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CONTENTS

Volume 9 June 1975 Number 1

BRIEF

DDT Residues in Starlings, 1974

Paul R. Nickerson [1] and Kyle R. Barbehenn [2]

ABSTRACT

In the preceding issue of this journal, the authors suggested that the mean level of DDT plus metabolites in starlings should drop below 0.1 ppm for the 1974 collection. They based their prediction on an analysis of the relationship between mean levels of DDT and its metabolites in starlings and estimates of domestic disappearance of DDT. The present brief summarizes initial findings from the 1974 starling collection. Authors indicate that their earlier estimates for disappearance of total DDT were optimistic: the geometric mean for 1974 was 0.282, a 36 percent reduction from the 1972 mean of 0.442.

Introduction

Based upon an analysis of the relationship between mean levels of DDT and its metabolites in starlings and estimates of domestic disappearance of DDT, authors suggested in the preceding issue of this periodical that the residue levels of these organochlorines in starlings should drop below a mean of 0.1 ppm for the 1974 collection (*1*).

Analytical Results

Residue analysis results from the 1974 collection are now in hand and it is apparent that the extrapolation from a small data base was overly optimistic. The geometric mean of DDT plus metabolites is 0.282 ppm for 1974.

Of the 122 sites sampled, 17 of the values exceeded 1.0 ppm and 2 (3G3 in Arkansas and 4C1 in Arizona; see Tables 1,3) reached a level of 9.2 ppm. Although the reduction of 0.160 ppm (36 percent) from the mean level of 1972 (0.442 ppm) is substantial it is clear that DDT remains by far the most abundant source of pesticide residues found in starlings two full growing seasons after the major uses of DDT were cancelled.

LITERATURE CITED

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

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RESIDUES IN FISH, WILDLIFE, AND ESTUARIES

Chlorinated Pesticides and Polychorinated Biphenyls in Marine Species, Oregon/Washington Coast, 1972 [1]

Robert R. Claeys,[2] Richard S. Caldwell,[3] Norman H. Cutshall,[4] and Robert Holton[4]

ABSTRACT

Concentrations of chlorinated pesticides and polychlorinated biphenyls (PCB's) were determined in three offshore marine species from the Oregon/Washington coast: pink shrimp, euphausiids, and flatfish; five species of bivalve mollusks from five estuaries along the Oregon coast; several fish species from the Coos Bay and Columbia River estuaries; and a summer run of steelhead from the Rogue River.

The compounds p,p'*-DDE and PCB's were detected most frequently. Euphausiids and pink shrimp contained approximately 2 ppb (μg/kg) wet-weight DDE and 8 and 25 ppb PCB's, respectively. Offshore flatfish contained an average of 9 ppb DDE and 29 ppb PCB's. DDE residues in estuarine mollusks approximated 0.5 ppb. PCB levels were not detectable (<3 ppb) except in collections from the mouth of the Columbia River where levels averaged 400 ppb PCB's and 17 ppb DDT. Selected Columbia River fish species contained 38 ppb DDE and 480 ppb PCB's; summer-run steelhead in the Rogue River contained 97 ppb DDE and 125 ppb PCB's.*

PCB chromatograms of most euphausiids closely resembled those of Aroclor 1254. Chromatograms of shrimp and flatfish indicated selective metabolism of two compounds in the Aroclor 1254 formulation. Biphenyls of higher chlorine content were also detected in the shrimp and flatfish.

Introduction

A global program to determine baseline levels of metals, hydrocarbons, and chlorinated hydrocarbons was initiated in 1971 by the International Decade for Ocean Exploration (IDOE) Program of the National Science Foundation. Baseline data for chlorinated hydrocarbons in the North Pacific Ocean are reported here. In addition, baseline levels in mollusks were determined in several Oregon estuaries as part of the National Estuarine Monitoring Program. Several species of fish were collected from two of these estuaries along with some summer-run steelhead (*Salmo gairdnerii*), a type of rainbow trout, from the Rogue River. Chlorinated hydrocarbon levels obtained under the IDOE Program from the Atlantic Ocean (*1*) and the Gulf of Mexico (*2*) surveys have already been published.

Sampling and Analytical Procedures

Pink shrimp (*Pandalus jordani*), euphausiids (*Euphausia pacifica*), and several species of flatfish were collected at ocean stations from Newport, Oreg., to the Straits of Juan de Fuca during September and October 1971 (Fig. 1). An otter trawl and an Isaacs-Kidd midwater trawl were used in these collections.

Estuarine bivalves were collected quarterly from December 1971 through October 1972 in five Oregon estuaries: Columbia River, Tillamook Bay, Yaquina Bay, Umpqua River estuary, and Coos Bay (Fig. 1). Species collected were the cockle clam (*Clinocardium nuttallii*), Eastern softshell clam (*Mya arenaria*), bay mussel (*Mytilus edulis*), Asiatic clam (*Corbicula fluminea*), and a species of Anodonta. The latter two species inhabit only fresh water and were the most abundant mollusks in the Columbia River; estuarine clams were not readily available. In addition, several species of estuarine fish were collected in the Coos Bay and Columbia River estuaries during January 1973 and

[1] Research conducted under National Science Foundation International Decade of Ocean Exploration Grant 6X28744, National Marine Fisheries Contract N-042-14-72(N), and U.S. DHEW Public Health Service Grant ES00040.
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August 1972, respectively; summer-run steelhead were obtained from the Rogue River in September 1970. Except for the steelhead, samples were frozen in glass jars washed with acetone. Special care was taken to avoid contamination because of the possible presence of polychlorinated biphenyls (PCB's) aboard ship.

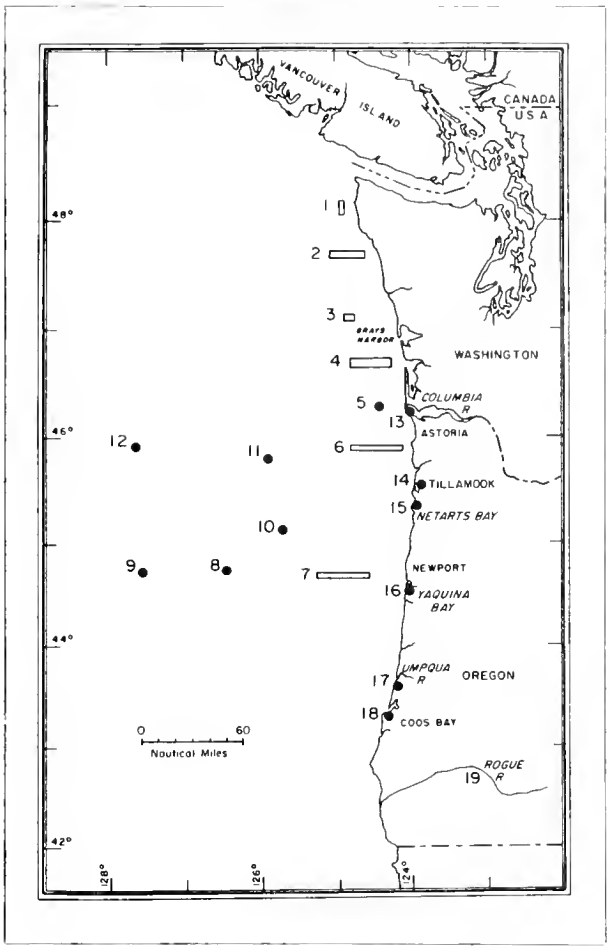

FIGURE 1. *Stations on Oregon/Washington coast sampled for residues in marine species*

Analytical procedures were similar to those of Porter et al. (*3*) except for hexane-acetonitrile partitioning; for that, analysts followed the method of Giuffrida et al. (*4*). Briefly, the shrimp, euphausiids, and small fish were ground whole in a meat grinder and a subsample not exceeding 3 g lipid or 100 g tissue was taken for analysis. Steelhead were analyzed individually by taking a cross section posterior to the anal opening. Mollusks were prepared and extracted as described by Butler (*5*). They were ground with a desiccant mixture of 10 percent QUSO (precipitated silica) and 90 percent anhydrous sodium sulfate. The sample and desiccant were mixed at an exact ratio of 1:3 by weight before taking a 120-g subsample. Fish and shrimp were extracted in a blendor with 2:1 hexane:acetone (v/v) and mollusks were extracted by Soxhlet with 1:1 hexane:acetone. A 25- 50-g sample was extracted, the solvent evaporated, and the residue weighed for an approximate lipid content.

Approximately 90 percent of the lipid was separated from the organochlorines by chromatographic column elution (*4*). The extract was evaporated under a stream of air and the lipid residue was mixed with florisil and loaded on a dry-packed florisil column. Pesticides were then eluted with 9:1 acetonitrile:water and partitioned into hexane after aqueous dilution. Additional cleanup was obtained on a second florisil column. PCB's, DDT, BHC, chlordane, mirex, and toxaphene compounds were eluted from the second column with 5 percent benzene in hexane (v/v). Dieldrin, endrin, heptachlor epoxide, and methoxychlor were eluted with hexane containing 10 percent ethyl ether and 0.25 percent acetone (v/v).

Major PCB isomers were separated from pesticides by a modification of the procedure of Armour and Burke (*6*) by substituting a 1 percent water deactivated silicic acid column. The 4-10 chloro PCB compounds were eluted with hexane and the 1-3 chloro PCB's and pesticide compounds were eluted with 5 percent aqueous methanol. Pesticides were partitioned into hexane after aqueous dilution of the methanol.

Compounds were normally separated and quantitated by gas-liquid chromatography on 122-cm-by-3-mm-ID pyrex columns filled with a 2:1 mixture of 7 percent QF-1 and 7 percent DC-11 liquid phases on high-performance chromosorb W, 100/120 mesh, or with 7 percent DC-11. Columns were operated at 195° C with 20 ml/min N_2 flow. The flow rate employed was 1.5 times the optimum rate for maximum PCB resolution. Both electron-capture and microcoulometric-halide detectors were employed. Sensitivity of the microcoulometric detector was 1-3 ng dieldrin or DDE.

Base hydrolysis was used to confirm the presence of DDD and DDT in selected samples by conversion to DDE and DDMU, respectively (*7*). PCB's remain stable although the α and γ BHC isomers are destroyed during this procedure. A 1:1 fuming HNO_3:concentrated sulfuric acid nitration test (*8*) was used to confirm the presence of chlordane and toxaphene; these are the only compounds which are not nitrated.

Special precautions were employed to improve analysis of low pesticide concentrations. Glassware was baked at 250°-300° C in a large oven (*9*) and other items such as glass wool, sodium sulfate, and florisil were baked at 450° C in a muffle furnace to reduce blank levels. In addition, blanks were analyzed before any samples were begun.

For PCB quantitation peak heights of the sample and standard were added. When peaks were missing, a zero was included in the summation. For two different reasons PCB values may be low: no attempt was made to

identify 8-10 chloro biphenyls; and 1-3 chloro biphenyls elute with the pesticide fraction from the silicic acid column.

Selected samples were spiked with known standards prior to extraction at a concentration of 10 higher than that previously analyzed. Mean recoveries were 75 percent for DDE, 63 percent for DDT, 83 percent for dieldrin, and 100 percent for Aroclor 1260 when silicic acid column separation of PCB's was employed (*10*). Recoveries from the silicic acid column were only 85 percent for DDE and DDT, thus accounting for low DDT recovery. Mean recovery of DDE for mollusks was 92 percent without silicic acid column separation. Values reported here are uncorrected for recovery or blank levels, except for mollusks, in which case blank levels were subtracted.

Results

Levels of chlorinated hydrocarbons in offshore species, estuarine fish, and Rogue River steelhead are given in Tables 1 and 2; offshore results are summarized in Table 3. Most of these data were presented in 1972 at a workshop of the International Decade of Ocean Exploration (*10*).

TABLE 1. *Chlorinated hydrocarbon concentrations in marine species, Washington/Oregon—1972*

Species		Concentration, µg kg wet weight				
		p,p'-DDE	*p,p'*-TDE	*p,p'*-DDT	Total DDT	PCB's
Euphausia pacifica	Samples analyzed	14	14	14	14	11
	Samples with residues	14	5	5	14	11
	Mean	2.2	0.2	0.6	3.0	7.5
	Range	0.2-5.8	0-0.6	0-4.0	0.2-5.9	1-22
Pandalus jordani	Samples analyzed	13	13	13	13	13
	Samples with residues	13	8	8	13	13
	Mean	1.9	0.3	0.5	2.7	25
	Range	0.9-3.7	0.2-1.0	0.2-3.0	1.1-5.0	11-69
Flatfish (genus and species unknown)	Samples analyzed	13	13	13	13	10
	Samples with residues	13	12	12	13	10
	Mean	8.5	1.0	1.0	10.5	29
	Range	3.4-18	0.7-1.7	0.6-2.0	4-19.7	16-121
Blanks	Samples analyzed	11	11	11	9	9
	Samples with residues	11	5	4	7	7
	Mean	0.06	0.03	0.03	0.12	<2
	Range	0.02-0.13	0-0.12	0-0.10	0-0.25	0-4

TABLE 2. *Chlorinated hydrocarbons in selected marine species collected off Oregon/Washington coast, September 1971*

Sampling Station	Location Latitude, Longitude	Concentration, µg/kg wet weight						
		p,p'-DDE	*p,p'*-TDE	*p,p'*-DDT	Total DDT	Dieldrin	Aroclor 1254	Aroclor 1260
		Euphausia pacifica						
7	44° 39′ 124° 31′	1.0	0.6	0.9	3		5	
7	44° 43′ 124° 41′	5.8			6		5	
7	44° 39′ 124° 52′	4.5			5		6	
7	44° 41′ 125° 09′	1.1			1		8	3
7	44° 39′ 125° 14′	3.3			3			3
8	44° 43′ 126° 29′	2.6			3		22	
8	44° 43′ 126° 29′	0.8			1		8	
9	44° 43′ 127° 35′	1.0			1		25	5
10	45° 10′ 125° 39′	1.1			1		4	
11	45° 46′ 125° 49′	2.3	0.1	0.5	3			13
12	45° 56′ 127° 40′	3.3	0.4 [1]	0.5 [1]	4			1
5	46° 21′ 124° 27′	1.8			2		4	
4	46° 31′ 124° 30′	0.2 [2]			0.2		NA	

(Continued next page)

TABLE 2 (cont'd.). *Chlorinated hydrocarbons in selected marine species collected off Oregon/Washington coast, September 1971*

