level of 0.002 ppm DDT and 0.005 ppm DDE might have been expected. Such estimated serum concentrations of the compounds for the study of 1961 (*6*) are similar to concentrations found now for the children and adolescents from Hooper Bay.

This comparison suggests that the body burden of these materials has remained relatively stable regardless of the route of exposure, and authors have no indication of recent local usage of any pesticide. Table 4 shows that chlorohydrocarbon levels in the serum of children of Hooper Bay are similar or only modestly lower than in children from most other areas (*9,11,13,14*). Children in South Carolina (*9*), especially black children, have demonstrated relatively high mean serum DDE and DDT levels, and reference adult populations had even higher levels.

The absence of chlorohydrocarbons in dietary samples reported in the previous Alaskan study (*6*) is in contrast to findings here, although differences in analytical techniques and corresponding sensitivities in measurements may well account for this.

TABLE 4. *Mean serum levels of chlorohydrocarbons in different populations of five States*

Reported Studies[1]	Age, yr	Chlorohydrocarbon, ppm	
		DDE	DDT
Hooper Bay, Alaska	6-17	0.011	<0.002
South Carolina (*9*)			
Whites	6-9	0.0246	0.0066
Blacks	6-9	0.0552	0.0185
Whites	Adults	0.0285	0.0112
Blacks	Adults	0.1222	0.0263
Florida (*11*)	—	0.0157	0.0042
Idaho (*14*)	3-10	0.0079	0.0021
	11-15	0.0130	0.0030
	16-20	0.0149	0.0030
Utah (*13*)	<21	0.0134	0.0036
	≥21	0.0209	0.0066

[1]Numbers in parentheses represent literature references cited in present study

The levels of residues in seal fat, in seal oil, and in sea duck meat found in the present study are notably lower than those in fat of seals taken off eastern Scotland (5.5 ppm DDE and 7.8 ppm DDT), northern and western Scotland (3.4 and 3.8 ppm), and Cabot Strait (5.9 and 5.5 ppm) and Magdalene Island (1.2 ppm and 0.36 ppm) in the Gulf of Saint Lawrence, Canada (*8*). Furthermore, the levels found in this study do not approach those reported in fat samples of nonmigratory harbor seals from some regions of the eastern North Pacific Ocean (*1*). Geometric means of ΣDDT and PCB's were 611 ppm in seals from Puget Sound and 11 ppm in seals from Pribilof Islands. Data on the levels of DDE in various tissues from immature males and nursing pups of the northern fur seal from the Pribilof Islands or the coast of Washington (*2,3*) indicate that fat levels of the compound are seven times as high as those in liver. The immature males would thus be expected to contain some 5 ppm DDE in their fat, a value in keeping with those found in seals from North Atlantic waters.

If generally representative, the relatively low levels of chlorohydrocarbons found in the fat and oil samples reported here suggest that lower dietary exposures, at least from an indigenous meat supply, should prevail for Eskimos of western Alaska. This assumption is not borne out by levels of DDE and DDT in serum from the children of Hooper Bay. Environmental levels of the chemically stable compound, DDT, in that locale should not be affected by a recent moratorium on its use, since its introduction into the region would have been largely windborne and in notably smaller quantity than if it had been used in local agriculture. It is possible that prepackaged food available to many Alaska Natives, especially in school lunch programs, is a source of the chlorohydrocarbons in the children's blood. Modest dietary exposure and body burdens of the chlorohydrocarbons appear to have been maintained during the past decade or longer.

LITERATURE CITED

(*1*) *Anas, R. E. 1974.* DDT plus PCB's in blubber of harbor seals. Pestic. Monit. J. 8(1):12-14.

(*2*) *Anas, R. E., and A. J. Wilson, Jr. 1970.* Organochlorine pesticides in fur seals. Pestic. Monit. J. 3(4):198-200.

(*3*) *Anas, R. E., and A. J. Wilson, Jr. 1970.* Organochlorine pesticides in nursing fur seal pups. Pestic. Monit. J. 4(3):114-116.

(*4*) *Curley, A., M. F. Copeland, and R. D. Kimbrough. 1969.* Chlorinated hydrocarbon insecticides in organs of stillborn and blood of newborn babies. Arch. Environ. Health 19(5):628-632.

(*5*) *Curley, A., and R. Kimbrough. 1969.* Chlorinated hydrocarbon insecticides in plasma and milk of pregnant and lactating women. Arch. Environ. Health 18(2):156-164.

(*6*) *Durham, W. F., J. F. Armstrong, W. M. Upholt, and C. Heller. 1961.* Insecticide content of diet and body fat of Alaskan natives. Science 134(3493):1880-1881.

(7) *Holden, A. V. 1972.* Monitoring organochlorine contamination of the marine environment by the analysis of residues in seals, in marine population and sea life. Fishing News (Books) Ltd., London, pp 226-272.

(8) *Holden, A. V., and K. Marsden. 1967.* Organochlorine pesticides in seals and porpoises. Nature 216(5122):1274-1276.

(9) *Keil, J. E., W. Weston III, C. B. Loadholt, S. H. Sandifer, and J. J. Colcolough. 1972.* DDT and DDE residues in blood from children, South Carolina, 1970. Pestic. Monit. J. 6(1):1-3.

(10) *O'Leary, J. A., J. E. Davis, W. F. Edmondsons, and G. A. Reich. 1970.* Transplacental passage of pesticides. Am. J. Obstet. Gynecol. 107(1):65-68.

(11) *Radomski, J. L., W. B. Deichmann, A. A. Rey, and I. Merkin. 1971.* Human pesticide blood levels as a measure of body burden and pesticide exposure. Toxicol. Appl. Pharmacol. 20(2):175-185.

(12) *Stanley, R. L., and H. T. Le Favoure. 1965.* Rapid digestion and cleanup of animal tissues for pesticide residue analysis. J. Assoc. Off. Agric. Chem. 48(3):666-667.

(13) *Warnick, S. L. 1972.* Organochlorine pesticide levels in human serum and adipose tissue, Utah—fiscal years 1967-71. Pestic. Monit. J. 6(1):9-13.

(14) *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.

(15) *Wolman, A. A., and A. J. Wilson, Jr. 1970.* Occurrence of pesticides in whales. Pestic. Monit. J. 4(1):8-10.

RESIDUES IN FISH, WILDLIFE, AND ESTUARIES

Mercury, Arsenic, Lead, Cadmium, and Selenium Residues in Fish, 1971-73—National Pesticide Monitoring Program

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ABSTRACT

As part of the National Pesticide Monitoring Program, the Fish and Wildlife Service, U.S. Department of Interior, analyzed selected fish samples from 100 monitoring stations for residues of mercury, arsenic, lead, cadmium, or selenium in 1971-73. At most stations, detectable residues of all metals were present in more than 95 percent of the composite samples. Fishes with mercury residues exceeding 0.5 mg/kg wet weight in the whole fish were mainly predators. Fishes with residues of arsenic, lead, cadmium, and selenium exceeding 0.5 mg/kg included predatory and nonpredatory species. The number of composite samples in which residues of these elements exceeded 0.5 mg/kg decreased from 1971 to 1973, whereas the percentage of samples with detectable residues increased slightly. Only selected samples were analyzed in 1973; therefore, these figures should be used only cautiously as trend data. Species of fish collected varied considerably between geographic regions but were similar from year to year within each region.

Introduction

The Fish and Wildlife Service (FWS) has contributed to the National Pesticide Monitoring Program by determining residues of various pollutants in fish. Authors have analyzed for organochlorines since 1967, mercury since 1969, and lead, cadmium, selenium, and the metaloid arsenic since 1971. Results of analyses were published for organochlorines through 1969 (*4,6*) and for mercury through 1970 (*5*). The present report presents results of analyses of heavy metals conducted on fishes collected 1971-73 at 100 stations throughout the United States (Fig. 1). On the basis of 1971 and 1972 results from 100 stations only, selected samples were analyzed for metals in 1973; caution should be exercised in interpreting these data. Except for Redhorse and fishes collected in Hawaii, common names of fishes used throughout this report are those designated by the American Fisheries Society (*1*). Redhorse is used to designate unidentified members of the genus *Moxostoma*. Fishes from the Hawaiian streams were Tilapia (*Tilapia mossambica*), Cuban limia (*Limia vittata*), and Chinese catfish (*Clarias fuscus*).

Methods

FISH COLLECTIONS

Fish were collected by FWS biologists, personnel of State fish and game agencies, and local commercial fishermen. Collection gear included a variety of nets and traps, hook and line, and electrofishing equipment. The use of chemical collecting agents was not permitted. As in previous reports (*1,7*) three composites of three species, each consisting of two to five adult fish, were to be collected at each of the stations from September to November. In the Hawaiian stations up to 26 fish were analyzed. Sample collections included a replicate for each species in 1971, but for only one of the three species from each station in 1972 and 1973. After length and weight of the fish had been determined, each composite was wrapped in foil, frozen, and shipped to the analytical laboratory for preparation and residue analyses. Localities of collection, species, size, and number of fish appear in Tables 1-3.

LABORATORY METHODS

1971—Two subsamples were taken from ground whole body composites: a 1-g sample for mercury and a 15-g sample for arsenic, cadmium, and lead. Mercury determinations followed the procedures of Okuno et al. (*13*).

Arsenic was measured by the Jarrell-Ash procedure (*7*) with the following modifications: a 1:1 (v/v) mixture of concentrated sulfuric acid (H_2SO_4) and nitric acid (HNO_3) was used to digest the 15-g samples, no perchloric acid was added during digestion, and the final volume was adjusted to 60 ml with distilled water. A subsample of the

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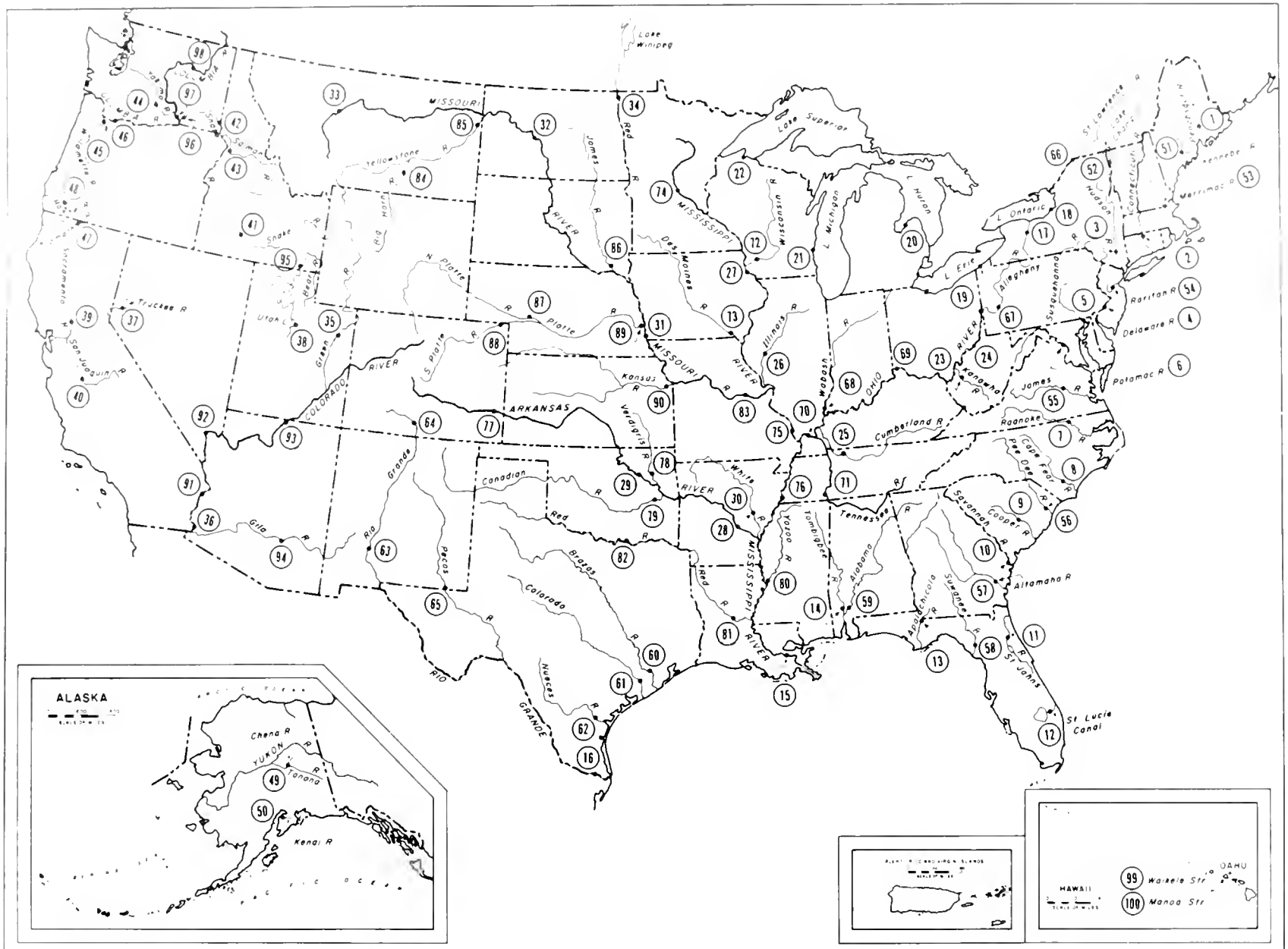

FIGURE 1. *Fish sampling stations, National Pesticide Monitoring Program, 1971-73*

digest representing 2.5 g of sample was analyzed by atomic absorption.

The digest from the arsenic procedure was also used for determining the presence of lead and cadmium. A subsample representing 10 g of sample was placed in a beaker and adjusted to 60 ml with distilled water, three drops of 1 percent (v/v) thymol blue were added, and the pH was adjusted to 5-6 with aqueous solutions of NaOH and H_2SO_4. This solution was transferred to a 250-ml separatory funnel, 10 ml of a 1 percent aqueous solution of a chelator (diethyldithiocarbamic acid, sodium salt) was added, the funnel was shaken for 2 minutes, and the extract was allowed to stand for 10 minutes. A 10-ml portion of water-saturated methyl isobutyl ketone (MIBK) was added, and the funnel was shaken for 2 minutes to extract the metals into the MIBK. The aqueous solution was drawn off, discarded, and the MIBK was collected in a 16-by-125-mm culture tube. This solution was aspirated into the flame of an atomic absorption spectrophotometer.

Recoveries of the metals were determined from the analyses of fish samples fortified at different levels with each metal. The overall mean from triplicate analyses for arsenic at three levels (0.1, 0.25, 0.5 ppm) was 82 percent with a standard deviation of 9.3 percent. The mean and standard deviations for lead (0.1, 1, 5 ppm) and cadmium (0.05, 0.25, 0.5 ppm) were 109 percent ± 21.0 percent and 99 percent ± 17.7 percent, respectively.

1972—Homogenized samples for mercury determinations were dried in a microwave oven for 15 minutes before combustion, but were otherwise analyzed as described for 1971. For lead and cadmium, 1-g subsamples of ground whole-body composites were dried in a beaker on a hotplate, charred with infrared lamps, and ashed in a muffle furnace at 500°C for 4 hours. After cooling, the residue was dissolved in 1 ml concentrated HNO_3, then heated until dry and white. To the cooled residue, 1 ml of concentrated HNO_3 was added, then diluted to 20 ml with water. The solution was warmed on a hotplate, cooled, and adjusted to a pH of 3 ± 0.2, then quantitatively transferred to a 125-ml separatory funnel with 2 ml water. A 1-ml portion of a 1 percent (w/v) aqueous solution of ammonium pyrrolidine-dithiodi-carbamate was added to the funnel and mixed. After 2 minutes, 10 ml of MIBK was added, the funnel was shaken for 1 minute, solvents were allowed to separate, and the lower aqueous layer was drawn off and discarded. A 10-ml solution of 5 percent HNO_3 was added to the funnel and shaken for 30 seconds. Solvents were allowed to separate, and the lower aqueous layer was collected. This sample solution was analyzed for both lead and cadmium, using a carbon rod atomizer on an absorption spectrophotometer.

Arsenic and selenium residues were determined in separate 1-g subsamples of the ground whole-body composites. Analyses for both followed the Jarrell-Ash (*7*) procedure with the following modifications: samples were placed in a Chromel wire sample holder and the holder was hung on the hook of a ground glass stopper placed in a 2-liter combustion flask containing 20 ml of 25 percent hydrochloric acid (HCl) solution for arsenic determinations, or 20 ml of a 1:1 (v/v) mixture of 50 percent HCl and 25 percent H_2SO_4 for selenium determinations. Flasks were flushed with oxygen, stoppered, and the contents were ignited with an infrared igniter. After combustion, flasks were allowed to stand 1 hour in order for the acid solution to entrain combustion products.