Sampling Station	Location: Latitude, Longitude	Concentration, μg/kg wet weight						
		p,p'-DDE	*p,p'*-TDE	*p,p'*-DDT	Total DDT	Dieldrin	Aroclor 1254	Aroclor 1260
4	46° 41′ 124° 46′	2.1 [2]	0.6 [2]	3 [2]	7	5 [2]	NA	
3	47° 11′ 124° 48′	1.3 [1]	0.6 [1]	4 [1]	6	4 [1]	NA	
		Pandalus jordani						
7	44° 39′ 124° 35′	2.4	0.7	0.3	3		9	10
7	44° 43′ 124° 41′	3.7	0.2	0.3	4		11	
6	45° 55′ 124° 14′	1.1			1		12	
6	45° 55′ 124° 28′	1.2			1		36	8
6	45° 56′ 124° 41′	2.0			2		9	
5	46° 21′ 124° 27′	0.9	0.5	0.3	2		35	10
4	46° 37′ 124° 26′	2.5	0.3	0.2	3		33	
4	46° 39′ 124° 39′	1.4			1		14	
4	46° 41′ 124° 37′	1.8	0.4	0.6	3		16	
3	47° 06′ 124° 41′	1.9	1.0		3		19	50
3	47° 06′ 124° 47′	1.0	0.5	0.2	2		15	
3	47° 11′ 124° 48′	2.0 [2]		3 [2]	5		44	
2	47° 39′ 125° 05′	3.0	0.3 [1]	1.1 [1]	4		20	
		Sand Shrimp						
6	45° 55′ 124° 14′	<1.3			1		ND	
2	47° 39′ 124° 36′	<0.3					7	
2	47° 40′ 124° 54′	1.1	0.3	0.3	2		28	
1	48° 06′ 124° 51′						6	
		Sergestid Shrimp						
7	44° 43′ 124° 41′	25		4.1	29		17	
		Galathea Shrimp						
4	46° 41′ 124° 37′	1.4			5		5	
		Flatfish						
6	45° 54′ 124° 02′	6.4	0.7	1.1	8		ND	12
6	45° 55′ 124° 14′	10.4	1.0	1.1	13		52	
6	45° 56′ 124° 12′	10 [2]	<3 [2]	<5 [2]	18		NA	
6	45° 55′ 124° 28′	12.6	0.9	0.8	14		24	
6	45° 56′ 124° 41′	12.7	1.7 [1]	1.8 [1]	25		28	
4	46° 37′ 124° 14′	11.0	1.8 [1]	2.0 [1]	15		85	36
4	46° 37′ 124° 26′	3.4	1.0	1.2	6		25	
2	47° 28′ 124° 41′	6.7	1.0	1.5	9		28	
2	47° 39′ 124° 36′	5.0	0.9		6		24	

(Continued next page)

TABLE 2 (cont'd.). *Chlorinated hydrocarbons in selected marine species collected off Oregon/Washington coast, September 1971*

Sampling Station	Location: Latitude, Longitude	Concentration, μg/kg wet weight						
		p,p'-DDE	*p,p'*-TDE	*p,p'*-DDT	Total DDT	Dieldrin	Aroclor 1254	Aroclor 1260
2	**47° 39'** **124° 36'**	5.7	NA	NA	6		12	
2	47° 40' 124° 54'	10.0	0.6	0.7	17		18	
2	47° 41' 124° 46'	5.7	0.9	0.7	7		16	
2	47° 39' 125° 05'	17.4	0.8	0.9	19		30	
2	**47° 39'** 125° 05'	16.6	0.8	0.9	18		18	
2	**47° 39'** 125° 05'	20.0	NA	NA	20		21	
1	48° 06' 124° 51'	4.3	0.8	0.9	6		16	
		Salpa						
9	44° 43' 127° 35'	0.1					20	
		Clupea harengus pallasii						
4	46° 37' 124° 14'	19	4.0	1.6	25		146	
		Small Fish						
1	48° 12' 124° 56'	107	2 [1,2]	6 [1,2]	115	3 [1,2]	NA	

NOTE: NA = not analyzed.
ND = no data because of interference with analytical process.
Blank spaces imply residues below detectable levels.
Representative *Euphausia pacifica* sample contained 1.8 percent lipid; *Pandalus jordani*, 2.0 percent; sand shrimp, 2.4 percent.
[1] Alcoholic base hydrolysis.
[2] Microcoulometric detector confirmation.

TABLE 3. *Chlorinated hydrocarbons in estuarine fish and Rogue River steelhead, 1970-73*

Species	Concentration, μg/kg wet weight						
	p,p'-DDE	*p,p'*-TDE	*p,p'*-DDT	Total DDT	Dieldrin	Aroclor 1254	Aroclor 1260
Coos Bay Estuary, January 1973, Station 18							
Striped Seaperch *(Embiotoca lateralis)*	5			5		23 [1]	
Sand Sole *(Psettichthys melanostictus)*	7			7		26 [1]	
Staghorn Sculpin *(Leptocottus armatus)*	3			3		14 [1]	
Starry Flounder *(Platichthys stellatus)*	6			6			27 [1]
Blank	0.02			0.02	NA	2	
Percent recovery of sample spiked at 17 ppb			87		81		
Columbia River Estuary, August 1972, Station 13 [2]							
Starry Flounder *(Platichthys stellatus)*	18	8	8	34	310		
Tom Cod *(Microgadus proximus)*					90		
Peamouth Chub *(Mylochilus causinus)*	81	62		143	1160		
Finescale Sucker *(Catostomus syncheilus)*	14	28	11	53	350		
Blank	<1	<1	<1		<1		
South Rogue River, September 1970, Station 19							
Steelhead *(Salmo gairdneri)* [3]							
2 [4]	73			73	28	100	
9	110			110	15	150	
1,6 [5]	140			140	9	NA	
8,10 [5]	62			62	29	NA	
5,7 [5]	72			72		NA	
3,4 [5]	126			126	24	NA	

NOTE: NA = not analyzed.
Representative starry flounder sample contained 2.5 percent lipid; representative steelhead contained 10.6 percent lipid.
Blank spaces imply residues below detectable levels.
[1] Microcoulometric confirmation.
[2] Aroclor 1254 concentrations not reported for species from station 13 because of interference with analytical process.
[3] South Rogue River column 1 shows Oregon State University identification numbers for samples not identified by species.
[4] Species also contained 6 μg/kg chlordane and 6 μg/kg thiodan.
[5] Sample too small for PCB analysis.

Offshore collections showed little geographical differences. DDE was frequently the only DDT-related compound present, averaging about 2 ppb in euphausiids and pink shrimp and 9 ppb in flatfish. PCB levels were slightly higher, averaging 8, 25, and 29 ppb for euphausiids, pink shrimp, and flatfish, respectively.

Figure 2 compares a typical shrimp chromatogram with those of Aroclor 1254 and 1260. Although most euphausiid PCB chromatograms resembled Aroclor 1254, peaks 21 and 23 were low or absent in pink shrimp and flatfish. Peak number 34 was also absent but peak 37 was usually present. Tentative indentification has been previously reported (*11*). Peaks 21 and 23 are both five chlorobiphenyls; peaks 34 and 37 are seven chlorobiphenyls.

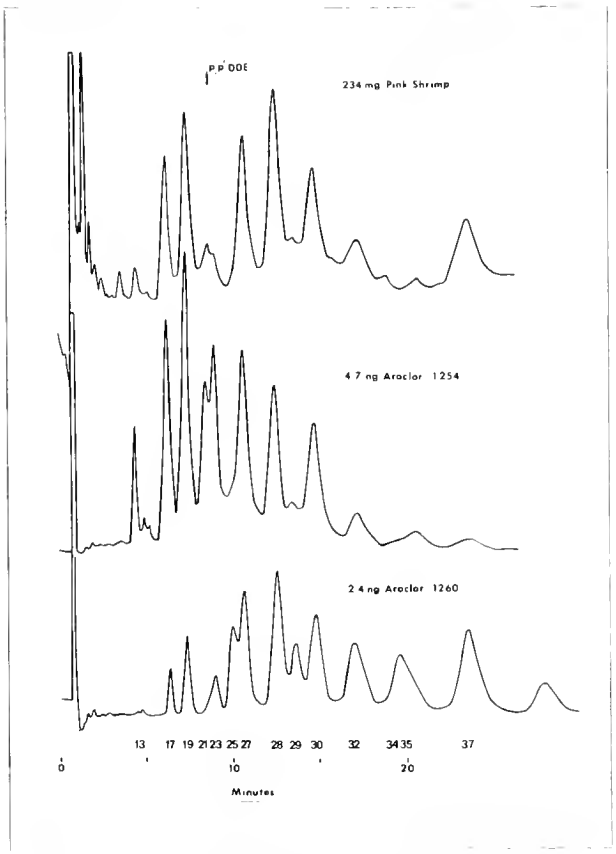

FIGURE 2. *Typical chromatograms of the PCB fraction, pink shrimp extract*

Dieldrin may have been present in the offshore species; but because of poor lipid separation, many peaks were present in the eluant containing dieldrin, making positive identification and quantitation difficult. In about one-half the pink shrimp and euphausiid collections and nearly all flatfish samples an apparent dieldrin peak was present. A second chromatographic column, 3 percent diethylene glycol succinate, was used for further confirmation.

Where dieldrin was indicated, levels were 0.2-0.5 ppb except for two euphausiid samples which contained about 5 ppb. In these latter two samples microcoulometric chloride detection positively confirmed dieldrin. These samples, collected 25 miles west of Grays Harbor (sampling stations 3 and 4), also contained higher levels of DDT and DDD. Dieldrin was also positively confirmed in a small unidentified fish collected near the Straits of Juan de Fuca (station 1). Dieldrin blank levels ranged from 0.004 to 0.33 ppb ($\bar{x} = 0.11$ ppb). Thus the apparent dieldrin peak in many samples may represent blank levels.

Fish collected from Coos Bay showed relatively low levels of DDE and PCB's (Table 3). PCB chromatograms resembled those found in the pink shrimp, i.e., Aroclor 1254 with two peaks missing; starry flounder chromatograms resembled those of Aroclor 1260.

Columbia River fish contained much higher levels of chlorinated hydrocarbons (Table 3), particularly PCB's (90-1160 ppb), than those found in Coos Bay fish. Starry flounder was the only species collected from both estuaries. Columbia River samples had six times the level of ΣDDT and 11 times the level of PCB's than had Coos Bay specimens. Interfering peaks prevented determination of dieldrin levels in these samples.

Summer-run steelhead from the Rogue River contained highest levels of DDE (97 ppb) and dieldrin (21 ppb) of all species sampled. In addition, 6 ppb chlordane and thiodan were found in several samples. PCB levels in Rogue River fish were lower than in Columbia River fish.

Results for mollusks are summarized in Table 4. The only chlorinated hydrocarbon pesticide found consistently throughout the sampling area was *p,p'*-DDE and, occasionally, *p,p'*-TDE and *p,p'*-DDT. Concentrations of DDT and related compounds were very low except in the Columbia River estuary. There were no significant seasonal variations. The Coos Bay *Mya* population had higher DDT residues (1.6-3.0 ppb) than had other clam populations from estuaries with small coastal mountain watersheds, i.e., Umpqua, Tillamook, and Yaquina. Only a single species, *Clinocardium nuttallii*, was analyzed from Netarts Bay; no chlorinated hydrocarbon compounds were detected.

Levels of DDT compounds in mollusks from the Columbia River were in marked contrast to those in mollusks from the other Oregon estuaries. Unfortunately, neither *Clinocardium* nor *Mya* was available from this system so comparisons must be made using different species. Except for a single sample of *Mytilus edulis* taken from the south jetty during the winter period, only *Anodonta* sp. and *Corbicula fluminea* were collected at this location. Levels of ΣDDT in *Anodonta* ranged from 14.9 ppb during the spring to 2 ppb in the fall. In contrast, ΣDDT in *Corbicula* ranged from

53 to 78 ppb. No marked seasonal variation was evident in this latter species either in ΣDDT or in the proportion of metabolites.

The only other pesticide detected in mollusks during the sampling period was dieldrin, which was present in all three Columbia River species analyzed during the winter and spring but was not detected in the summer and fall collections. Concentrations in mollusk tissues never exceeded 4 ppb.

During the first three sampling periods PCB's were found only in tissues of Columbia River bivalves. The PCB's found are believed to be a mixture of Aroclor 1254 and Aroclor 1260. *Corbicula* samples had consistently higher levels of PCB's than had Anodonta samples. In the former species concentrations ranged from 390 to 1,170 ppb. The highest level was found in the spring sampling period; levels did not exceed 570 ppb during the three remaining seasons. Levels of PCB's in *Anodonta* ranged from 160 ppb to levels

TABLE 4. *Chlorinated hydrocarbons in Oregon estuarine mollusks, 1972*

Species	Date	Concentration, μg kg wet weight			
		p,p'-DDI	*p,p'*-TDE	*p,p'*-DDT	PCB'S
		Columbia River			
Corbicula fluminea	2/24	21	20	12	570
	4/14	ND	ND	ND	1170
	7/28	35	28	15	390
	10/5	30	17	10	420
Anodonta	4/14	7	4	3	160
	7/28	7	2	1	35
	10/4	2	NS	NS	NS
Mytilus edulis	2/24	NS	NS	NS	44
		Coos Bay			
Mya arenaria	1/25	0.6	0.8	2	NS
	4/17	0.7	NS	1.6 [1]	NS
	7/12	0.7	0.7	3	NS
	9/30	ND	NS	NS	26
Clinocardium nuttalli	1/25	NS	NS	NS	NS
	4/17	NS	NS	NS	NS
	7/12	0.3	NS	0.4	NS
	9/30	ND	NS	NS	NS
		Tillamook			
Mya arenaria	1/14	NS	NS	NS	NS
	4/13	NS	NS	NS	NS
	7/9	0.2	NS	0.3	NS
	10/5	0.6	NS	NS	NS
Clinocardium nuttalli	1/14	NS	NS	NS	NS
	4/13	0.5	NS	0.4	NS
	7/9	0.1	NS	NS	NS
	10/5	0.6	NS	NS	NS
		Umpqua			
Mya arenaria	1/13	0.6	<0.7	<0.5	NS
	1/13	0.6	NS	NS	NS
	4/17	1.0	0.5 [1]	0.4 [1]	NS
	7/11	0.2	0.3	NS	NS
	10/2	1.2	NS	NS	NS
Mytilus edulis	1/26	0.7	NS	NS	NS
	5/19	1.0	NS	NS	NS
	7/12	0.8	0.3	NS	NS
	10/2	1.8	NS	NS	NS
		Yaquina			
Mya arenaria	1/24	0.2	NS	NS	NS
	4/15	0.5	NS	NS	NS
	7/8	0.2	NS	NS	NS
	9/25	0.6	NS	NS	5
Clinocardium nuttalli	1/1	NS	NS	NS	NS
	4/15	0.2	0.5	NS	NS
	7/8	0.2	NS	NS	NS
	9/25	0.3	NS	NS	7
Blanks [2,3]	Winter	0.2	0.3	0.5	19
	Spring	0.2	0.2	0.4	9
	Summer	0.1	0.2	0.4	5
	Fall	0.2	0.2	0.4	1

NOTE: Values have been corrected for sea water blanks.
ND = no data because of interference with analytical process.
NS = residues not significant (less than twice the blank values).
[1] Confirmed by base hydrolysis.
[2] Values assume 30-g sample weight.
[3] Average of two blanks.

lower than those determined for blank samples. Like *Corbicula, Anodonta* displayed the highest PCB level in the spring. During the fall sampling period, low levels (5-7 ppb) of PCB's were detected in the two bivalve species from Yaquina Bay, and 26 ppb PCB's were found in the Coos Bay *Mya* population.