For the arsenic determination, the sample solution was transferred to a 100-ml pear-shaped flask and 20 ml of 40 percent (w/v) hydroxylamine hydrochloride was added; after the solution had been allowed to equilibrate for 15 minutes, 1 ml of a 6 percent aqueous solution of potassium iodide was added. After another 15 minutes, 2 ml of a 40 percent $SnCl_2$ solution was added and allowed to stand another 15 minutes; a Teflon-covered magnetic stirring bar was dropped into the flask and the flask was connected to an arsine generator. The solution was stirred briefly, 1 g of 20 mesh zinc was added and mixed for 2 minutes, and the generated arsine was swept with helium into the burner of an atomic absorption spectrophotometer.

Selenium sample solutions were decanted from the combustion flasks and rinsed with 20 ml acid (50 percent HCl and 25 percent H_2SO_4). A 10-ml portion of this solution (0.25 g sample equivalent) was placed in a pear-shaped flask with 30 ml of the HCl-H_2SO_4 acid mixture and 1 ml of stannous chloride ($SnCl_2$). A stirring bar was placed in this flask and the generator was connected as in the procedure for arsenic analysis. A magnetic stirrer was placed under the flask and 2 g of 20 mesh zinc was added; after 15 seconds of stirring, the hydrogen selenide generated was swept into the burner of the atomic absorption spectrophotometer.

Mercury recovery studies were made to compare microwave drying with the former P_2O_5 procedure for drying samples. Analysis of each of three samples using both drying procedures showed no significant differences ($P = 0.55$). Recoveries of lead and cadmium were determined by fortifying samples at varying levels ranging from 0.1 to 1 ppm for lead, and 0.01 to 0.1 ppm for cadmium. The overall mean recovery and standard deviation for lead was 90 percent ± 11.6 percent and 100 percent ± 13.6 percent for cadmium. For arsenic, the overall recovery from samples fortified with levels ranging from 0.05 to 0.3 ppm was 91 percent ± 18 percent. Selenium was determined by the procedure of Church and Robison (*3*). Recoveries of selenium by the procedure averaged 100 percent with a standard deviation of 15 percent.

1973—Mercury, lead, and cadmium were determined as in 1972. Arsenic was determined as in 1972, except that the

zinc used in generating arsine was 200-400 mesh in a slurry of distilled water (10 g zinc to 20 ml distilled water), and an electrodeless discharge lamp (EDL) and power supply were used in place of the hollow cathode lamp. Selenium was measured as described for 1972, but the light source was an EDL.

DETECTION LIMITS AND STANDARDS

The limits of detection of the metals in the composite fish samples were the same in all 3 years. Expressed as mg/kg wet weight, detection levels of each metal were mercury, 0.01; arsenic, 0.05; lead, 0.10; cadmium, 0.05; and selenium, 0.05. Analyses for metal residues were conducted on subsamples of composites prepared as described by Henderson et al. for laboratory C (6).

During all analyses, standard solutions of each metal were used for quantification and reagent blanks were used to detect possible contamination.

CROSS-CHECK ANALYSES

In cross-check analyses, total mercury was determined by the techniques described by the Joint Mercury Residues Panel (*10*) and modified as described by Henderson et al. (5). Arsenic and selenium residues were determined as described in the eleventh (*8*) and twelfth (9) editions, respectively, of the methods book of the Association of Official Analytical Chemists. Lead and cadmium residues were determined as follows: to a 12.5-g sample portion, 5 ml of 10 percent magnesium nitrate was added, the samples were then dried and charred on a hotplate and ashed overnight at 500°C. The samples were wetted with nitric acid, dried on a hotplate, and ashed again at 500°C for 20 minutes. After the sample had cooled, 2 ml concentrated HCL and 15 ml H_2O were added. Samples were boiled and stored in 50-ml volumetric flasks. Final determinations were made with a Perkin-Elmer model 303 spectrophotometer.

PRESENTATION OF RESULTS

The Denver Wildlife Research Center (DWRC) was contracted to conduct the initial analyses and the Wisconsin Alumni Research Foundation (WARF) was contracted to conduct cross-check analyses on selected samples. Also, DWRC conducted a methods check by repeating the analyses on several samples for all 3 years. Samples for cross-checking were selected according to results of initial analysis or the history of high residues at a particular station. A level of 0.5 mg/kg or greater was the criterion generally applied for selection. Mercury, arsenic, lead, and cadmium were analyzed in the samples from 1971, and selenium was added in 1972. In 1973, the rising costs of analytical work precluded the measurement of all metals. Therefore, only selected samples were analyzed for mercury, arsenic, lead, and cadmium, but all samples were analyzed for selenium residues to provide data for 2 consecutive years, 1972 and 1973. The initial and the cross-check data for 1971–73 are presented in Tables 1-3. Results of the initial run and of the in-house rerun by DWRC varied by less than one order of magnitude. For this reason and for a degree of brevity, rerun results are not presented.

The National Academy of Sciences recommends that to protect fish and predatory aquatic organisms, total mercury burdens in these organisms should not exceed 0.5 mg/kg net weight (*12*). For the present purposes, authors have considered that any level exceeding 0.5 mg/kg in whole body components is a high level at which mercury, arsenic, lead, cadmium, or selenium would harm fish. To show annual trends for these elements in all fish, each residue value from the initial analyses was placed into at least one of the following categories: composites analyzed, composites with residues, composites with residues at or below detectable levels, composites with residues between detectable levels and 0.5 mg/kg, or composites with residues above 0.5 mg/kg (Table 4).

Results

Mercury residues were present in all samples of fish collected (Tables 1-3). Of the 100 stations sampled, 25 in 1971, 12 in 1972, and 11 in 1973 yielded composites in which mercury concentrations exceeded 0.5 mg/kg. Henderson et al. (5) reported composites exceeding 0.5 mg/kg from 9 stations in 1969 and 20 in 1970. Only stations 1-50 were sampled in 1969. These data indicate a general increase of mercury contamination from 1969 to 1971 and a decrease from 1971 to 1973.

Henderson et al. (5) also pointed out that certain predator fishes such as bass, perch, and squawfish had the highest mercury residues. Of 12 species in the present study in which mean residues exceeded 0.5 mg/kg during any of the 3 years, 7 were predators: chain pickerel, white perch, smallmouth bass, largemouth bass, whitebass, sauger, and Northern squawfish; and 5 could be considered nonpredator, i.e., nonpiscivorous: bowfin, carp, yellow and brown bullhead, and channel catfish.

Residues of mercury, arsenic, and selenium were generally present in more than 90 percent of samples in the present study (Table 4); lead was detected in 56 percent and cadmium in 76 percent of the 584 composites analyzed in 1971.

Arsenic residues (Tables 1-3) were generally lower than those of mercury; concentrations in mg/kg ranged up to 3.40 in 1971, 1.70 in 1972, and 1.24 in 1973. Residues in excess of 0.5 mg/kg were detected in composites from eight stations during the 3 years. Unlike mercury residues, arsenic residues above 0.5 mg/kg were not confined to the predatory fishes.

Lead residues above 0.5 mg/kg were present in fish from 16 stations in 1971, 34 stations in 1972, and 10 stations in

1973 (Tables 1-3). The highest concentrations in mg/kg were detected in fish from the Hawaiian streams: 1.4 in 1971, 5.2 in 1972, and 1.4 in 1973. Like arsenic residues, lead residues above 0.5 mg/kg were not confined to the predatory fishes.

Composites with cadmium residues above 0.5 mg/kg were few in 1971 (less than 1 percent) and 1972 (4 percent), and, of the 75 selected samples analyzed in 1973, none exceeded 0.5 mg/kg (Table 4). This suggests a decrease in the level of detectable residues of this metal, particularly since authors biased these results by selecting the samples to be analyzed during 1973 from stations at which residues in some samples exceed 0.5 mg/kg during 1972. Like lead and arsenic, cadmium residues above 0.5 mg/kg are not restricted to the predatory fishes. Cadmium is an extremely dangerous metal that accumulates readily in fish, has chronic effects, and is considered a threat to fishery resources (*12*).

The selenium analyses conducted only in 1972 and 1973 showed residues in essentially all samples (Table 4). Residues exceeding 0.5 mg/kg were distributed equally between predatory and nonpredatory fishes. Naturally occurring selenium has been detected in various environmental segments, but the biological significance of selenium residues is unknown (*12*).