Discussion

Relative concentrations of DDT and PCB compounds differed in the three offshore species. Residues of ΣDDT were 3 ppb in both euphausiids and pink shrimp, but PCB levels differed between the two species by a factor of three: 7.5 versus 25 ppb, respectively (Table 3). Levels of DDT in flatfish were three times higher than in euphausiids and pink shrimp, but PCB levels were similar to those in the pink shrimp. Considering that all three species have nearly the same lipid content, approximately 2 percent, other factors probably account for these differences. Both euphausiids and pink shrimp feed on zooplankton and smaller animals. Euphausiids are found in the water column, however, and pink shrimp are found near the ocean floor. Another possible explanation for the difference between these levels is that the two species were collected from different geographic locations. Most euphausiids were collected west of Newport (station 7); pink shrimp were collected farther north at stations 2 and 5.

DDT levels reported by Giam et al. (*2*) for the Gulf of Mexico are considerably higher. DDT levels for Gulf shrimp (family Panaeidae) ranged from 33 to 165 ppb; PCB chromatograms lacked sufficient resemblance to an Aroclor formulation for quantitation. DDT levels in Gulf fish were also much higher than those from the study reported here, but PCB levels were comparable.

Atlantic Ocean levels (*1*) are similar to those reported from the present study of the Northeast Pacific. Icelandic shrimp (*Pandalus borealis*) contained 1 and 18 ppb DDT and PCB compounds, respectively.

In 1968 Stout (*12*) reported pesticide residues in fish and shellfish in the Northeast Pacific. Residues in hake collected along the Oregon/Washington coast ranged from 115 to 285 ppb total DDT; DDE represented only 26-36 percent of the total DDT residue. Some PCB interference may have accounted for higher DDD and DDT residues. In the authors' 1972 collections, DDE often represented the major portion of the total DDT residue; Columbia River collections, which showed signs of recent DDT contamination, were the exception.

Little is known about biological effects of PCB's on the marine environment. Duke et al. (*13*) exposed shrimp (*Penaeus duorarum*) to 5 ppb Aroclor 1254 in sea water for 20 days. Shrimp that died after 10 days had only 1,600 ppb PCB's; those living after 20 days had 3,300 ppb PCB's. Thus mortality probably was not caused by PCB poisoning. If 1,600 ppb is taken as a toxic residue level for shrimp, then pink shrimp (*Pandalus jordani*) in the Northeast Pacific contain only 1/60 the toxic residue level. Similar studies for DDE were not located.

DDE and PCB levels in the Coos Bay fish were slightly less than those found in the offshore flatfish collections (5 vs. 9 ppb DDE and 22 vs. 29 ppb PCB's, respectively).

Traces of chlordane and thiodan found in the steelhead may have originated from agricultural use in Medford, Oreg., a fruit-growing area. Only minor quantities of these chemicals are presently being applied in this area. Dieldrin found in those collections may have originated in the Rogue River, although dieldrin was also found in a few offshore collections.

PCB chromatograms of shrimp samples indicate selected metabolism of some isomers. All shrimp species had very low peaks for isomers 21 and 23 although euphausiids contained the expected ratio of isomers. The lower quantities of isomers 21 and 23 in flatfish may be a result of their feeding on pink shrimp. The larger fish, herring, salpa, and steelhead, had chromatograms closely resembling Aroclor 1254. PCB chromatograms of common murres collected in this area were very similar to the shrimp chromatogram (*11*). It is significant that three of the four fish collected in the Coos Bay estuary had PCB patterns closely resembling Aroclor 1254. The pattern of the fourth, a starry flounder, resembled Aroclor 1260.

Except for the Columbia River collections, organochlorine residues reported here for Oregon estuarine mollusks are consistently lower than those reported for mollusks from many other coastal States. Coos Bay mollusks had higher ΣDDT residues than had mollusks from the small coastal drainage estuaries, but even these did not exceed 5 ppb. In contrast, a very high percentage of mollusks sampled in other States contained between 11 and 100 ppb ΣDDT; significant numbers contained even more than 100 ppb (*5*).

Residues found in Columbia River *Corbicula* (53-78 ppb) more closely paralleled those reported in other States, but *Anodonta* collected in the same area contained less than 15 ppb ΣDDT. In general, a higher level of DDT tissue residues would be anticipated in Columbia River mollusks considering the enormous area of agricultural land drained by this river system. However, high levels of ΣDDT found in *Corbicula* may also be a result of the extraordinary ability of this species to accumulate organochlorine compounds.

Like DDT, PCB's accumulated far more heavily in *Corbicula* than in the other mollusks examined. The higher levels of PCB's in the Columbia River fish suggest that PCB contamination of the Columbia River greatly exceeded that of adjacent coastal waters.

Acknowledgment

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Residues of Organochlorine Pesticides and Polychlorinated Biphenyls and Autopsy Data for Bald Eagles, 1971-72 [1]

Eugene Cromartie, William L. Reichel, Louis N. Locke, Andre A. Belisle, T. Earl Kaiser, Thair G. Lamont, Bernard M. Mulhern, Richard M. Prouty, and Douglas M. Swineford

ABSTRACT

Thirty-seven bald eagles found sick or dead in 18 States during 1971-72 were analyzed for organochlorine pesticides and polychlorinated biphenyls (PCB's). DDE and PCB's were detected in all bald eagle carcasses; 30 carcasses contained DDD and 28 contained dieldrin. Four eagles contained possibly lethal levels of dieldrin and nine eagles had been poisoned by thallium. Autopsies revealed that illegal shooting was the most common cause of mortality. Since 1964 when data were first collected, 8 of the 17 eagles obtained from Maryland, Virginia, South Carolina, and Florida possibly died from dieldrin poisoning; all four specimens from Maryland and Virginia were from the Chesapeake Bay Tidewater area.

Introduction

The purpose of this paper is to report and evaluate residue and autopsy data on bald eagles *(Haliaeetus leucocephalus)* collected in 1971 and 1972. Data for specimens collected in 1964 through 1970 have been previously reported (*1-3*).

Sampling

Bald eagles found dead or moribund in the field are collected by Federal, State, and private cooperators, packed in dry ice, and shipped air express to the Patuxent Wildlife Research Center in Laurel, Md., where they are stored intact in plastic bags at −25° C. Thus sampling for the present study was not systematic because of the relatively low population and protected status of these birds. Table 1 shows the collection areas of the 37 birds analyzed; 25 birds were collected in 1971 and 12 in 1972. Decomposed specimens were not analyzed.

TABLE 1. *Distribution of eagles collected by State and year of death, 1971-72*

State	No. Eagles Collected	
	1971	1972
California	1	
Florida	1	
Illinois	4	
Indiana		1
Iowa	1	
Maine		1
Michigan		1
Minnesota		2
Missouri	4	1
New Mexico		1
New York		1
Ohio	1	
South Carolina	1	
Texas		1
Utah	2	
Virginia	1	2
Wisconsin	1	
Wyoming	8	1
TOTAL	25	12

Autopsy and Analytical Procedures

Procedures for autopsy followed those reported previously by Belisle et al. (*3*). After removal of the skin, feet, wings, liver, and gastrointestinal tract, the carcass was ground and homogenized in a Hobart food cutter. A 10-g aliquot of the carcass and the entire brain were

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

mixed separately with anhydrous sodium sulfate in a blendor and extracted for 7 hours with hexane in a Soxhlet apparatus. Extracts were evaporated, lipid weights were determined, and the extracts were redissolved in 20 ml hexane. A 10-ml aliquot of extract containing not more than 0.5 g lipid was cleaned on a florisil column.

The florisil had been washed and recalcined at 675° C according to Hall's method (*4*) and partly deactivated with 1.0-1.5 percent water to permit the elution of dieldrin with the other pesticides. Approximately 21 g of the treated florisil was placed in each 2-by-20-cm column with a 250-ml reservoir and topped with 1 cm anhydrous sodium sulfate. Columns were prewashed with 50 ml hexane and the extract was eluted with 200 ml 6 percent ethyl ether in hexane.

The florisil eluate was concentrated to 5 ml and a 4-ml aliquot was placed on a silicic acid column to separate pesticides from PCB's. Armour and Burke's separation method (*5*) was used with the following modifications: the silicic acid, Mallinckrodt Silicar CC-4, was heated at 130° C for 24 hours in a pan covered with aluminum foil containing a few pinholes; celite and air pressure were eliminated; and the petroleum ether eluate was collected in two separate fractions of 100 ml and 300 ml followed by 200 ml of the polar eluate. The adsorbent usually was deactivated with 3 percent water, and the flask was sealed with paraffin tape, shaken for 3 hours on a reciprocating shaker, and allowed to equilibrate for 24 hours before use. The amount of water was adjusted by running standards to assure that all the DDE was in the second fraction.

Using this procedure, hexachlorobenzene (HCB) and mirex were collected in the first 100 ml petroleum ether, PCB's and DDE were in the second fraction, and the remaining pesticides were in the polar eluate. Silicar CC-4 did not require celite or air pressure to maintain the specified flow rate. Covering the pan with aluminum foil during the heating process eliminated certain interfering background peaks.

Samples were 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 possible errors from PCB interference; other pesticides were measured by digital integration of area, and PCB's were estimated by comparing total peak area with Aroclor 1254 or 1260.

Residues in 15 specimens (40 percent) were positively identified with an LKB gas-liquid chromatograph/mass spectrometer (GLC/MS). Operating procedures have been described (*3*) except that a 1 percent SE-30 column was temperature-programmed. Program rate was 2° C/min; initial temperature was 135° C, rising to a maximum of 220° C.

Average recoveries from spiked mallard carcass tissue were: DDE, 96 percent; DDD, 103 percent; DDT, 110 percent; dieldrin, 101 percent; heptachlor epoxide, 104 percent; mirex, 106 percent; oxychlordane, 98 percent; *cis*-chlordane, 100 percent; *cis*-nonachlor, 98 percent; HCB, 69 percent; and Aroclor 1254, 101 percent. Residue levels for eagle samples were not corrected for recovery. The lower limit of sensitivity was 0.05 ppm; residue levels less than 0.05 ppm were not reported "trace" as in the previous reports.

Samples were not analyzed for oxychlordane, *cis*-chlordane, *cis*-nonachlor, or HCB in 1971. GLC/MS analyses using temperature programming revealed both *cis*-chlordane and *trans*-nonachlor. In one sample, only *trans*-nonachlor was detected. Authors were unable to obtain a GLC column for the electron-capture detector that would separate both compounds without interference from another pesticide. The peak was quantitated as *cis*-chlordane because standards of these compounds have the same detector response.

Thallium levels in eagle kidneys were determined by flame atomic absorption using the method described by Curry et al. (*6*) except that a sampling boat was not used. The lower limit of sensitivity was 2.0 ppm.

Results and Discussion

RESIDUES

Table 2 summarizes residues of organochlorine pesticides and PCB's in 37 bald eagle carcasses and brains; all data are reported on a wet-weight basis. All carcasses contained PCB and DDE residues, 30 contained DDD, and 28 contained dieldrin.

Four specimens had concentrations of dieldrin in the brain within the range known to have caused death by dieldrin. Table 3 shows dieldrin levels in the brains of these specimens to range from 4.0 to 7.8 ppm. Stickel et al. (*7*) concluded from an experimental study on Japanese quail *(Coturnix coturnix)* and from residues in brains of several kinds of animals found dead in the field following heavy dieldrin treatments that a concentration of 4-5 ppm indicated that the animal was in the danger zone. Linder et al. (*8*) concluded from studies of capsule-dosed pheasants that a level of 3-4 ppm, or greater, of dieldrin in the brain indicates death by dieldrin.

During the 1964-72 period, 190 eagles were analyzed; 19 (10 percent) of these specimens were suspected cases of dieldrin poisoning. The incidence of dieldrin poisoning is high, particularly among specimens from Maryland, Virginia, South Carolina, and Florida. Of the 17 eagles collected (3 from Md., 4 from Va., 4 from S.C., and 6 from Fla.), 8 (47 percent) were possible victims

TABLE 2. *Pesticide and PCB residues in 37 bald eagles, 1971-72*

Compound	Year	Residues, ppm wet weight					
		Carcass			Brain		
		No. Specimens [1]	Median [1]	Range	No. Specimens [1]	Median [1]	Range
p,p'-DDE	1971	25	5.7	0.77- 210.0	25	0.95	0.07- 89.0
	1972	12	11.0	0.83- 110.0	12	3.3	0.14- 55.0
p,p'-DDD	1971	18	0.40	0.10- 33.0	9	0.19	0.05- 9.9
	1972	12	0.54	0.14- 18.0	8	0.35	0.06- 2.9
p,p'-DDT	1971	4	0.33	0.26- 3.2	2	0.08	0.05- 0.11
	1972	5	0.42	0.12- 0.94	1	0.34	-
Dieldrin	1971	16	0.72	0.10- 33.0	12	0.30	0.05- 7.8
	1972	12	0.65	0.14- 12.0	8	0.61	0.23- 4.6
Heptachlor epoxide	1971	9	0.36	0.06- 5.5	6	0.18	0.05- 1.5
	1972	5	0.72	0.06- 2.7	3	0.35	0.11- 1.7
Mirex	1971	10	0.30	0.10- 1.3	4	0.10	0.10- 0.13
	1972	6	0.26	0.06- 0.60	2	0.13	0.11- 0.13
Oxychlordane	1972	6	0.34	0.18- 1.4	6	0.09	0.05- 0.34
cis-Chlordane [2]	1972	10	0.30	0.11- 7.4	7	0.11	0.05- 1.7
cis-Nonachlor	1972	6	0.29	0.07- 0.95	2	0.59	0.19- 0.98
Hexachlorobenzene	1972	4	0.30	0.11- 0.50	4	0.14	0.05- 0.18
PCB's	1971	25	8.6	0.30- 290.0	24	1.1	0.10-150.0
	1972	12	26.0	0.60-1200.0	11	16.0	0.65-190.0

[1] Number of specimens containing residues; the median is based on this number.
[2] And/or *trans*-nonachlor.