Excessive levels of metals, greater than 0.5 mg/kg, were found in some fish from most river systems, but such high levels apparently occurred more frequently in certain stations than in others. Of the 11 stations with excessive mercury levels in 1973, 6 were from the Atlantic coastal streams (one each on the Stillwater and Kennebec Rivers, Maine; Merrimac River, Mass.; Pee Dee River, S. C.; Savannah and Altamaha Rivers, Ga.); 1 on the Gulf coastal streams (Tombigbee River, Ala.); 1 on the Mississippi River system (Little River, Minn.); 3 on the Columbia River system (1 on the Willamette and 2 on the Columbia River). Of those 11 stations, 6 exceeded 0.5 mg/kg during 1972 and 1973 and 3 (Kennebec River, Maine; Savannah River, Ga.; Tombigbee River, Ala.) had residues that exceeded 0.5 mg/kg during all the years reported. McKim, who was quoted in a paper by Olson et al. (*14*), exposed brook trout to methyl-mercuric chloride and determined residues in muscle tissue to be within 90-100 percent of those in the whole body. This suggests that not only should the fish and their predators be protected, but that fish from some rivers should not be consumed by humans.

Olson et al. (*14*) exposed fathead minnows (*Pimephales promelas*) to concentrations of methylmercury ranging from 0.018 to 0.247 mg/liter. After 48 weeks, analysis of whole body samples showed mean residues ranging from 1.47 to 10.9 mg/kg total mercury. For the most part, these residues exceed levels of the present study. However, fish from the control water of Olson's experiment, in which no methylmercury was added and residues averaged <0.01 ppm, had mean residues of 0.21 mg/kg (95 percent confidence interval, 0.17 to 0.25 mg/kg); water used in the experiment was unfiltered water from Lake Superior. In 1973, residues in samples from Lake Superior, Bayfield, Wis., ranged from 0.09 to 0.40 mg/kg. Olson et al. (*14*) point out the potential significance of low concentrations of mercury in natural waters. In a biochemical evaluation of methylmercuric chloride, Christensen (*2*) showed only a decrease in glutamic oxaloacetic transaminase (GOT) activity (L-aspartate: 2-oxoglutarate aminotranslerase, EC 2.6.1.1.) in brook trout embryos, and a decrease in weight and an increase in GOT activity in alevins. He further concluded that the concentrations used (1.03 μg/liter) in the study would be unsafe for the species if exposure were extended from egg through adult. These laboratory studies combined with residue data in the present study suggest that the health of many species collected is in danger.

Arsenic levels exceeding 0.5 mg/kg were found in fish from five stations (Tombigbee River, Ala.; Lake Michigan; Lake Superior; Red River, Okla.); those from the Great Lakes had high residues more frequently than the others. A study by the National Academy of Sciences and National Academy of Engineering showed residues up to 100 mg/kg in shellfish; sea water normally contains 2 to 3 μg /liter (*12*). Authors point out that acute effects of arsenic have been investigated, but little is known about sublethal chronic effects except that arsenic is readily accumulated by marine organisms (*12*).

Geographic distribution of high levels of lead appears to have decreased between 1972 and 1973. For instance, of the 14 stations located from the Stillwater River, Maine, south to the Pee Dee River (Northern Atlantic coastal streams), 9 exceeded 0.5 mg/kg in 1972 and 4 exceeded 1.0 mg/kg in 1973. Only 5 of the 14 stations had concentrations exceeding 0.5 mg/kg and none had composites with residues above 1.0 mg/kg. On the Mississippi River system in 1972, 13 of 35 stations had composites with residues above 0.5 mg/kg; 6 of those exceeded 1.0 mg/kg and 1 exceeded 5.0 mg/kg. In 1973, only 1 station, Des Moines River, Iowa, exceeded 0.5 mg/kg. This trend generally prevailed where excessive lead residues were found in 1972. There are, however, two stations that do not follow this encouraging trend. In 1973, fish from the Columbia River at Grand Coulee, Wash., and Manoa Stream, Hawaii, had composites with residues of 1.0 mg/kg and 1.4 mg/kg, respectively. The former represents an increase and the latter represents only a slight decrease. The source of these residues should be investigated.

As indicated earlier, results of the in-house methods check by DWRC corresponded closely with the study each year; data are not included in this report. The in-house methods check represents the quality control of the laboratory and shows that the data presented are accurate

and can be interpreted within the limits of the methods used. Validity of the present findings is further enhanced by the fact that the cross-check data are from another laboratory which used slightly different techniques, yet agree closely with data here. Furthermore, examination of the results between replicated samples at one station also indicates that the residues are representative of environmental levels.

NAS and NAE have stated, ". . . at present, it is not possible to predict accurately the amount of total metal in any environment that may be lethal, biologically active or contributory to toxicity . . ." (*12*). Authors submit that the data presented in this program are indicative of environmental levels of arsenic, lead, cadmium, and water with a wide variation in such characteristics as hardness and pH, and that criteria should be established for each metal and water. For an update on the effects of pollution on fish, authors recommend an excellent review by McKim et al. (*11*) which includes chemical and biological methodology used, the effects of water quality, pesticides, industrial pollutants, including metals, and domestic and radioactive wastes.

Residues in river fish analyzed in the present study are based on wet weight, whole fish. The concentrations of residues in the edible portions would probably be lower.

Acknowledgments

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LITERATURE CITED

(*1*) *American Fisheries Society 1970.* A list of common and scientific names of fishes from the United States and Canada. Spec. Publ. No. 6. Washington, D. C. 149 pp.

(*2*) *Christensen, G. M. 1975.* Biochemical effects of methylmercuric chloride, cadmium chloride and lead nitrate on embryos and alevins of the brook trout, *Salvelinus fontinalis*. Toxicol. Appl. Pharmacol. 32:191-197.

(*3*) *Church, M. R., and W. H. Robison. 1974.* A rapid, routine absorption spectrometry method for the determination of selenium at sub-microgram levels in animal tissue. Int. J. Environ. Anal. Chem. 3(1):323-331.

(*4*) *Henderson, C., A. Inglis, and W. L. Johnson. 1971.* Organochlorine insecticide residues in fish—fall 1969 (National Pesticide Monitoring Program). Pestic. Monit. J. 5(1):1-11

(*5*) *Henderson, C., A. Inglis, and W. L. Johnson. 1972.* Mercury residues in fish, 1969-1970—National Pesticide Monitoring Program. Pestic. Monit. J. 6(3):144-159.

(*6*) *Henderson, C., W. L. Johnson, and A. Inglis. 1969.* Organochlorine insecticide residues in fish (National Pesticide Monitoring Program). Pestic. Monit. J. 3(3):145-171.

(*7*) *High Sensitivity Arsenic Determination by Atomic Absorption. 1971.* Jarrell-Ash Applications Laboratory, Jarrell-Ash. Co., Waltham, Mass. 5 pp. mimeograph.

(*8*) *Horwitz, W., ed. 1970.* Official methods of analysis, 11th ed. Association of Official Analytical Chemists, Washington, D.C. 1015 pp.

(*9*) *Horwitz, W., ed. 1975.* Official methods of analysis, 12th ed. Association of Official Analytical Chemists, Washington, D.C. 1094 pp.

(*10*) *Joint Mercury Residues Panel Report. 1961.* Analyst 86 (1026):608–614.

(*11*) *McKim, J. M., D. A. Benoit, K. E. Biesinger, W. A. Brungs, and R. E. Siefert. 1975.* Effects of pollution on freshwater fish. J. Water Pollut. Control Fed. 47(6):1711-1768.

(*12*) *National Academy of Sciences, National Academy of Engineering. 1972.* Section III—Freshwater aquatic life and wildlife, and Section IV—Marine aquatic life and wildlife. Pages 106-296 *in* Water Quality Criteria. Ecological Research Series. EPA-R3-73-033 March 1973. NAS, Washington, D.C.

(*13*) *Okuno, I., R. A. Wilson, and R. E. White. 1972.* Determination of mercury in biological samples by flameless atomic absorption after combustion and mercury-silver amalgamation. J. Assoc. Offic. Anal. Chem. 55(1):96-100.

(*14*) *Olson, G. F., D. I. Mount, V. M. Snarski, and T. W. Thorslund. 1975.* Mercury residues in fathead minnows, *Pimephales promelas* Rafin., chronically exposed to methylmercury in water. Bull. Environ. Contam. Toxicol. 14(2):129-134.