TABLE 3. *Data on four suspected cases of dieldrin poisoning of adult eagles, 1971-72*

State	Year	Sex	Dieldrin Residue in Brain, ppm	Autopsy Findings [1]
Iowa	1971	F	7.8	Open, no fat deposits
South Carolina	1971	M	6.5	Emaciation
Virginia	1971	M	4.0	Open, no fat deposits
Virginia	1972	F	4.6	Open, no fat deposits

[1] Open = no diagnosis could be made on the basis of autopsy findings.

of dieldrin poisoning. Two eagles suspected of dieldrin poisoning were collected from each State. It is of special concern that all four eagles from Maryland and Virginia suspected of dieldrin poisoning were from the Chesapeake Bay tidewater area. No specimens were collected from North Carolina or Georgia.

A large group of bald and golden eagles found dead near Casper, Wyo., in May 1971 were suspected of having been killed by ingestion of poisoned bait. Specimens were analyzed for cyanide, strychnine, sodium fluoroacetate (1080), and thallium. Residues of thallium in the kidneys ranged from 14 to 59 ppm. Eight of the eleven bald eagles from this group which were suitable for residue analysis are included in this report. In an eagle from Utah, the kidney contained 63 ppm thallium. It was concluded from autopsies and chemical analyses that these eagles had died from thallium ingestion.

AUTOPSY

Results of the autopsies are summarized in Table 4. Illegal shooting, the most common cause of mortality, was responsible for the death of 35 percent of the eagles.

Three eagles suspected of dieldrin poisoning were in good flesh but lacked deposits of fat. The other bird listed as emaciated showed marked atrophy of the pectoral and leg muscles, and had no fat deposits.

TABLE 4. *Probable causes of bald eagle mortality, 1971-72*

Cause of Death	No. Eagles
Shooting	13
Thallium poisoning	9
Dieldrin poisoning	4
Nephrosis	1
Drowning	1
Drowning; coccidiosis	1
Coccidiosis	1
Strychnine poisoning	1 [1]
Impact	1
Electrocution	1
Open [2]	4
TOTAL	37

[1] Specimen from New Mexico; analyzed for strychnine by Denver Wildlife Research Center, Denver, Colo.
[2] No diagnosis could be made on the basis of autopsy findings or chemical analysis.

Coccidiosis caused by *Isospora* sp. was apparently responsible for the death of an eagle from Minnesota. It was a contributing factor in the death of an emaciated adult female found downstream from Flaming Gorge Dam, Utah; immediate cause of her death was reported as drowning.

Drowning was also the immediate cause of the death of an adult female eagle from Michigan that had high levels of DDE (55 ppm) and PCB's (190 ppm) in the brain. The eagle, which had been observed perched on a snag over the water, suddenly fell into the water and drowned. No injuries were found, and both aerobic and anaerobic cultures of liver, heart blood, and intestinal tract failed to reveal any pathogenic bacteria.

The thallium-poisoned eagles usually had normal amounts of adipose tissues, were in good flesh, and had no gross lesions except congestion of vessels overlying the cerebellum. Microscopically, there were no acid-fast intranuclear inclusion bodies which sometimes indicate lead poisoning, and examination of the kidney sections stained by the Pritschow technique proved to be equivocal.

An adult female eagle from Missouri had a shattered lower left leg, the result of an earlier gunshot wound. She had valvular endocarditis, probably the result of a secondary bacterial infection from the leg wound. *Escherichia coli* appeared in the heart blood but not in the lungs and liver; thus the cause of death is listed as shooting (Table 4).

Conclusion

Bald eagles are subject to a wide variety of environmental insults, including infectious agents, chemical pollutants, and human-related trauma. Levels of pesticides and PCB's in eagles continue to be high, reflecting widespread contamination by these compounds.

Acknowledgments

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Mercury Concentrations in Fish, North Atlantic Offshore Waters—1971

R. A. Greig,[1] D. Wenzloff,[1] and C. Shelpuk [2]

ABSTRACT

Mercury concentrations were determined in muscle and liver of 41 species of fish and a limited number of plankton, sediment, and invertebrate samples collected from North Atlantic offshore waters in 1971. The average mercury concentration in fish muscle was 0.154 ppm with a standard deviation of 0.124. Invertebrate samples had mercury concentrations which were generally less than 0.1 ppm. In a single lobster sample, however, 0.31 ppm mercury was found in the tail muscle and there was 0.60 ppm in the liver. Mercury levels in all 9 plankton and 10 sediment samples taken were less than 0.05 ppm.

Introduction

Recently, much has been published about mercury in freshwater lakes in Japan, Sweden, Canada, and the Great Lakes area of the United States. Mercury discharged into these waters was found to accumulate in tissues of fish and other organisms to levels that in certain species were considered potentially dangerous to human health (*1*).

This mercury was traced to many industrial and domestic uses, such as the manufacture of sodium hydroxide and chloralkali plants, paper manufacturing, plastics production, and application of fungicides to control yeast and mold growth on grass and in pulp mills.

The degree and source of mercury contamination of freshwater fish and waters were readily established. Levels in marine fish and waters, however, were not so easily determined. The Food and Drug Administration (FDA), U.S. Department of Health, Education, and Welfare, conducted a survey of mercury levels in several species of both domestic and foreign marine fisheries products and found that certain species of tuna and swordfish contained mercury above the 0.5 ppm action level, the maximum allowable concentration in fish intended for sale.

As a result of these findings, a program was initiated within the National Marine Fisheries Service, U.S. Department of Commerce, to determine mercury levels in other marine fish as part of an overall program on the effects of chemical contamination of living marine resources. The present paper reports on part of this program, a survey of mercury concentrations in groundfish collected from U.S. waters of the North Atlantic Ocean.

Experimental Methods

SAMPLE COLLECTION

Fish and invertebrates were collected by otter trawl during the annual assessment of groundfish stocks conducted by the National Marine Fisheries Service, Northeast Fisheries Center, Woods Hole, Mass. After the catch, fish and invertebrates were sorted and dissected aboard the vessel. Livers and a 1-inch-thick steak immediately posterior to the head were taken from each fish. Invertebrate samples varied: whole squid were analyzed although scallop samples were composed of only the edible muscle and lobster samples consisted of the digestive diverticula and tail muscle.

Bottom sediments were obtained from selected areas with a Smith-McIntyre sampler. Samples were removed for analysis with a plastic tube 1 1/2 inch in diameter and 6 inches long, which was inserted into the bottom sediment, capped, and frozen.

[1] National Marine Fisheries Service, Middle Atlantic Coastal Fisheries Center, Milford Laboratory, Milford, Conn. 06460.
[2] J. P. Stevens Co., Box 428, Piedmont, S.C.

Approximate geographic sampling areas are shown in Figure 1. Common and scientific names of fish and invertebrates obtained in the survey are presented in Table 1.

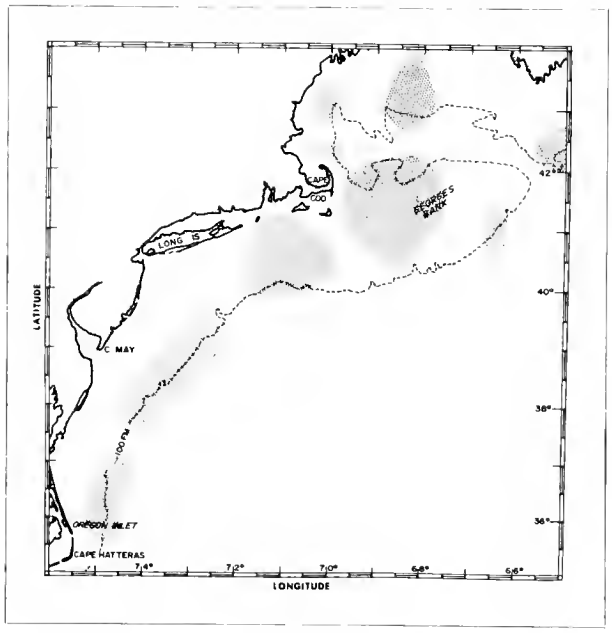

FIGURE 1. *Collection sites of fish sampled for mercury concentrations, North Atlantic offshore waters—1971*

TABLE 1. *Fish sampled for mercury concentrations, North Atlantic offshore waters—1971*

COMMON NAME	SCIENTIFIC NAME
American plaice	*Hippoglassoides platessoides*
American shad	*Alosa sapidissima*
Angel shark	*Squalus dumerili*
Atlantic cod	*Gadus morhua*
Atlantic herring	*Clupea harengus harengus*
Atlantic mackerel	*Scomber scombrus*
Atlantic wolffish	*Anarhichas lupus*
Beardfish	*Polymixia lowei*
Blackbelly rosefish	*Helicolenus dactylopterus*
Black sea bass	*Centropristis striata*
Butterfish	*Peprilus triacanthus*
Cusk	*Brosme brosme*
Daubed shanny	*Lumpenus maculatus*
Fawn cusk-eel	*Lepophidium cervinum*
Fourspot flounder	*Paralichthys oblangus*
Gulf Stream flounder	*Citharichthys arctifrans*
Haddock	*Melanogrammus aeglefinus*
Lanternfish	Unclassified
Little skate	*Raja erinacea*
Longhorn sculpin	*Myoxocephalus octodecemspinosus*
Mailed sculpin	*Triglops nybelini*
Northern searobin	*Prionotus carolinus*
Ocean pout	*Macrozoarces americanus*
Pollock	*Pollachius virens*
Redfish	*Sebastes marinus*
Red hake	*Urophycis chuss*
Round herring	*Etrumeus teres*
Silver hake	*Merluccius bilinearis*
Spiny dogfish	*Squalus acanthias*
Spot	*Leiostomus xanthurus*
Striped searobin	*Prionotus evolans*
Thorny skate	*Raja radiata*
White hake	*Urophycis tenuis*
Windowpane flounder	*Scophthalmus aquosus*
Winter flounder	*Pseudopleuronectes americanus*
Winter skate	*Raja binoculata*
Witch flounder	*Glyptocephalus cynoglossus*
Yellowtail flounder	*Limanda ferruginea*

SAMPLE PREPARATION FOR CHEMICAL ANALYSIS

At the laboratory fish steaks were thawed, skinned, and boned. Muscle and liver tissues of 5-10 fish from each station were combined into single composite samples for mercury analysis although some muscle and liver tissues were also analyzed individually. Invertebrates were pooled into composites of 10 animals per station. Samples were homogenized in an electric blendor composed of stainless steel blades and a glass jar.

Plankton samples were processed in a Vir-Tis model 10-100 freeze-drier for 48 hours. Plankton data are reported on a wet-weight basis. Entire sediment samples about 3-5 inches deep and 1½ inches in diameter were thoroughly mixed by hand in a plastic bag prior to analysis.

MERCURY ANALYSIS

Samples were analyzed according to the procedure of the Division of Laboratories, Ontario Ministry of the Environment (*2*). Plankton samples and ground flesh or liver samples ranging from 0.1 to 0.5 g were weighed into 30-ml Kjeldahl flasks. Ten ml 4:1 reagent grade concentrated sulfuric acid:nitric acid were added and the sample was shaken in a 50°-60° C water bath. Digestion was considered complete after 1½-2 hours when a clear solution was obtained. Flasks and samples were cooled at room temperature for 1 hour and placed in ice while 15 ml 6 percent potassium permanganate was slowly added to each sample. After addition of permanganate, samples were left overnight at room temperature.

A 20 percent sulfuric acid solution was added and samples were transferred to glass washing bottles equipped with fritted stems. Twenty ml reductant consisting of 100 ml concentrated sulfuric acid, 15 g sodium chloride, 30 g hyroxylamine sulfate, and 60 g stannous sulfate made up to 1,000 ml with distilled water were added to the sample and stirred for 1 minute. Mercury was swept by air through a 2.5-cm cell mounted in the light path of a Perkin Elmer model 305 atomic absorption spectrophotometer. Air flow rate was adjusted to give about 60 percent recorder response for 0.3 μg mercury. Peak heights of sample recorder response were compared to those of standards carried through the same digestion procedure described above for quantitation.

The method was checked for accuracy by comparing its results with those obtained by other procedures. A sample of oil-packed yellow fin tuna prepared by the National Canners Association was analyzed for mercury residues by nine laboratories using a variety of methods. The average mercury level obtained was 0.86 ppm; range was 0.80-1.02 ppm. The tuna sample studied at this laboratory was routinely analyzed with small batches of samples taken in the present study. An average value of 0.90 ppm with a relative standard deviation of 17.94 percent was obtained for 39 replicate determinations.

The procedure for mercury analysis of sediment samples was obtained from the Chemistry Laboratory Manual—Bottom Sediments, December 1969, compiled by the Great Lakes Region Committee on Analytical Methods, Federal Water Quality Administration, a predecessor of the U.S. Environmental Protection Agency. Samples ranging between 0.2 and 0.5 g were weighed into 125-ml Erlenmeyer flasks and 10 ml distilled water and 5 ml of 1:3 lactic acid:HCl (aqua regia) were added. Samples were heated for 2 minutes in a 95° C water bath and cooled in tap water for 10-15 minutes. Fifty ml distilled water and 15 ml of a 6 percent potassium permanganate solution were added to each flask. Then samples were reduced and analyzed by atomic absorption spectrophotometry as described for fish tissue except that sediment samples were analyzed the day they were digested.

Percent recoveries of $HgCl_2$ added to fish muscles and sediment prior to digestion are given in Table 2. Mercury was added to fish muscle before any acids or other reagents and was not allowed to equilibrate with muscle prior to addition of acid. Mercury added to sediment was allowed to stand for 2 hours prior to addition of water and acid. Sensitivity was about 0.05 ppm.

TABLE 2. *Percent recovery of mercury from fish and sediment, North Atlantic offshore waters—1971*

Species	Mercury Added, μg [1]	No. Replicates Analyzed	Recovery, %	
			Range	Average
Fishmeal	0.05	6	81.9-118.1	95.4
Swordfish	0.1	6	100.7-127.9	113.7
Yellow perch	0.2	6	80.9-108.0	96.9
Carp	0.2	6	89.7-102.3	95.1
Yellowfin tuna	0.3	5	95.4-105.1	98.6
Skipjack tuna	0.5	5	103.1-111.9	108.2
Sediment	0.3	6	105.0-119.0	111.5

[1] $HgCl_2$ used for mercury addition.

Results

Mercury concentrations among individual specimens were similar for most fish species although variations among individuals were observed for cusk and spiny dogfish (Table 3). One cusk collection had mercury concentrations ranging from 0.14 to 1.33 ppm in the liver and from 0.15 to 0.59 ppm in the muscle. In a second collection, variation among individuals was less: residues ranged from 0.16 to 0.34 ppm in the muscle and from 0.13 to 0.40 ppm in the liver.

Variation among four of six collections of spiny dogfish individuals was substantial. Mercury levels in these samples were: 0.20-0.61 ppm, 0.35-0.69 ppm, 0.35-0.93 ppm, and 0.22-0.65 ppm. Mercury content among individuals in the other two collections ranged only from 0.17 to 0.29 ppm and from 0.14 to 0.29 ppm.

MERCURY LEVELS AND FEEDING HABITS

In an attempt to correlate mercury concentrations with feeding habits, fish were grouped according to similar feeding patterns. The majority collected were bottom-feeders, others were primarily pelagic and plankton feeders and a few species could not be grouped into a particular feeding habit and were listed as miscellaneous. Feeding habits and mercury concentrations did not correlate (Table 4).

MUSCLE

Highest levels of mercury in fish muscle were found in cusk, spiny dogfish, northern searobin, and striped searobin (Table 5). The highest mercury concentrations in these samples were 0.49, 0.53, 0.35, and 0.35 ppm, respectively. The 36 other fish species had mercury levels in muscle that were less than 0.30 ppm. Mercury levels in all fish muscle sample averaged 0.154 ± 0.124 ppm.

LIVER

Highest mercury levels in fish livers were detected in blackbelly rosefish, cusk, northern searobin, and American shad (Table 5). The highest mercury levels in these samples were 0.40, 0.83, 0.56, and 0.67 ppm, respectively. The other 36 species of fish had mercury levels below 0.30 ppm in the liver (Table 5). Concentrations in livers of all fish examined averaged 0.164 ± 0.157 ppm.

MUSCLE AND LIVER

Mercury residues in fish samples averaged 0.154 ppm in muscle and 0.164 ppm in liver. Investigators have shown that liver accumulates metals to a greater extent than do most other tissues and organs (*3-5*). Data in this study, however, reflected an important difference: similar concentrations of mercury occurred in muscle and liver for most species examined. Exceptions to this rule were spiny dogfish, blackbelly rosefish, American shad, and Atlantic herring. Levels in spiny dogfish were two to three times higher in muscle than in liver, whereas in the other species mercury concentrations were greatest in the liver. Ratios of mercury levels in liver to those in muscle for other species were blackbelly rosefish, 2:1; American shad, 13:1; and Atlantic herring, 5:1.

PLANKTON, SEDIMENT, AND INVERTEBRATES

Mercury levels in all 9 plankton and 10 sediment samples were less than 0.05 ppm (Table 6). Pandallis shrimp, scallops, and squid generally had mercury levels less than 0.05 ppm (Table 7). However, the mercury levels of one squid sample and one shrimp sample were 0.06 ppm and 0.09 ppm, respectively. The single lobster sample obtained had mercury levels of 0.31 ppm in the tail meat and 0.60 ppm in liver (Table 7).

Discussion

This study measures total mercury: organic and inorganic forms. Methylmercury is considered more toxic to humans than are inorganic mercury salts and thus its occurrence in fish is of more toxicological significance

TABLE 3. *Mercury concentrations in individual fish samples, North Atlantic offshore waters—1971*

Species	Tissue	No. Fish Analyzed	Mercury Content, ppm wet weight		
			Range	Average	Standard Deviation
American dab	muscle	5	0.03-0.16	0.08	0.064
Atlantic cod	muscle	4	0.10-0.15	0.14	0.081
	liver	4	0.08-0.15	0.12	0.017
	muscle	5	0.10-0.38	0.24	0.135
	liver	5	0.10-0.36	0.18	0.109
Atlantic herring	liver	5	0.20-0.44	0.26	0.103
Atlantic wolffish	muscle	5	0.08-0.25	0.16	0.063
Blackbelly rosefish	muscle	5	0.12-0.31	0.22	0.095
Cusk	muscle	6	0.16-0.34	0.27	0.089
	liver	6	0.13-0.40	0.24	0.095
	muscle	6	0.15-0.59	0.41	0.189
	liver	6	0.14-1.33	0.65	0.440
Fourspotted flounder	muscle	5	0.09-0.19	0.16	0.031
Haddock	liver	5	0.05-0.09	0.06	0.014
Little skate	muscle	5	0.05-0.18	0.12	0.060
	liver	5	0.06-0.15	0.10	0.033
Mackerel	muscle	5	0.07-0.10	0.08	0.016
Pollock	muscle	5	0.06-0.12	0.10	0.029
	liver	5	0.05-0.09	0.06	0.016
Redfish	muscle	6	0.15-0.29	0.20	0.050
Red hake	muscle	5	0.05-0.09	0.06	0.000
Silver hake	muscle	5	0.06-0.14	0.09	0.034
Spiny dogfish	muscle	4	0.17-0.29	0.23	0.052
	muscle	10	0.20-0.61	0.34	0.160
	muscle	5	0.35-0.69	0.54	0.135
	muscle	5	0.35-0.93	0.58	0.270
	muscle	5	0.22-0.65	0.44	0.154
	muscle	5	0.14-0.29	0.18	0.064
Thorny skate	muscle	5	0.11-0.41	0.19	0.116
	muscle	4	0.15-0.36	0.26	0.113
	liver	4	0.12-0.17	0.15	0.033
White hake	muscle	5	0.08-0.17	0.12	0.037
	liver	5	0.05-0.18	0.12	0.055
Windowpane flounder	muscle	5	0.06-0.18	0.10	0.045
Winter flounder	muscle	5	0.06-0.12	0.08	0.022
	liver	5	0.12-0.26	0.18	0.044
Witch flounder	muscle	5	0.08-0.11	0.09	0.000
	liver	5	0.07-0.17	0.12	0.045
Yellowtail flounder	muscle	5	0.07-0.13	0.10	0.022

TABLE 4. *Mercury concentrations in fish grouped according to feeding habits, North American offshore waters—1971*

Fish	No. Collections Analyzed [1]	Mercury Content, ppm wet weight			
		Muscle		Liver	
		Range	Average	Range	Average
Bottom Feeders					
American dab	2	0.06-0.08	0.07	0.11-0.14	0.13
Atlantic cod	2	0.14-0.25	0.20	0.11-0.20	0.16
Atlantic wolffish	2	<0.05-0.15	0.08	<0.05-0.06	<0.05
Blackbelly rosefish	1	0.22	0.22	0.40	0.40
Black sea bass	1	0.08	0.08	0.18	0.18
Cusk	4	0.15-0.49	0.31	0.14-0.83	0.42
Fourspot flounder	2	0.16	0.16	0.23-0.27	0.25
Gulf Stream flounder	2	0.05	0.05	ND	ND
Haddock	2	<0.05-0.09	0.06	<0.05	<0.05
Little skate	2	0.13-0.16	0.15	0.10-0.23	0.17
Longhorn sculpin	2	0.08-0.09	0.09	0.09-0.16	0.13
Ocean pout	2	<0.05-0.11	0.07	<0.05-0.09	0.06
Red hake	2	<0.05-0.05	<0.05	<0.05-0.08	0.06
Striped searobin	1	0.35	0.35	0.38	0.38
Thorny skate	2	0.21-0.26	0.24	0.09-0.15	0.12
White hake	2	0.10-0.12	0.11	0.12-0.16	0.14
Windowpane flounder	1	0.10	0.10	0.12	0.12
Winter flounder	3	0.06-0.14	0.09	0.07-0.18	0.11
Winter skate	1	0.15	0.15	0.18	0.18
Witch flounder	2	0.07-0.10	0.09	0.13-0.16	0.15
Yellowtail flounder	2	0.10-0.24	0.17	0.17-0.25	0.21
Pelagic Feeders					
Pollock	2	0.08-0.10	0.09	<0.05-0.06	<0.06
Redfish	2	0.10-0.20	0.15	0.15	0.15
Spot	1	<0.05	<0.05	<0.05	<0.05
Silver hake	1	0.09	0.09	0.10	0.10
Plankton Feeders					
American shad	1	0.05	0.05	0.67	0.67
Atlantic herring	2	<0.05-0.09	0.06	0.26-0.28	0.27
Mackerel	1	0.08	0.08	ND	ND
Miscellaneous					
Angel shark	1	0.08	0.08	<0.05	<0.05
Cusk-eel	1	0.11	0.11	0.19	0.12
Spiny dogfish	8	0.07-0.53	0.32	<0.05-0.19	0.10

NOTE: ND = no data.
[1] Each collection includes 6-10 animals.

than is the occurrence of total mercury. Reports conflict concerning methylmercury:total mercury ratios in fish. Japanese investigators report that methylmercury does not exceed about 15 percent of the total mercury in fish whereas Swedish scientists have reported that these mercury concentrations are mostly methylmercury (*6*).

The Food and Drug Administration bases its administrative guideline of 0.5 ppm mercury in fish on total mercury content. Thus data presented here can be compared to the guideline. The only muscle samples in this survey that approached this level were those in cusk and spiny dogfish. Cusk measuring 61-67 cm had an average mercury content of 0.49 ppm. Levels in three groups of spiny dogfish muscle averaged 0.44, 0.47, and 0.53 ppm, whereas levels in five other groups of dogfish ranged from 0.07 to 0.34 ppm. The average of 0.154 ± 0.124 ppm for all fish muscle samples shows most fish well below the guideline level.

With the exception of cusk and spiny dogfish, fish examined in this study do not have abnormal mercury concentrations in relation to levels in marine fish reported by other investigators. Twelve of 15 species of Oregon groundfish had mercury levels in the range of 0.08-0.24 ppm. Yellow rockfish, lingcod, and spiny dogfish had average levels of 0.37, 0.35, and 0.60 ppm, respectively (*7*). The latter concentration was higher than the level reported for spiny dogfish in the present study.

Of about 21 species of marine fish and shellfish, only swordfish consistently had mercury levels at or over 0.5 ppm in an FDA study of marine and freshwater fish (*8*). Three thousand samples of canned tuna had an average mercury content of 0.25 ppm; less than 4 percent of these samples had levels over 0.5 ppm. The average mercury content of 19 other species of marine fish and shellfish was 0.3 ppm although most were below 0.1 ppm.

Mercury levels in fish landed in England and Wales have also been determined (*9*). Investigators there reported that mercury levels in fish from deep-water fishing areas averaged 0.06 ppm. Those caught away from coastal waters in the North Sea had an average concentration of 0.10 ppm whereas residues in fish caught in

TABLE 5. *Mercury concentrations in composite fish samples, North Atlantic offshore waters—1971*

Species	Sample Data					Mercury Content		
						Average, ppm wet weight		
	Latitude	Longitude	Depth, fathoms [1]	Date	Length, cm [1]	Muscle	Whole Animal	Liver
American dab	42° 48′	70° 38′	15-62	4-17	32-36	0.08		0.14
	41° 21′	68° 46′	28-62	10-19	ND	0.06		0.11
American shad	ND	ND	23-62	ND	ND	0.05		0.67
Angel shark	36° 11′	74° 48′	58-105	4-4	43-58	0.08		<0.05
Atlantic cod	41° 44′	69° 40′	58-115	10-18	ND	0.25		0.20
	42° 12′	70° 06′	15-62	11-4	54-61	0.14		0.11
Atlantic herring	41° 38′	68° 37′	28-62	10-18	ND	<0.05		0.26
	40° 23′	71° 02′	28-62	3-10	20	0.09		0.28
Atlantic wolffish	42° 42′	66° 07′	30-52	4-25	78-93	0.15		<0.05
	42° 55′	65° 01′	50-105	11-7	20-74	0.07		<0.05
Beardfish	37° 07′	74° 33′	58-105	4-5	13-14		0.06	
Blackbelly rosefish	39° 11′	72° 32′	95-200	10-7	16-34	0.22		0.40
Black sea bass	36° 50′	74° 42′	28-62	4-5	22-24	0.08		0.18
Butterfish	36° 37′	75° 20′	10-32	4-3	10		0.06	
Cusk	42° 46′	66° 37′	48-105	11-13	61-67	0.49		0.83
	42° 48′	70° 07′	55-130	4-18	44-68	0.27		0.23
Daubed shanny	43° 44′	69° 08′	5-62	4-21	8-12		0.05	
Fawn cusk-eel	40° 13′	71° 04′	58-105	10-8	25-29	0.11		0.19
Fourspot flounder	40° 24′	71° 57′	28-62	3-11	16-19	ND		0.27
	39° 09′	73° 12′	28-62	10-6	21-34	0.16		0.23
Gulf Stream flounder	38° 01′	74° 14′	28-62	10-5	6-12	0.05		ND
Haddock	41° 32′	69° 31′	10-35	10-18	ND	0.09		<0.05
	41° 01′	67° 06′	28-62	3-16	46-68	<0.05		<0.05
Lanternfish	41° 35′	61° 55′	95-200	10-22	ND		<0.05	
Little skate	40° 22′	68° 46′	28-62	10-16	ND	0.16		0.23
	40° 57′	71° 18′	13-33	3-30	45-50	0.13		0.10
Longhorn sculpin	40° 46′	68° 35′	10-34	10-17	ND	0.09		0.16
	41° 12′	71° 17′	13-33	3-10	25	0.08		0.09
Mackerel	39° 59′	71° 40′	28-62	3-11	30-35	0.08		ND
Mailed sculpin	43° 35′	66° 41′	50-115	4-23	8-13		<0.05	
Northern searobin	37° 53′	74° 41′	10-32	10-9	24-27	0.35		0.56
Ocean pout	40° 23′	73° 06′	11-32	3-31	45-55	0.11		0.09
	40° 55′	71° 63′	11-35	3-10	46	<0.05		<0.05
Pollock	42° 48′	66° 37′	48-105	4-24	51	0.08		<0.05
	41° 25′	69° 08′	58-115	10-19	ND	0.10		0.06
Redfish	41° 42′	69° 16′	58-115	3-24	38	0.20		0.15
	41° 57′	69° 02′	58-115	10-19	41-57	0.10		0.15
Red hake	40° 24′	71° 57′	28-62	3-11	25-30	<0.05		<0.05
	40° 33′	71° 57′	28-62	9-30	27-34	0.05		0.08
Round herring	40° 09′	73° 31′	11-32	10-4	15-16		<0.05	
Silver hake	39° 55′	72° 05′	28-62	10-7	28-31	0.09		0.10
Spiny dogfish	42° 20′	65° 35′	48-105	4-29	68-75	0.23		0.07
	42° 17′	66° 34′	90-160	3-21	ND	0.32		0.06
	44° 16′	66° 51′	50-135	11-15	81-84	0.34		0.09
	40° 32′	71° 20′	28-62	3-11	37	0.07		<0.05
	36° 28′	75° 08′	10-32	4-3	80-92	0.53		0.19
	38° 14′	73° 44′	58-105	4-8	82-95	0.47		0.07
	40° 29′	72° 26′	11-32	10-1	60-86	0.44		0.15
	40° 43′	70° 26′	11-35	10-15	ND	0.18		0.12
Spot	37° 29′	75° 13′	10-32	10-10	27-29	<0.05		<0.05
Striped searobin	36° 00′	74° 53′	28-62	4-4	28-37	0.35		0.38
Thorny skate	42° 41′	66° 12′	30-52	4-25	60-93	0.21		0.09
	44° 07′	66° 35′	15-62	11-15	60-81	0.26		0.15
White hake	42° 44′	69° 40′	90-155	4-18	57-68	0.12		0.12
	42° 16′	70° 22′	15-62	11-3	27-72	0.10		0.16
Windowpane flounder	41° 09′	70° 47′	11-35	9-29	22-31	0.10		0.12
Winter flounder	40° 11′	67° 56′	15-62	4-21	22-46	0.07		0.08
	40° 42′	72° 31′	11-32	10-1	28-35	0.14		0.18
Winter skate	40° 46′	68° 35′	10-34	10-17	ND	0.15		0.18
Witch flounder	38° 13′	73° 51′	95-200	4-8	31-36	0.07		0.16
	40° 32′	70° 57′	28-62	10-8	42-50	0.10		0.13
Yellowtail flounder	40° 16′	73° 24′	11-32	3-31	28-32	0.24		0.17
	40° 29′	71° 49′	28-62	9-30	33-38	0.10		0.25