TABLE 1. *Concentrations of mercury, arsenic, lead, and cadmium in whole fish, 1971—National Pesticide Monitoring Program*

Station Number and Location	Species	No. Fish	Average Size		Residues, mg/kg wet weight			
			Length, in.	Weight, lb	Mercury	Arsenic	Lead	Cadmium
Atlantic Coast Streams								
1 Stillwater River	White sucker	5	12.5	0.8	0.20	<0.05	0.26	<0.05
Old Town, Maine	White sucker (R)	5	12.5	0.8	0.28	<0.05	ND	<0.05
	Yellow perch	5	7.5	0.2	0.32	<0.05	ND	<0.05
	Yellow perch (R)	5	7.9	0.2	0.32	<0.05	0.26	0.05
	Chain pickerel	5	15.1	0.7	0.35	<0.05	0.16	<0.5
					(0.45)	(<0.05)	(<0.2)	(<0.05)
	Chain pickerel (R)	5	15.0	0.7	0.39	<0.05	ND	ND
51 Kennebec River	White sucker	5	12.7	0.8	0.18	<0.05	ND	<0.05
Hinckley, Maine	White sucker (R)	5	13.8	0.9	0.18	0.05	ND	ND
	Yellow perch	5	10.3	0.5	0.50	<0.05	ND	<0.05
					(0.83)	(<0.05)	(0.4)	(<0.05)
	Yellow perch (R)	5	9.1	0.3	0.50	<0.05	ND	ND
	Smallmouth bass	5	13.0	1.1	0.46	<0.05	0.21	ND
	Smallmouth bass (R)	2	14.4	1.4	1.20	<0.05	ND	<0.05
					(1.88)	(<0.05)	(0.5)	(<0.05)
52 Lake Champlain	Pumpkinseed	5	7.3	0.4	0.12	0.10	ND	<0.05
Burlington, Vt					(0.23)	(0.08)	(0.4)	(<0.05)
	Pumpkinseed (R)	5	6.9	0.3	0.18	<0.05	0.78	ND
	Yellow perch	5	8.9	0.3	0.37	<0.05	0.57	<0.05
					(0.31)	(<0.05)	(0.7)	(0.06)
	Yellow perch (R)	5	10.0	0.4	0.31	<0.05	ND	ND
	Chain pickerel	3	16.2	1.0	0.39	0.05	0.13	<0.05
	Chain pickerel (R)	2	13.8	0.7	0.34	<0.05	0.11	<0.05
53 Merrimac River	White sucker	5	12.0	0.7	0.15	<0.05	0.36	<0.05
Lowell, Mass								
	White sucker (R)	5	11.1	0.5	0.46	<0.05	0.36	<0.05
	Pumpkinseed	5	6.2	0.2	0.38	<0.05	0.24	ND
	Pumpkinseed (R)	5	4.4	0.1	0.42	<0.05	0.16	ND
	Yellow perch	5	10.7	0.6	0.14	<0.05	ND	ND
	Yellow perch (R)	5	10.7	0.6	0.42	<0.05	ND	ND
2 Connecticut River	White catfish	5	12.1	0.8	0.17	0.04	0.41	0.14
Windsor Locks, Conn	White catfish (R)	5	12.9	1.1	0.21	0.06	0.51	0.17
	Yellow perch	5	8.8	0.3	0.25	<0.05	0.20	<0.05
	Yellow perch (R)	5	10.0	0.6	0.20	<0.05	0.12	<0.05
	White perch	4	8.6	0.4	0.38	<0.05	0.23	0.39
	White perch (R)	4	10.0	0.6	0.44	0.05	0.15	<0.05
3 Hudson River	Goldfish	5	9.4	0.8	0.06	0.11	1.30	0.12
Poughkeepsie, N.Y.	Goldfish (R)	5	9.9	0.8	0.19	0.08	0.52	0.15
	Pumpkinseed	5	6.1	0.1	0.13	0.07	ND	<0.05
	Pumpkinseed (R)	5	6.0	0.2	0.07	0.05	0.12	<0.05
	Largemouth bass	5	10.9	0.9	0.19	<0.05	ND	<0.05
	Largemouth bass (R)	5	10.8	0.9	0.10	0.05	ND	<0.05
54 Raritan River	Golden shiner	5	7.6	0.2	0.12	0.10	0.13	<0.05
Highland Park, N.J.	Golden shiner (R)	6	6.3	0.1	0.26	0.10	ND	<0.05
	White sucker	5	13.4	1.2	0.11	0.08	0.32	0.10
	White sucker (R)	5	12.3	1.0	0.18	<0.05	0.24	0.05
	White perch	5	9.7	0.7	0.34	0.08	0.16	<0.05
	White perch (R)	5	9.6	0.6	0.32	0.07	ND	<0.05
4 Delaware River	White sucker	5	14.6	1.3	0.06	0.06	0.51	0.06
Camden, N.J.	White sucker (R)	5	13.9	1.2	0.06	0.05	0.54	<0.05
	Brown bullhead	5	11.7	0.8	0.12	0.06	0.38	<0.05
	Brown bullhead (R)	5	10.9	0.7	0.04	0.06	0.36	<0.05
					(0.05)	(0.06)	(0.45)	(<0.05)
	White perch	5	9.5	0.5	0.25	0.06	0.78	<0.05
	White perch (R)	5	9.8	0.6	0.20	<0.05	0.47	<0.05
5 Susquehanna River	Carp	4	18.0	3.0	0.12	0.09	0.12	ND
Conowingo Dam, Md.	Carp (R)	4	18.9	3.3	0.05	0.20	ND	0.10
	Channel catfish	5	15.2	1.1	0.04	0.07	0.14	<0.05
	Channel catfish (R)	5	15.4	1.3	0.02	0.06	0.17	<0.05
	Yellow perch	5	8.6	0.3	0.08	0.06	ND	<0.05
	Yellow perch (R)	5	8.4	0.3	0.10	0.08	ND	<0.05
6 Potomac River	Carp	5	17.2	2.6	0.26	0.13	0.11	0.08
Little Falls, Md.	Carp (R)	5	15.7	2.0	0.19	0.11	0.21	0.11
	Redhorse[1]	5	13.5	1.0	0.18	<0.05	ND	0.06
	Redhorse (R)	5	14.7	1.2	0.15	0.06	ND	0.09
	Smallmouth bass	5	14.1	1.4	0.32	<0.05	ND	ND
	Smallmouth bass (R)	4	10.2	0.5	0.14	<0.05	ND	0.05
55 James River	Redhorse sucker	2	16.5	1.8	0.15	0.05	ND	ND
Richmond, Va.	Redhorse sucker (R)	2	16.0	1.6	0.10	<0.05	ND	0.23
	Channel catfish	2	21.5	3.6	0.23	<0.05	ND	0.05
	Channel catfish (R)	2	17.0	1.4	0.11	<0.05	ND	ND
	Largemouth bass	5	11.6	0.9	0.24	<0.05	ND	ND
	Largemouth bass (R)	5	8.6	0.3	0.23	<0.05	ND	ND

(*Continued next page*)

TABLE 1 (cont'd.) *Concentrations of mercury, arsenic, lead, and cadmium in whole fish, 1971 —National Pesticide Monitoring Program*

Station Number and Location	Species	No. Fish	Average Size		Residues, mg/kg wet weight			
			Length, in.	Weight, lb.	Mercury	Arsenic	Lead	Cadmium
7 Roanoke River Roanoke Rapids, N.C.	Redhorse	4	18.7	2.5	0.13	< 0.05	ND	ND
	Redhore (R)	4	19.8	2.9	0.12	< 0.05	ND	0.17
	Brown bullhead	3	9.7	0.3	0.06	< 0.05	ND	ND
	Largemouth bass	5	10.5	0.7	0.14	0.10	ND	0.06
	Largemouth bass (R)	5	9.3	0.5	0.11	0.06	ND	ND
8 Cape Fear River Elizabethtown, N.C.	Gizzard shad	5	8.7	0.2	0.10	0.09	0.20	< 0.05
	Gizzard shad	5	10.0	0.4	0.10	0.05	0.35	< 0.05
	Brown bullhead	5	9.5	0.3	0.14	< 0.05	0.10	ND
	Brown bullhead (R)	5	9.6	0.3	0.22	< 0.05	0.13	< 0.05
	Largemouth bass	3	11.1	0.6	0.46	0.09	0.15	ND
56 Pee Dee River Dongola, S.C.	White catfish	5	14.5	1.6	0.33	< 0.05	ND	0.06
	White catfish (R)	5	14.9	2.0	0.36	0.05	ND	< 0.05
	Bluegill	4	5.5	0.2	0.04	0.09	0.21	< 0.05
	Bluegill (R)	4	5.0	0.1	ND	ND	ND	ND
	Bowfin	4	18.5	2.5	1.03	0.20	ND	ND
	Bowfin (R)	4	17.6	2.1	0.43	0.22	ND	ND
9 Cooper River Summerton, S.C.	Carp	2	23.2	6.8	0.04	0.08	ND	< 0.05
	Carp (R)	2	23.5	7.3	0.29	0.05	0.11	ND
	Bluegill	5	6.5	0.2	0.12	0.05	ND	ND
	Bluegill (R)	5	6.2	0.2	0.08	0.12	ND	ND
	Largemouth bass	5	11.0	0.6	0.05	0.05	0.23	< 0.05
	Largemouth bass (R)	5	11.2	0.8	0.12	0.05	0.21	ND
10 Savannah River Savannah Ga.	Carp	2	20.3	4.1	ND (< 0.05)	< 0.05 (< 0.05)	0.14 (0.3)	< 0.05 (< 0.05)
	Carp (R)	2	20.9	4.4	0.36 (0.41) < 0.05 (< 0.05)	ND (< 0.2)	ND (< 0.05)	
	Bluegill	2	11.2	1.0	0.44 (0.54)	< 0.05 (0.12)	ND (0.8)	0.50 (< 0.05)
	Bluegill (R)	3	8.8	0.6	0.10 (0.28)	0.06 (0.10)	0.21 (0.3)	< 0.05 (< 0.05)
	Largemouth bass	3	10.9	1.0	0.60 (0.72)	0.06 (< 0.05)	ND (< 0.2)	ND (< 0.05)
	Largemouth bass (R)	4	10.9	0.7	0.34	< 0.05	ND	ND
57 Altamaha River Doctortown, Ga.	Spotted sucker	4	17.2	2.2	0.23	0.06	0.16	0.12
	Spotted sucker (R)	4	18.2	2.7	0.22	0.06	ND	0.10
	Bluegill	5	7.6	0.4	0.12	0.09	ND	ND
	Bluegill (R)	5	7.4	0.4	0.12	0.09	ND	ND
	Largemouth bass	4	13.4	1.3	0.36	< 0.05	ND	ND
	Largemouth bass (R)	4	12.2	1.1	0.43	< 0.05	ND	< 0.05
11 St. Johns River Welaka Fla.	Striped mullet	2	21.3	3.1	ND	0.34	0.15	< 0.05
	Striped mullet (R)	3	19.1	3.1	ND	0.26	ND	0.05
	Channel catfish	5	10.7	0.4	0.02	< 0.05	ND	ND
	Channel catfish	4	11.1	0.4	ND	< 0.05	ND	ND
	Largemouth bass	3	17.1	2.9	0.64	0.06	ND	ND
	Largemouth bass (R)	3	15.4	2.3	0.10	0.05	ND	< 0.05
12 St. Lucie Canal Indiantown Fla.	Channel catfish	3	16.6	1.8	0.09	< 0.05	ND	ND
	Channel catfish (R)	2	21.8	3.8	0.13	< 0.05	ND	0.06
	Bluegill	4	6.5	0.2	0.04	0.06	ND	ND
	Bluegill (R)	4	6.4	0.2	0.07	0.09	ND	ND
	Largemouth bass	4	11.5	1.2	0.26	0.08	ND	ND
	Largemouth bass (R)	4	12.4	1.2	0.32 0.35	0.10 0.09	0.13 ND	< 0.05 0.05
			Gulf Coast Streams					
5 Suwannee River Old Town Fla.	Spotted sucker	4	12.5	1.0	0.15	0.05	ND	< 0.05
	Spotted sucker (R)	4	13.8	1.4	0.22	< 0.05	ND	< 0.05
	Redbreast sunfish	5	7.6	0.2	0.17	< 0.05	ND	< 0.05
	Redbreast sunfish (R)	5	7.9	0.3	0.12	0.05	ND	< 0.05
	Largemouth bass	4	13.4	1.6	0.42	0.22	ND	ND
	Largemouth bass (R)	4	12.1	1.4	0.76	0.05	ND	< 0.05
4 Apalachicola R. Fort Woodruff, Fl. Fla.	Spotted sucker	3	15.6	2.1	0.15	0.10	ND	< 0.05
	Channel catfish	3	10.8	0.7	0.06	0.05	ND	ND
	Channel catfish (R)	3	9.7	0.5	0.06	0.05	ND	ND
	Largemouth bass	4	10.0	0.5	0.09	0.07	ND	ND
	Largemouth bass (R)	4	9.4	0.4	0.09	0.09	ND	ND
Apalachicola River Chattahoochee Fla.	[illegible]	4	16.1	2.0	0.02	0.24	ND	< 0.05
	[illegible] (R)	4	15.0	1.7	0.19	0.16	0.12	< 0.05
	[illegible]	5	8.0	0.4	0.08	0.05	0.14	< 0.05
	[illegible]	5	7.6	0.4	0.16	0.05	ND	ND
	[illegible]	4	17.1	3.2	0.59	0.07	ND	0.10
	[illegible]	5	16.6	2.6	0.09	0.07	ND	< 0.05

(Continued next page)

TABLE 1 (cont'd.). *Concentrations of mercury, arsenic, lead, and cadmium in whole fish, 1971 —National Pesticide Monitoring Program*

Station Number and Location	Species	No. Fish	Average Size		Residues, mg/kg wet weight			
			Length, in	Weight, lb	Mercury	Arsenic	Lead	Cadmium
14. Tombigbee River McIntosh, Ala	Carp	3	19.7	3.9	0.10	0.07	ND	< 0.05
	Carp (R)	3	19.6	3.8	0.42	0.11	ND	ND
	Striped mullet	3	15.8	1.9	0.07	0.50	ND	ND
	Striped mullet (R)	3	15.6	1.8	0.30	0.70	0.13	0.05
	Largemouth bass	4	15.7	2.0	1.10	0.13	ND	0.05
	Largemouth bass (R)	5	14.7	1.6	1.10	0.09	ND	ND
15. Mississippi River Luling, La	Carp	3	14.2	2.1	0.04	0.08	0.15	< 0.05
	Carp (R)	3	14.4	1.9	0.02	0.07	ND	< 0.05
	Bigmouth buffalo	3	18.6	4.8	0.11	0.07	0.22	0.06
	Bigmouth buffalo (R)	3	19.2	4.9	0.15	0.12	0.23	0.05
	Channel catfish	3	14.2	1.3	0.07	0.05	0.30	< 0.05
	Channel catfish (R)	3	15.7	1.8	0.12	0.05	0.37	< 0.05
60. Brazos River Richmond, Tex	Smallmouth buffalo	2	21.4	7.0	0.17	0.07	0.13	< 0.05
	Smallmouth buffalo (R)	3	19.1	4.0	0.09	0.06	0.19	< 0.05
	Blue catfish	3	14.3	1.6	0.09	< 0.05	0.26	< 0.05
	Longnose gar	3	25.1	1.6	0.34	< 0.05	ND	ND
	Spotted gar	3	22.4	2.1	0.44	0.05	0.10	< 0.05
61. Colorado River Wharton, Tex	River carpsucker	5	11.8	1.1	0.16	0.06	0.21	< 0.05
	River carpsucker (R)	5	14.3	1.4	0.11	0.07	0.17	ND
	Channel catfish	3	15.5	1.0	0.05	< 0.05	0.13	< 0.05
	Flathead catfish	3	22.5	4.7	0.30	ND	0.10	< 0.05
	Longnose gar	3	26.1	1.7	0.24	ND	0.14	< 0.05
	Longnose gar (R)	3	24.2	1.6	0.31	0.05	0.12	< 0.05
62. Nueces River Mathis, Tex	Gizzard shad	6	9.7	0.4	0.06	0.10	0.10	< 0.05
	Gizzard shad (R)	6	7.3	0.2	0.02	0.16	0.15	< 0.05
	Blue catfish	6	12.8	0.6	0.11	< 0.05	0.13	< 0.05
	Blue catfish (R)	6	11.3	0.4	0.10	< 0.05	0.16	< 0.05
	Black crappie	6	7.0	0.3	0.06	0.16	< 0.10	< 0.05
	White crappie	6	8.7	0.3	0.13	0.14	0.11	< 0.05
16. Rio Grande Brownsville, Tex.	Gizzard shad	3	9.6	0.3	0.02	0.32	0.20	< 0.05
					(0.06)	(0.43)	(0.5)	(0.06)
	Gizzard shad (R)	3	10.6	0.4	0.15	0.23	0.10	ND
	Channel catfish	3	13.4	1.1	0.10	< 0.05	0.24	ND
	Channel catfish (R)	3	11.9	0.6	0.11	< 0.05	0.26	ND
	Blue catfish	3	13.5	1.4	0.11	0.12	0.26	ND
	Blue catfish (R)	3	13.0	1.1	0.11	< 0.05	0.44	ND
					(0.08)	(0.06)	(0.5)	(< 0.05)
63. Rio Grande Elephant Butte, N. Mex	Channel catfish	6	13.2	1.3	0.48	< 0.05	ND	< 0.05
	White bass	2	15.8	2.0	0.58	0.24	ND	< 0.05
	White bass (R)	3	16.2	2.0	0.68	0.14	ND	ND
	Longear sunfish	5	4.9	0.1	0.03	0.22	ND	< 0.05
	Largemouth bass	2	16.9	2.8	0.68	0.15	ND	< 0.05
	Largemouth bass (R)	2	16.6	2.7	0.53	0.11	ND	ND
64. Rio Grande Alamosa, Colo	Carp	3	10.1	0.5	0.02	< 0.05	0.27	< 0.05
	Carp (R)	3	10.4	0.5	0.30	0.06	0.14	ND
	White sucker	5	8.0	0.2	0.04	0.06	0.22	< 0.05
	White sucker (R)	3	10.7	0.5	0.04	0.07	0.35	< 0.05
	Brown trout	3	13.6	0.9	0.07	< 0.05	0.20	ND
	Brown trout (R)	3	12.7	0.6	0.21	< 0.05	0.19	< 0.05
65. Pecos River Red Bluff Lake, Tex	Gizzard shad	5	7.4	0.2	< 0.01	0.08	0.11	< 0.05
	Gizzard shad (R)	4	9.2	0.3	0.04	0.28	ND	ND
	Smallmouth buffalo	3	14.7	1.2	0.16	0.16	0.12	< 0.05
	Smallmouth buffalo (R)	3	14.8	1.5	0.18	0.06	0.12	< 0.05
	Channel catfish	3	15.8	1.3	0.06	< 0.05	ND	< 0.05
	Channel catfish (R)	3	17.3	1.8	0.17	< 0.05	ND	< 0.05
17. Genessee River Scottsville, N.Y	White sucker	5	14.4	1.1	0.14	0.06	< 0.10	< 0.05
	White sucker (R)	4	14.1	1.0	0.16	0.08	0.10	< 0.05
	Rock bass	5	8.0	0.4	0.32	< 0.05	0.30	< 0.05
	Rock bass (R)	5	7.5	0.4	0.28	0.05	< 0.10	ND
	Walleye	5	19.3	3.0	0.64	0.08	0.10	< 0.05
	Walleye (R)	5	13.4	0.9	0.28	0.11	0.12	ND
66. St. Lawrence River Massena, N.Y	White sucker	5	13.9	1.1	0.12	0.05	0.14	ND
	White sucker (R)	5	14.1	1.2	0.11	0.05	0.21	ND
	Yellow perch	5	9.2	0.3	0.36	0.06	0.10	ND
	Yellow perch (R)	5	8.4	0.2	0.23	< 0.05	0.19	ND
	Smallmouth bass	5	12.2	0.9	0.34	0.28	ND	ND
	Smallmouth bass (R)	5	12.1	0.9	0.38	0.34	ND	ND
18. Lake Ontario Port Ontario, N.Y N.Y	Yellow perch	5	11.4	0.8	0.65	0.15	0.20	< 0.05
					(0.58)	(0.18)	(0.4)	(< 0.05)
	Yellow perch (R)	5	11.3	0.8	0.50	0.10	0.16	ND
	White perch	5	10.0	0.6	0.36	0.14	0.85	< 0.05
	White perch (R)	5	9.6	0.6	0.46	0.14	1.40	< 0.05
					(0.56)	(0.31)	(0.4)	(< 0.05)
	Rock bass	5	8.3	0.5	0.45	0.10	ND	ND
					(0.45)	(0.12)	(0.4)	(< 0.05)
	Rock bass (R)	5	8.4	0.6	0.52	0.10	0.51	< 0.05
					(0.48)	(0.14)	(0.4)	(< 0.05)