NOTE: ND = no data.
[1] Values reported in ranges only; depth range represents a bottom contour from which the fish was taken.

the Irish Sea were twice as high. The average level of about 0.15 ppm for all groundfish examined in the present study falls midway between North Sea and Irish Sea data.

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TABLE 6. *Mercury concentrations in plankton and sediment, North Atlantic offshore waters—1971*

Sample Data				Mercury Content
Latitude	Longitude	Depth, fathom	Date	Average, ppm wet weight
Plankton				
42° 50′	64° 32′	50-100	4-27	<0.05
43° 33′	68° 44′	55-110	4-21	<0.05
42° 13′	69° 59′	55-130	11-4	<0.05
43° 05′	68° 40′	60-120	11-17	<0.05
41° 29′	66° 47′	28-62	10-22	<0.05
36° 03′	74° 52′	28-62	4-4	<0.05
36° 51′	75° 20′	10-32	4-3	<0.05
39° 19′	73° 51′	10-32	4-1	<0.05
37° 14′	74° 58′	10-32	10-12	<0.05
Sediment				
42° 50′	64° 32′	50-100	4-27	<0.05
43° 33′	68° 44′	55-110	4-21	<0.05
43° 12′	70° 05′	55-130	11-8	<0.05
43° 05′	68° 40′	60-120	11-17	<0.05
43° 14′	68° 42′	60-120	11-17	<0.05
36° 03′	74° 52′	28-62	4-4	<0.05
36° 51′	75° 26′	10-32	4-3	<0.05
39° 19′	73° 51′	10-32	4-1	<0.05
40° 19′	70° 29′	23-62	10-15	<0.05
37° 14′	74° 58′	10-32	10-12	<0.05

TABLE 7. *Mercury concentrations in invertebrates, North Atlantic offshore waters—1971*

	Sample Data					Mercury Content		
						Average, ppm wet weight		
Species	Latitude	Longitude	Depth, fathoms	Date	Length, cm	Muscle	Whole Animal	Liver
Lobster *(Homarus americanus)*	39° 21′	72° 15′	95-200	4-9	6-19	0.31 [1]		0.60
Pandallid shrimp (unclassified)	42° 04′	68° 44′	58-115	4-19	ND		0.09	
	42° 48′	70° 38′	15-62	4-17	ND		<0.05	
	41° 19′	61° 20′	10-35	3-23	ND		<0.05	
Scallops *(Placopecten magellanicus)*	38° 10′	74° 07′	28-62	10-6	5-7	<0.05		—
Squid *(Illex illecebrosus)*	40° 13′	71° 07′	58-105	3-11	ND		<0.05	
	39° 38′	72° 60′	28-62	10-4	ND		<0.05	
	40° 02′	71° 11′	95-200	10-8	18-22		<0.05	
	36° 19′	74° 48′	95-200	4-4	ND		0.06	

NOTE: ND = no data.
[1] Lobster muscle sample from tail only.

Baseline Concentrations of Polychlorinated Biphenyls and DDT in Lake Michigan Fish, 1971 [1]

Gilman D. Veith [2]

ABSTRACT

Responding to the recommendations of the Lake Michigan Interstate Pesticide Committee, the author aimed to establish baseline data on polychlorinated biphenyls (PCB's) and DDT in Lake Michigan fish in 1971. Because the past 2 years had witnessed unprecedented legislative action to protect food resources and other aquatic species near the top of the food chain from persistent hazardous chemicals, the author also attempted to gauge the impact of cooperative legislative action on the quality of large lakes.

Thirteen species of fish taken from 14 regions of Lake Michigan in the fall of 1971 were analyzed for PCB's and DDT analogs. Mean wet-weight concentrations of PCB's similar to Aroclor 1254 ranged from 2.7 ppm in rainbow smelt to 15 ppm in lake trout. Most trout and salmon longer than 12 inches contained PCB's at concentrations greater than the tolerance level of 5 ppm established by the Food and Drug Administration, U.S. Department of Health, Education, and Welfare. Mean concentrations of total DDT ranged from less than 1 ppm in suckers to approximately 16 ppm in large lake trout. The presence of the major chlorinated hydrocarbons was confirmed by gas-liquid chromatography/mass spectrometry; additional PCB confirmations were obtained through perchlorination. The most abundant PCB's were tetra-, penta-, hexa-, and heptachlorobiphenyls which are similar to commercially prepared Aroclor 1254; lesser chlorinated PCB's were present in fish from nearshore waters.

Introduction

This paper identifies and quantifies the most abundant organochlorine compounds, particularly polychlorinated biphenyls (PCB's) and DDT, in Lake Michigan fish in 1971. By establishing data on PCB's and DDT in Lake Michigan fish as recommended by the Lake Michigan Interstate Pesticide Committee, the author of the present study aimed to develop a 1971 baseline to predict trends of these chemicals in the lake. Lake Michigan contains much higher concentrations of potentially hazardous and persistent organic chemicals than the other Great Lakes, in part because of their widespread usage in the watershed and their disproportionally brief flushing period and low biomass density. Previous studies have shown that fish from Lake Michigan approach the action levels for dieldrin set by the Food and Drug Administration (FDA), U.S. Department of Health, Education, and Welfare (*1*); a major percentage of Lake Michigan fish exceeded the 5 ppm action level for DDT in 1969 (*2*). Similarly, Veith (*3*) has shown that PCB concentrations similar to Aroclor 1254 were greater than 15 ppm or three times the FDA action level in large fish captured from Lake Michigan in 1969.

Despite the comparatively high levels of DDT, dieldrin, and PCB's in Lake Michigan, there is no unequivocal evidence that they are endangering aquatic life. Concentrations of these chemicals appear to be below 10 parts per trillion (ppt) in the pelagic water and less than 100 ppt in nearshore waters. However, considerable indirect evidence suggests that the buildup of organochlorine compounds may threaten biological resources of the lake. Other reports have reviewed the chronic toxicity of pesticides and PCB's (*4-7*).

[1] Supported by U.S. Environmental Protection Agency Project 16020 PBE, University Engineering Experiment Station, and University of Wisconsin Department of Civil and Environmental Engineering, Madison, Wis.

[2] National Water Quality Laboratory, U.S. Environmental Protection Agency, 6201 Congdon Boulevard, Duluth, Minn. 55804.

States surrounding Lake Michigan have made a major effort to restock the lake with brown, lake, and rainbow trout and coho and chinook salmon. Between 1963 and 1970, over 600,000 rainbow trout were released by Wisconsin alone (*8,9*). However, Reinert (*2*) previously noted that DDT and dieldrin levels in eggs of these fish are similar to concentrations which inhibited reproduction in the studies of Burdick et al. (*10*) and Macek (*11*). Johansson et al. (*12*) have shown that 15 ppm PCB's (lipid basis) in salmon eggs produced mortality in 50 percent of the samples tested. Death can be expected in all eggs when the PCB lipid content reaches 25 ppm.

Although continued stocking of fish may maintain a food resource, many fish contain residue body burdens which make them unfit for consumption. The effect of these fish on mink production in the North Central States has been studied in detail: before DDT and dieldrin concentrations in these fish had been well documented, Hartsough (*13*) indicated that the fish were suspected to inhibit mink reproduction; Aulerich et al. (*14*) clearly demonstrated that the fish had been the cause of the minks' reproductive failure; and Aulerich and Ringer (*15*) reported that DDT and DDD did not have significant adverse effects on mink. Furthermore, dieldrin was lethal to mink at 2.5 ppm in the food when fed for extended periods, but did not appear to affect reproduction at twice this concentration during the gestation period. Aulerich et al. concluded that feeding coho salmon to mink did not cause reproduction problems, but that the disorder is associated with other species of fish and ". . . appears to be dependent upon the species of fish and its environment" (*16*). Finally, after the earlier reports that PCB's were present in Lake Michigan fish, Ringer et al. (*17*) demonstrated that 10 ppm Aroclor 1254 in coho salmon produced 71 percent mortality in mink and that a mixture of 10 ppm PCB's and 0.5 ppm dieldrin in coho feed produced 100 percent mortality. No kits were born alive when the diet contained 5 ppm or more Aroclor 1254 alone. This clearly indicates that biological resources of Lake Michigan may seriously endanger other species even though concentrations of toxicants are not severe enough to produce readily discernible effects within the aquatic communities.

Equally important is the coincidence of high chlorinated hydrocarbon levels in herring gull and other bird populatons coupled with reproductive failures and subsequent population decline (*18*). Anderson (*19*) found that the eggs of the Great Lakes herring gull contained the highest chlorinated hydrocarbon levels ever reported for that species. He also found that the degree of eggshell thinning in the Lake Michigan gull, whose population declined dramatically in the early 1960's, varied from 9 percent in 1953-56 to 18 percent in 1965. In comparison, eggs of gulls on Lake Huron and Lake Superior have exhibited shell thinning of 7 percent and 8 percent, respectively, and those from gulls on the East Coast have remained essentially unchanged. Double-crested cormorants from Wisconsin had eggshells 20 percent thinner than those of gulls, and their eggs had the highest DDE concentrations of any cormorant eggs sampled from interior North America. Golden eagles, which feed primarily on mammals, do not show eggshell thinning as dramatic as that of bald eagles, which feed on fish (*19*).

Lake Michigan is the only Great Lakes watershed where major persistent chemicals have been curtailed. Although use of chlorinated pesticides in agriculture was probably diminishing in the late 1960's, the Lake Michigan Enforcement Conference recommended regulatory actions on many uses in 1968. This recommendation led to restrictions on DDT including its sale in Illinois, Michigan, and Wisconsin. A more detailed summary is presented by Lueschow (*20*). Monsanto Company, the sole producer of PCB's in the United States, restricted PCB sales in 1970; by April 1971 they were sold only to close-system users.

To measure the impact of the unprecedented cooperative legislative action regarding these chemicals, and to establish baseline data, the Lake Michigan Interstate Pesticide Committee recommended that this study be funded.

Sampling Procedures

Fish were collected in September and October 1971 with gill nets and pond nets from the four regions of Lake Michigan outlined in Figure 1. Whole fish were stored frozen (−20° C) in aluminum foil or polyethylene bags for 60 days or less and homogenized while frozen by repeatedly passing them through a meat grinder. All metal surfaces were rinsed with acetone, polyethylene bags were examined for interferences, and the grinder bearing and seal were checked periodically to assure that the sample was not contaminated during storage or preparation.

Analytical Procedures

REAGENTS

Sodium sulfate (Fisher Scientific Co.) was washed with three volumes of 1:1 hexane-acetone and dried at 130° C. To prevent further contamination from cap liners or containers, the Na_2SO_4 was stored in large glass bottles with aluminum foil liners in the cap.

The florisil (Kensington Chemical, Fisher Scientific Co.) was extracted in an all-glass Soxhlet extractor for 24 hours with the azeotrope of hexane and acetone to remove traces of organic impurities. The solvent was evaporated from the florisil at 100° C, and the solid was heated at 650° C for 2.5 hours for activation. If not used immediately after heating, the florisil was heated to 105° C before use.