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TABLE 1 (cont'd.). *Concentrations of mercury, arsenic, lead, and cadmium in whole fish, 1971 —National Pesticide Monitoring Program*

Station Number and Location	Species	No. Fish	Average Size		Residues, mg/kg wet weight			
			Length, in	Weight, lb	Mercury	Arsenic	Lead	Cadmium
19 Lake Erie	White sucker	5	14.6	1.3	0.13	0.11	ND	ND
Erie, Pa.	White sucker (R)	5	14.4	1.4	0.14	0.16	0.18	0.06
	Freshwater drum	5	13.3	1.1	0.29	0.11	0.20	<0.05
	Freshwater drum (R)	5	13.3	1.3	0.13	0.09	0.20	<0.05
	Yellow perch	5	9.5	0.5	0.09	<0.05	ND	<0.05
	Yellow perch (R)	5	9.0	0.4	0.13	<0.05	0.12	<0.05
20 Lake Huron	Carp	4	16.7	2.4	0.02	<0.05	ND	<0.05
Bay Port, Mich.	Carp (R)	4	17.7	2.7	0.04	0.08	0.15	<0.05
	Channel catfish	5	17.0	1.6	0.11	0.12	ND	<0.05
	Channel catfish (R)	5	17.3	1.7	0.12	0.16	0.11	<0.05
	Yellow perch	5	9.4	0.4	0.04	<0.05	0.11	ND
	Yellow perch (R)	5	9.1	0.3	0.02	<0.05	ND	ND
21 Lake Michigan	Bloater	3	9.5	0.5	0.07	2.80	0.54	<0.05
Sheboygan, Wis.	Bloater (R)	2	9.3	0.4	0.13	3.40	ND	<0.05
	Lake trout	5	26.0	6.4	0.52	1.00	ND	<0.05
	Lake trout (R)	5	25.1	6.6	0.49	1.30	0.10	0.05
	Yellow perch	5	9.8	0.3	0.16	0.07	0.15	ND
	Yellow perch (R)	3	9.6	0.3	0.15	0.07	0.13	ND
22 Lake Superior	Bloater	5	8.5	0.5	0.20	0.80	1.00	<0.05
Bayfield, Wis.	Bloater (R)	5	8.4	0.4	0.13	0.90	0.31	0.09
	Lake whitefish	5	19.7	2.4	0.01	0.60	0.13	<0.05
	Lake whitefish (R)	5	20.0	2.8	0.09	0.60	ND	0.20
	Lake trout	5	19.0	3.2	0.42	0.27	ND	<0.05
	Lake trout (R)	4	22.0	4.4	0.46	0.27	ND	<0.05
67 Allegheny River	Carp	4	16.4	1.9	0.04	<0.05	0.30	0.07
Natrona, Pa.	Carp (R)	4	18.8	3.8	0.12	0.06	0.13	0.07
	Yellow perch	4	9.6	0.5	0.27	<0.05	0.14	<0.05
					(0.10)	(<0.05)	(0.4)	(<0.05)
	Yellow perch (R)	5	7.9	0.2	0.08	ND	ND	<0.05
					(0.08)	(<0.05)	(0.7)	(<0.05)
	Walleye	4	12.4	0.7	0.19	<0.05	0.13	<0.05
	Walleye (R)	5	16.4	1.5	0.19	0.08	0.12	0.06
23 Kanawha River	Carp	5	11.3	0.9	0.01	<0.05	ND	ND
Winfield, W. Va.	Carp (R)	5	12.0	1.0	ND	<0.05	ND	ND
	Brown bullhead	5	10.9	0.8	0.08	<0.05	0.18	0.13
	Brown bullhead (R)	5	11.5	0.8	0.04	0.07	0.14	ND
	White crappie	5	9.2	0.5	0.09	<0.05	ND	<0.05
	White crappie (R)	5	9.2	0.05	0.14	<0.05	ND	ND
68 Wabash River	Carp	3	19.8	4.3	0.28	0.07	ND	0.12
New Harmony, Ind.	Carp (R)	3	19.2	3.5	0.25	0.07	ND	0.05
	Channel catfish	3	16.0	1.6	4.50	<0.05	0.16	<0.05
	Channel catfish (R)	3	17.7	1.9	0.29	<0.05	0.11	0.05
	White crappie	5	9.2	0.4	0.18	0.11	ND	<0.05
	White crappie (R)	5	9.5	0.4	0.16	0.08	ND	<0.05
24 Ohio River	Carp	2	19.1	3.9	0.14	0.52	0.34	0.08
Marietta, Ohio					(0.11)	(0.40)	(0.3)	(0.07)
	Carp (R)	2	14.0	1.4	0.15	0.28	0.40	0.09
	Channel catfish	4	14.8	1.1	0.19	<0.05	0.10	ND
	Channel catfish (R)	4	13.1	0.7	0.30	<0.05	0.28	<0.05
	Largemouth bass	4	12.6	1.5	0.25	0.11	0.12	<0.05
					(0.26)	(0.07)	(0.3)	(<0.05)
	Largemouth bass (R)	4	13.3	1.4	0.22	0.07	ND	ND
69 Ohio River	Carp	5	15.3	1.9	0.09	<0.05	0.28	0.08
[illegible], Ohio	Carp (R)	5	14.4	1.7	0.09	0.08	0.15	<0.05
	Channel catfish	4	14.5	1.3	0.17	ND	0.20	<0.05
	Channel catfish (R)	4	14.3	0.9	0.18	<0.05	0.16	<0.05
	Sauger	5	12.9	0.8	0.14	0.06	<0.10	<0.05
	Sauger (R)	5	12.7	0.7	0.13	0.07	<0.10	<0.05
70 [illegible]	Carp	4	18.4	3.6	0.23	0.25	ND	0.10
[illegible]	Carp (R)	4	17.3	2.8	0.12	0.25	0.13	0.12
	Channel catfish	5	14.1	0.9	0.18	0.22	0.29	<0.05
	Channel catfish (R)	5	14.6	1.0	0.14	0.17	0.14	<0.05
	White crappie	5	10.4	0.7	0.18	0.13	ND	0.30
	White crappie (R)	5	10.1	0.6	0.42	0.16	ND	<0.05
25 Cumberland	[illegible]	4	10.8	0.5	0.11	0.06	ND	<0.05
Clarksville	[illegible] (R)	4	9.5	0.4	0.05	<0.05	ND	<0.05
	[illegible] gill	4	5.5	0.1	0.09	ND	0.23	<0.05
	[illegible] (R)	4	6.0	0.1	0.04	<0.05	ND	<0.05
	[illegible] outh bass	2	9.6	0.6	0.10	0.10	ND	0.05

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TABLE 1 (cont'd.). *Concentrations of mercury, arsenic, lead, and cadmium in whole fish, 1971 —National Pesticide Monitoring Program*

Station Number and Location	Species	No. Fish	Average Size		Residues, mg/kg wet weight			
			Length, in.	Weight, lb	Mercury	Arsenic	Lead	Cadmium
71. Tennessee River	Carp	3	17.3	2.4	0.23	0.13	ND	<0.05
Savannah, Tenn.	Carp (R)	3	17.3	2.7	0.20	0.07	ND	<0.05
Tenn.	Channel catfish	3	13.4	0.8	0.28	0.10	ND	<0.05
	Channel catfish (R)	4	12.5	0.7	0.34	0.08	0.12	<0.05
	Largemouth bass	3	12.9	1.2	0.24	0.21	ND	<0.05
	Largemouth bass (R)	3	12.9	1.1	0.14	0.18	ND	0.07
72. Wisconsin River	Carp	3	18.7	3.4	0.25	0.05	<0.10	<0.05
Woodman, Wis.	Carp (R)	4	20.5	4.0	0.19	0.06	ND	<0.05
	Channel catfish	4	16.3	1.4	0.20	ND	0.10	<0.05
	Channel catfish (R)	4	17.4	1.6	0.66	<0.05	<0.10	<0.05
					(0.19)	(<0.05)	(0.2)	(<0.05)
	Sauger	4	11.3	0.4	0.55	<0.05	<0.10	<0.05
	Sauger (R)	4	13.9	1.0	1.10	<0.05	ND	ND
					(0.77)	(<0.05)	(0.3)	(<0.05)
	Smallmouth bass	4	10.8	0.7	0.06	<0.05	ND	ND
					(0.46)	(<0.05)	(<0.2)	(<0.05)
	Smallmouth bass (R)	4	14.6	1.7	0.99	<0.05	<0.10	<0.05
					(0.96)	(<0.05)	(<0.2)	(<0.05)
73. Des Moines River	Carp	5	12.5	0.9	0.01	<0.05	0.83	<0.05
Keosauqua, Iowa					(<0.05)	(<0.05)	(0.2)	(<0.05)
	Carp (R)	5	13.0	1.2	0.05	ND	0.32	<0.05
	Channel catfish	5	12.6	0.7	0.06	ND	0.11	ND
	Channel catfish (R)	5	13.0	0.7	0.05	ND	0.17	<0.05
	Walleye	5	13.6	0.8	0.16	<0.05	ND	ND
	Sauger	3	13.9	0.9	0.08	ND	0.11	<0.05
26. Illinois River	Carp	5	15.1	1.6	0.04	<0.05	ND	0.05
Beardstown, Ill.	Carp (R)	5	13.9	1.4	0.08	0.08	0.18	<0.05
	Bigmouth buffalo	3	16.4	3.0	0.06	0.13	ND	<0.05
	Bigmouth buffalo (R)	3	18.7	4.2	0.05	0.13	0.12	<0.05
	White crappie	4	8.9	0.4	0.08	0.16	ND	0.07
	White crappie (R)	4	9.4	0.5	0.05	0.18	ND	0.07
74. Mississippi River	White sucker	4	18.8	2.9	0.96	<0.05	ND	<0.05
Little Falls, Minn.	White sucker (R)	4	18.6	2.8	0.43	<0.05	ND	0.05
	Black bullhead	4	7.1	0.3	0.22	<0.05	0.10	<0.05
	Black bullhead (R)	4	7.0	0.3	0.26	<0.05	ND	ND
	Northern pike	3	18.2	1.4	0.42	<0.05	0.10	<0.05
	Northern pike	3	13.7	0.4	0.18	<0.05	ND	ND
27. Mississippi River	Carp	5	17.9	3.5	0.15	<0.05	0.53	<0.05
Guttenburg, Iowa	Carp (R)	5	19.5	4.4	0.18	<0.05	0.27	<0.05
	Bluegill	5	6.3	0.2	0.12	<0.05	0.30	ND
					(0.12)	(0.11)	(0.7)	(<0.05)
	Bluegill (R)	5	6.7	0.3	0.04	<0.05	0.15	<0.05
	Largemouth bass	5	13.8	2.0	0.26	<0.05	0.14	ND
	Largemouth bass (R)	5	13.2	1.9	0.33	<0.05	0.21	<0.05
75. Mississippi River	Carp	5	18.5	3.0	0.06	0.05	ND	<0.05
Cape Girardeau, Mo.	Carp (R)	5	18.6	3.2	0.15	0.07	0.22	0.08
	Channel catfish	5	16.0	1.2	0.12	<0.05	<0.10	<0.05
	White crappie	3	10.4	0.6	0.12	0.10	<0.10	<0.05
	White crappie (R)	2	11.8	1.2	0.10	0.16	ND	ND
76. Mississippi River	Carp	2	21.3	5.2	0.06	0.26	0.17	0.07
Memphis, Tenn.	Carp (R)	2	20.8	5.0	0.06	0.12	0.12	0.06
	Carpsucker	2	18.5	4.0	0.10	0.11	ND	<0.05
	Carpsucker (R)	2	17.0	2.8	0.08	0.37	0.13	<0.05
28. Arkansas River	Carp	2	16.9	2.1	0.09	0.05	ND	0.05
Pine Bluff, Ark.	Carp (R)	2	17.7	2.4	0.08	<0.05	ND	0.07
	Smallmouth buffalo	2	17.4	3.3	0.03	0.08	ND	<0.05
	Smallmouth buffalo (R)	2	18.3	3.5	0.14	0.33	ND	0.06
	Flathead catfish	2	19.4	2.8	0.16	<0.05	ND	0.06
	Flathead catfish (R)	2	21.6	4.8	0.48	<0.05	ND	0.05
29. Arkansas River	Carp	5	12.8	0.8	0.12	<0.05	<0.10	<0.05
Keystone Reservoir, Okla.	Carp (R)	5	14.6	1.4	0.08	0.13	0.13	<0.05
	Channel catfish	5	16.1	1.1	0.14	0.26	0.10	<0.05
	Channel catfish (R)	5	16.7	1.2	0.15	0.07	0.11	<0.05
	Bluegill	5	5.7	0.1	0.07	0.07	<0.10	ND
	Bluegill (R)	4	5.6	0.1	0.03	<0.05	<0.15	<0.05
77. Arkansas River	Carp	5	13.7	1.2	2.70	<0.05	0.13	<0.05
John Martin Reservoir,					(<0.05)	(<0.05)	(<0.2)	(<0.05)
Colo.	Carp (R)	5	13.5	1.2	0.04	<0.05	<0.10	ND
					(<0.05)	(<0.05)	(<0.2)	(<0.05)
	Channel catfish	4	15.0	1.3	0.05	<0.05	0.15	<0.05
	Channel catfish (R)	3	13.2	0.8	0.06	ND	0.26	<0.05
	Black bullhead	5	9.9	0.6	0.16	ND	0.16	<0.05
	Black bullhead (R)	3	9.2	0.4	0.11	ND	0.10	ND

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