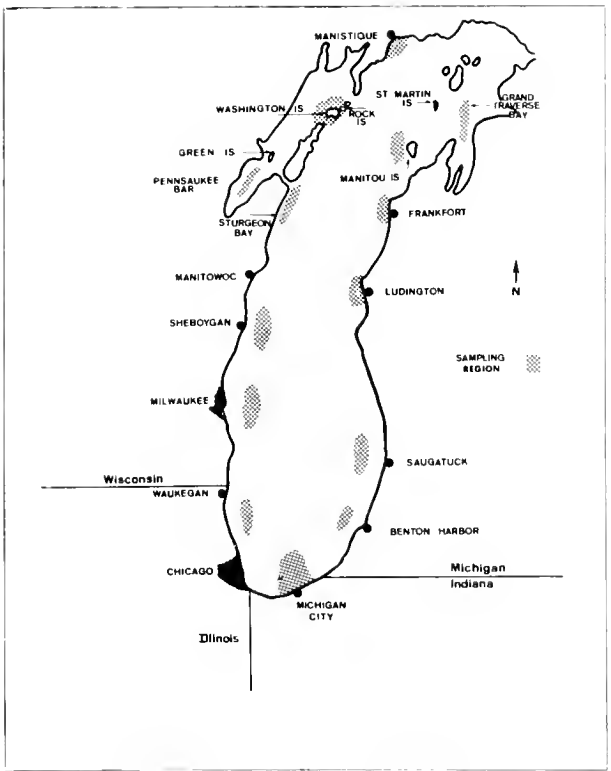

FIGURE 1. *Sampling regions for collecting fish, Lake Michigan—1971*

Other analytical components included:

Silicic acid:	Mallinckrodt Chemical, AR grade, Ramsey and Patterson. Used directly from reagent bottle.
Hexane:	Skelly B. Redistilled in glass from Dri-Sodium, Fisher Scientific Co.
Acetone:	Fisher Scientific Co., MCB. Redistilled in glass from Dri-Sodium, Fisher Scientific Co.
Ethyl ether and methylene chloride:	Mallinckrodt Chemical. Pesticide-quality solvents. Used directly from reagent bottle after periodic checks showed no interferences.
Glass wool:	Soaked in acetone, rinsed with 1:1 acetone:hexane mixture.
Glassware:	Washed thoroughly with hot detergent; rinsed once with hot water, twice with distilled water, again with 1:1 mixture of redistilled acetone:hexane.

PREPARATION OF SAMPLES

Procedures to extract and remove the bulk of the lipids have been described previously (*21*). Because of the high relative concentration of *p,p'*-DDE in Lake Michigan fish, DDE was quantitated directly by diluting 10 percent of the nonpolar florisil eluate to the appropriate volume for gas-liquid chromatographic (GLC) analysis. PCB's were separated from TDE and DDT isomers with a modified Armour and Burke procedure which omitted Celite 545 (*22*).

Quantitative gas chromatographic analyses were conducted on an Aerograph 1745-20 gas chromatograph equipped with dual concentric-tube electron-capture detectors (^{3}H, 250 mc). Columns were 2.0-m-by-1.8-mm-ID glass coils packed with 3 percent OV-101 on 120/140-mesh Gas-Chrom Q. The carrier gas, purified N_2, was maintained at 20 ml min; the injector, column, and detector temperatures were 240°, 180°, and 220° C, respectively. Chromatograms were recorded on a Varian model A-25 dual pen recorder.

Previous work (*21*) showed that fish from Lake Michigan contain mixtures of PCB's that closely resemble the Aroclor 1254 produced by Monsanto Company, although PCB's both heavier and lighter than those most abundant in Aroclor 1254 were also present. The fish extracts contain predominantly those PCB's which elute at 70, 84, a doublet of 98 and 104, 125, 146, and 176; peak height of *p,p'*-DDE is represented here as 100 (Fig. 2). The presence of DDE precluded the use of the 98 and 104 PCB components in the quantitation, and PCB's based on Aroclor 1254 were determined by summing the heights of the 70, 84, 125, 146, and 174 PCB components when peak height of DDE is 100. This method also decreased the effect of minor compositional variations on the analytical result.

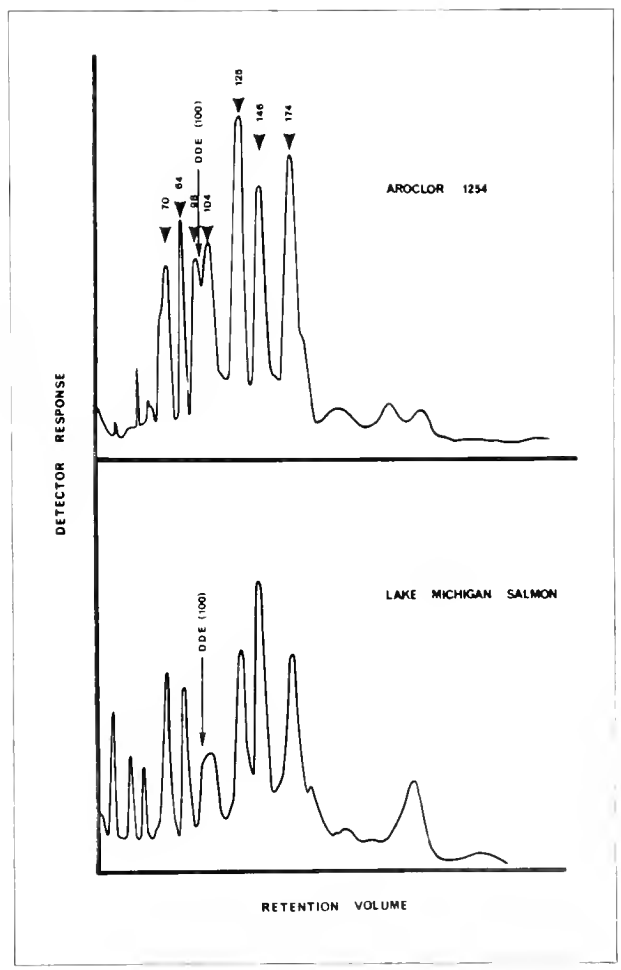

FIGURE 2. *Chromatograms of PCB mixtures in Aroclor 1254 and fish from Lake Michigan*

Recovery of PCB's from fish tissue averaged 85.1 ± 4.3 percent, whereas recovery of DDE was greater than 90 percent. The precision of the method outlined above is summarized in Table 1, which lists means and standard deviations of the analyses of six replicates of several fish species for PCB's, DDT, and lipids. The standard deviation for PCB analyses ranged from 5 percent in smaller fish to 14 percent in large coho salmon. The decrease in precision in analyses of large coho resulted from the difficulty of homogenizing larger fish. Precision was poorest in DDT analyses, where the standard deviation ranged from 8 to 23 percent with a mean of approximately 14 percent. This reduced precision results from losses during silicic acid chromatography which is used to quantitate the TDE and DDT isomers. The precision of DDE analyses was greater than those for DDT analyses, which was anticipated because of the fewer manipulations of the extracts. The standard deviation ranged from 7 to 18 percent, but the average deviation was approximately 10 percent. Because of the relatively simple procedure, lipid analyses were most precise, exhibiting standard deviations from 5 to 7 percent.

TABLE 1. *Precision of chlorinated hydrocarbon determinations for PCB's, DDE, DDT, and lipids in selected fish, Lake Michigan—1971*

Species	No. Replicates	Aroclor 1254	*p,p'*-DDE	*p,p'*-DDT	Lipid, %
Coho salmon (25 in.)	6	15.2±2.2	7.5±0.6	3.2±0.6	4.2±0.2
Coho salmon (27 in.)	6	13.1±1.3	5.5±0.4	1.8±0.4	10.0±0.6
Whitefish (13 in.)	6	4.1±0.2	0.35±0.04	0.56±0.04	16.2±0.9
Bloater (10 in.)	6	5.7±0.4	3.4±0.3	2.2±0.3	18.2±1.3
Alewife (8 in., composite)	6	4.0±0.2	1.1±0.2	1.0±0.2	5.7±0.3

NOTE: In columns 3-6, first number represents mean, second represents standard deviation.
Residues are ppm wet weight.

The determinable limit for PCB analysis was approximately 0.1 ppm; limits for *p,p'*-DDT, *o,p'*-DDT, *p,p'*-TDE, and *p,p'*-DDE were approximately 0.05 ppm.

CONFIRMATION OF MAJOR COMPONENTS

Major components of Lake Michigan fish extracts were characterized for a limited number of composite samples by standard gas-liquid chromatography/mass spectrometry techniques. In addition, the presence of PCB's in samples from each collection area was confirmed by perchlorination of PCB's to decachlorobiphenyl and subsequent analysis of the product by GLC (*23*). Aliquots of the hexane fraction of silicic acid columns were evaporated to dryness in a 5-ml vial fitted with a teflon-lined screw cap. Antimony pentachloride (0.2 ml) was added to the residue, and the vial was sealed and held at 180° C for 6 hours. Approximately 1 ml 6N MCl was added to the products to remove the $SbCl_5$ and the solution was extracted with five 1-ml hexane portions. The hexane was passed through a disposable pipette containing anhydrous Na_2SO_4 to remove traces of the aqueous solution. The sample was collected in a graduated centrifuge tube and diluted to the proper volume for GLC analysis. This technique also provided semiquantitative information for PCB's to supplement direct GLC analysis of the extracts. For those samples which contained PCB's similar to Aroclor 1254, estimates of total PCB's by perchlorination were within 15 percent of direct GLC analysis.

Results and Discussion

Approximately 850 fish were analyzed for PCB mixtures most closely resembling Aroclor 1254; a summary is presented in Table 2. Mean concentrations ranged from 2.7 ppm in smelt to 15.5 ppm in lake trout. Larger fish, such as brown, lake, and rainbow trout and chinook and coho salmon, contained PCB's at mean concentrations two to three times the 5 ppm action level established by FDA (*1*). Mean PCB concentrations in redhorse suckers, smelt, and whitefish were considerably less than 5 ppm. Mean concentrations in the alewife, carp, chub, and yellow perch were approximately 5 ppm; the range was 4.2-6.0 ppm. As expected, PCB levels increased with the percentage of fat and size of fish.

In Lake Michigan fish the mean concentration of total DDT, the sum of *p,p'*-DDT, *o,p'*-DDT, *p,p'*-TDE, and *p,p'*-DDE, ranged from 0.9 ppm in carp to 7.1 ppm in lake trout (Table 2). As with PCB's, fish with higher lipid concentrations contained greater concentrations of DDT.

The ratio of PCB's to total DDT ranged from 1.3 in redhorse suckers caught primarily in the northern waters to 7.6 in carp. The ratio of PCB's to DDT in the majority of the fish was between 1.7 and 2.8, and only in the carp, redhorse, yellow perch, and white sucker did the ratios fall outside this range. This ratio may become important in future studies to determine the rates at which the chemicals are eliminated from the Lake Michigan system.

Mean ratios of *o,p'*-DDT to *p,p'*-DDT ranged from 0.1 to 0.3; this ratio in the majority of the fish was 0.2. Since technical DDT generally contains about 30 percent of the *o,p'*-DDT isomer (ratio, 0.4), data from Lake Michigan fish suggest that degradation, other removal mechanisms, or both in the lake are slightly greater for the *o,p'* isomer than for the *p,p'* isomer. More than 80 percent of the total DDT residue is accounted for by *p,p'*-DDE and *p,p'*-DDT.

Not only did PCB concentrations vary considerably among the 13 species captured, but the range of PCB concentrations in a single lake species was generally

greater than 100 percent. The concentration range in red suckers was less, but all were captured in the same region of the lake. Although some variation in concentrations is expected because of the normal analytical error, the much larger ranges in Table 2 are undoubtedly due to other factors that limit usefulness of the mean concentrations presented. Previous research has shown that the lipid content, size of fish, season of capture, and concentration in the water may affect considerably the observed concentration of chlorinated hydrocarbons in tissue (2).

CHLOROBIPHENYLS

Regional variation in PCB concentrations and variations due to lipid content for each species are shown in Table 3. The wet-weight concentration of PCB's in ale-

TABLE 2. *Major chlorocarbons in fish, Lake Michigan—1971*

Species [1]	No. Fish Analyzed	Mean Fish Weight, g	Mean Lipid, %	Mean PCB's	Mean DDE	Mean ΣDDT	Mean PCB/ ΣDDT	Mean DDE/ ΣDDT	Mean *o,p'*-DDT/ *p,p'*-DDT
Alewife	85	100	6.5[3.9]	4.6[2.1]	1.7[0.8]	2.2[1.1]	2.4	0.8	0.2
Bloater	287	249	20.0[5.9]	6.0[2.2]	2.5[1.1]	3.8[2.8]	2.2	0.7	0.2
Brown trout	17	3,650	15.5[4.1]	7.3[2.8]	2.7[1.0]	4.2[1.6]	1.8	0.6	0.1
Carp	42	2,160	10.0[7.0]	4.2[3.6]	0.7[0.9]	0.9[1.2]	7.6	0.8	0.3
Chinook salmon	21	3,100	5.0[3.9]	11.4[4.0]	5.2[1.5]	6.8[2.5]	1.7	0.8	0.2
Coho salmon	56	2,720	6.5[2.1]	11.5[5.7]	4.8[2.3]	6.3[2.8]	2.1	0.7	0.2
Lake trout	134	1,620	16.6[4.3]	15.5[3.3]	5.0[2.8]	7.1[3.7]	2.5	0.7	0.2
Yellow perch	44	148	6.1[1.7]	5.8[3.5]	1.0[0.6]	1.6[1.1]	4.8	0.8	0.1
Rainbow trout	11	4,190	18.4[3.3]	9.3[4.1]	3.4[1.3]	4.2[1.8]	2.3	0.8	0.2
Redhorse sucker	16	902	8.6[1.2]	3.0[0.7]	1.6[0.5]	2.6[0.7]	1.3	0.6	0.2
Smelt	38	51	5.8[1.8]	2.7[1.3]	0.8[0.4]	1.2[0.6]	2.6	0.7	0.1
White sucker	51	1,130	5.9[2.8]	3.9[3.6]	1.0[0.5]	1.6[1.2]	3.4	0.7	0.1
Whitefish	43	1,170	17.6[4.4]	3.0[1.9]	0.8[0.3]	1.4[0.6]	2.8	0.7	0.2

NOTE: Expressions in brackets represent standard deviations.
Residues are ppm wet weight.
[1] Scientific names appear in Table 3.

TABLE 3. *Mean concentrations of PCB's and DDT in fish, Lake Michigan—1971*

Location	Capture Date	No. Fish Analyzed	PCB's	Percentage Fish Above 5 ppm PCB's	PCB's, lipid weight	*p,p'*-DDE	*p,p'*-TDE	*p,p'*-DDT	*o,p'*-DDT	Total DDT	Percentage Fish Above 5 ppm DDT
Alewife (*Alosa pseudoharengus*)											
Michigan City	10/15	10	4.4[2.0]	40	164	1.4	0.19	0.5	0.08	2.2	10
Benton Harbor	9/2	10	4.8[1.1]	40	60	1.8	0.23	0.5	0.08	2.7	0
Waukegan	8/23	2	2.5[0.1]	0	47	1.0	0.18	0.5	0.07	1.6	0
Saugatuck	4/11	12	5.3[2.2]	41	51	1.8	0.22	0.8	0.10	2.7	11
Sheboygan	10/15	4	5.5[1.4]	50	79	2.2	0.20	0.7	0.07	3.2	0
Ludington	7/3	16	4.4[1.4]	18	207	ND	ND	ND	ND	ND	ND
Frankfort	10/5	10	3.7[1.2]	20	62	1.3	0.16	0.4	0.06	1.9	0
Manitou Island	9/10	3	3.8[2.2]	33	51	3.2	0.33	1.3	0.16	5.0	30
Rock Island	9/11	3	8.9[12.0]	66	182	1.1	0.11	0.3	0.04	1.5	0
St. Martin Island	9/11	6	3.5[1.3]	16	82	1.0	0.14	0.3	0.05	1.5	0
Brown trout (*Salmo trutta*)											
Michigan City	10/15	1	11.9[0.0]	100	51	3.7	0.70	1.7	0.22	8.4	100
Sheboygan	7/13	5	7.9[3.0]	100	42	2.6	0.46	1.2	0.18	4.4	25
Gills Rock	9/16	10	6.7[2.5]	70	54	2.8	0.48	1.0	0.14	4.4	40
Carp (*Cyprinus carpio*)											
Michigan City	11/29	2	11.0[0.2]	100	72	3.3	0.81	0.3	0.14	4.6	50
Saugatuck	10/15	15	4.6[4.8]	26	71	0.6	0.20	0.1	0.02	0.9	0
Sheboygan	7/23	11	1.7[0.8]	0	30	0.2	0.07	0.0	0.01	0.3	0
Pensaukee Bar	11/1	9	4.2[1.4]	33	30	0.8	0.19	0.0	0.01	1.0	0
Manitou Island	9/16	5	5.8[0.8]	80	30	ND	ND	ND	ND	ND	ND
Bloater (*Coregonus hoyi*)											
Benton Harbor	9/2	10	5.0[1.2]	60	24	2.5	0.31	1.5	0.19	4.5	30
Saugatuck	6/16	18	8.1[1.9]	88	46	1.9	0.47	1.8	0.19	4.3	37
Saugatuck	6/18	24	7.8[2.2]	95	43	2.4	0.63	2.4	0.25	5.7	64
Saugatuck	6/19	15	6.9[1.8]	86	34	1.8	0.47	2.5	0.31	5.1	66
Milwaukee	9/19	11	4.6[1.2]	36	28	3.4	0.36	2.0	0.26	6.0	88
Sheboygan	7/13	13	5.1[1.5]	61	31	1.3	0.40	2.2	0.24	4.1	50
Sheboygan	7/22	13	6.1[1.8]	76	21	3.4	0.34	2.0	0.24	5.9	81

(Continued next page)

TABLE 3 (cont'd.). *Mean concentrations of PCB's and DDT in fish, Lake Michigan—1971*

Location	Capture Date	No. Fish Analyzed	PCB's	Percentage Fish Above 5 ppm PCB's	PCB's, lipid weight	*p,p'*-DDE	*p,p'*-TDE	*p,p'*-DDT	*o,p'*-DDT	Total DDT	Percentage Fish Above 5 ppm DDT
Sheboygan	8/19	6	3.8[0.6]	0	15	2.6	0.35	1.3	0.16	4.4	20
Sheboygan	8/27	7	5.0[1.3]	57	23	3.2	0.47	2.3	0.28	6.2	80
Sheboygan	10/15	6	3.7[0.8]	0	21	2.4	0.28	1.7	0.17	4.5	42
Ludington	7/3	43	7.4[1.8]	93	41	2.0	0.58	2.2	0.28	5.0	46
Frankfort	10/5	8	4.7[0.7]	12	28	2.2	0.33	1.2	0.16	3.8	0
Manitou Island	9/10	10	4.6[1.1]	30	24	3.1	0.50	1.8	0.26	5.6	50
Washington Island	9/9	6	4.1[0.6]	0	16	3.2	0.34	1.9	0.18	5.6	60
Rock Island	9/11	6	5.8[2.5]	66	97	2.8	0.36	1.1	0.08	4.4	20
Rock Island	9/14	7	5.6[1.6]	57	23	2.7	0.42	2.0	0.22	5.4	50
Rock Island	9/16	8	4.0[0.7]	12	18	2.8	0.29	1.3	0.14	4.5	40
St. Martin Island	7/19	9	3.4[0.6]	0	16	2.2	0.34	1.1	0.17	3.8	0
Manistique	5/27	9	4.8[0.7]	33	26	2.9	0.42	1.8	0.14	5.2	80
Chinook salmon (*Oncorhynchus tschawytscha*)											
Milwaukee	10/15	1	24.0[0.0]	100	117	6.6	1.67	4.7	0.53	13.6	100
Manitowoc	10/21	8	11.3[3.1]	100	209	6.3	0.62	1.2	0.21	8.3	100
Strawberry Creek	10/21	10	9.9[2.8]	100	373	4.5	0.39	1.0	0.17	8.0	88
Gills Rock	9/16	2	12.7[0.7]	100	278	5.5	0.44	1.2	0.20	7.3	100
Coho salmon (*Oncorhynchus kisutch*)											
Michigan City	4/17	8	3.6[1.7]	12	51	0.8	0.17	0.6	0.08	1.6	0
Michigan City	9/27	8	17.3[8.4]	87	255	5.3	0.46	1.2	0.20	7.2	85
Michigan City	10/7	6	14.0[4.0]	100	349	4.5	0.41	1.4	0.18	6.5	60
Sheboygan	10/21	9	12.1[2.8]	100	276	6.6	0.57	1.4	0.27	8.8	100
Ludington	8/28	4	11.2[3.3]	100	108	6.8	0.39	0.9	0.19	8.3	100
Platte River	10/7	10	12.9[1.3]	100	226	5.5	0.48	1.4	0.24	7.6	100
Gills Rock	9/16	11	12.6[4.1]	90	166	4.9	0.45	1.2	0.20	6.7	87
Lake trout (*Salvelinus namaycush*)											
Michigan City	10/15	4	14.9[2.0]	100	89	2.9	0.88	3.1	0.35	7.3	100
Michigan City	9/8	3	21.2[6.8]	100	121	9.5	1.12	3.9	0.45	14.9	100
Saugatuck	6/21	14	11.9[3.8]	100	70	4.7	0.65	2.1	0.27	7.6	88
Saugatuck	7/10	7	15.5[2.4]	100	78	6.9	0.70	2.0	0.24	9.8	100
Saugatuck	10/1	9	18.7[4.7]	100	113	6.7	0.84	2.8	0.27	10.6	100
Milwaukee	9/14	1	21.2[0.0]	100	90	10.1	0.96	3.0	0.47	14.5	100
Milwaukee	9/19	7	21.1[6.0]	100	114	10.6	1.05	3.3	0.45	15.4	100
Milwaukee	10/15	12	10.4[3.6]	100	127	2.3	0.44	1.3	0.15	4.2	20
Sheboygan	7/1	1	14.9[0.0]	100	58	ND	ND	ND	ND	ND	ND
Sheboygan	7/13	36	12.5[3.2]	100	82	4.3	0.51	1.7	0.24	6.8	64
Ludington	7/1	10	8.1[1.8]	100	51	3.3	0.52	1.6	0.22	5.6	60
Ludington	7/4	8	8.5[1.7]	100	58	3.2	0.63	2.0	0.30	6.1	66
Grand Traverse Bay	10/19	8	11.3[5.3]	75	56	6.0	0.73	2.0	0.30	9.0	77
Green Island	7/21	19	9.0[1.7]	100	48	3.8	0.50	1.5	0.21	6.0	72
Gills Rock	9/16	10	14.7[6.4]	100	83	5.5	0.62	1.9	0.24	8.3	62
Yellow perch (*Perca flavescens*)											
Michigan City	10/15	14	4.2[0.7]	14	72	0.8	0.15	0.4	0.04	1.3	0
Waukegan	8/28	9	6.1[1.5]	88	78	ND	ND	ND	ND	ND	ND
Milwaukee	10/13	10	10.9[3.1]	90	203	1.1	0.30	0.7	0.08	2.1	0
Ludington	7/6	3	6.2[1.3]	100	139	2.2	0.30	0.9	0.13	3.6	0
Frankfort	10/12	2	5.4[1.8]	50	69	1.7	0.43	2.2	0.14	4.5	0
Pensaukee Bar	8/25	10	2.7[2.1]	10	49	0.4	0.10	0.0	0.01	0.5	0
Rainbow trout (*Salmo gairdneri*)											
Michigan City	10/15	1	12.0[0.0]	100	66	ND	ND	ND	ND	ND	ND
Gills Rock	9/16	9	8.8[4.3]	77	47	3.1	0.34	0.9	0.16	4.5	40
Redhorse (*Moxostoma* sp.)											
Rock Island	9/11	7	2.8[0.9]	0	33	1.7	0.30	0.6	0.09	2.7	0
St. Martin Island	9/11	9	3.2[0.5]	0	37	1.5	0.35	0.8	0.09	2.7	0
Rainbow smelt (*Osmerus eperlanus modrax*)											
Michigan City	10/15	15	3.2[0.9]	0	45	0.9	0.11	0.4	0.04	1.4	0
Sheboygan	10/15	3	0.7[0.2]	0	18	0.6	0.12	0.3	0.03	1.0	0
Green Island	7/21	5	2.6[1.1]	0	57	0.7	0.12	0.2	0.02	1.0	0
Rock Island	9/11	8	2.9[1.7]	25	49	1.0	0.14	0.5	0.05	1.6	0
St. Martin Island	7/19	4	1.3[0.3]	0	31	0.7	0.09	0.2	0.04	1.0	0
White sucker (*Catostomus commersoni*)											
Michigan City	10/15	6	10.6[4.0]	100	100	1.8	0.32	1.8	0.08	4.6	66
Saugatuck	10/15	3	6.0[2.9]	66	149	0.7	0.14	0.2	0.03	1.0	0
Saugatuck	10/18	5	2.3[0.4]	0	40	ND	ND	ND	ND	ND	ND
Pensaukee Bar	8/6	7	3.2[3.1]	14	57	0.3	0.15	0.2	0.04	0.7	0
Grand Traverse Bay	10/19	14	2.3[0.7]	0	68	0.4	0.31	0.4	0.03	2.1	0
Green Island	7/21	1	2.1[0.0]	0	20	0.7	0.19	0.4	0.08	1.3	0
Rock Island	9/11	14	2.5[0.9]	0	46	0.9	0.20	0.3	0.04	1.4	0

(Continued next page)

TABLE 3 (cont'd.). *Mean concentrations of PCB's and DDT in fish, Lake Michigan—1971*

Location	Capture Date	No. Fish Analyzed	PCB's	Percentage Fish Above 5 ppm PCB's	PCB's, lipid weight	*p,p'*-DDE	*p,p'*-TDE	*p,p'*-DDT	*o,p'*-DDT	Total DDT	Percentage Fish Above 5 ppm DDT
Lake whitefish (*Coregonus clupeaformis*)											
Michigan City	10/15	4	6.1[0.9]	100	25	0.5	0.32	0.5	0.06	1.4	0
Saugatuck	6/19	7	2.7[0.5]	0	15	0.6	0.21	0.4	0.08	1.3	0
Saugatuck	6/21	2	3.1[1.3]	0	18	ND	ND	ND	ND	ND	ND
Grand Haven	9/6	7	5.8[0.9]	71	25	0.7	0.38	0.8	0.10	1.9	0
Grand Traverse Bay	10/19	13	1.8[0.3]	0	13	1.2	0.25	0.4	0.08	2.0	0
Rock Island	9/11	10	1.5[0.2]	0	9	0.7	0.16	0.4	0.05	1.4	0

NOTE: Expressions in brackets represent standard deviations.
ND = not determined.
Residues are ppm wet weight.

wives was greater in southern Lake Michigan than in the northern regions, although anomalies are apparent. Most alewives captured south of a line between Saugatuck and Sheboygan contained between 4.4 and 5.5 ppm PCB's, whereas those caught north of the line contained between 3.5 and 4.4 ppm. An interesting exception occurred in alewives from Rock Island just off the Door County Peninsula in Wisconsin; mean PCB concentration was 8.9 ppm.

Analysis of brown trout suggested similar trends: those from Michigan City at the southern end of the lake contained 11.9 ppm PCB's, whereas those from Sheboygan and Gills Rock contained 7.9 and 6.7 ppm PCB's, respectively.

Carp from Michigan City also had higher levels of PCB's than had those from the northern region. In contrast to the 11.0 ppm found in the Michigan City carp, those from Saugatuck and Sheboygan contained 4.6 and 1.7 ppm, respectively.

PCB's in bloaters in southern Lake Michigan ranged from 4.6 ppm near Milwaukee to 8.1 ppm near Saugatuck. In general, bloaters from the northern regions had concentrations below 5 ppm. The concentration of PCB's in the five groups of bloaters collected near Sheboygan during a 3-month period varied from 3.7 to 6.1 ppm, although the mean was below 5 ppm; no trend was indicated. The variation is somewhat less when data are expressed on a lipid basis: for example, PCB concentrations in the August 27 and October 15 bloaters were 5.0 and 3.7 ppm wet weight, respectively. In contrast, the concentration of PCB's in lipids was 23 ppm and 21 ppm, respectively. Thus much of the observed variation is caused by the variation in lipid content of fish.

All chinook salmon captured in Wisconsin contained more than 5 ppm PCB's; mean concentrations ranged from 9.9 ppm in Strawberry Creek (Sturgeon Bay) to 24 ppm at Milwaukee.

In concentrations of PCB's among coho salmon, authors observed little evidence of a trend dependent upon sampling region. Except for coho caught early in 1971 near Michigan City, mean concentrations of PCB's ranged from 11.2 ppm in salmon near Ludington to 17.3 ppm in those near Michigan City.

Among lake trout PCB concentrations were greatest in those from Michigan City, Saugatuck, and Milwaukee, where mean concentrations were generally between 15 and 21 ppm. Trout from the northern areas such as Sheboygan, Ludington, Grand Traverse Bay, and Gills Rock contained considerably less, and mean concentrations ranged between 8 and 15 ppm.

Mean concentration of PCB's was unexpectedly high, 10.9 ppm, in the 10 yellow perch caught near Milwaukee. Perch from other regions averaged less by a factor of two, and those from lower Green Bay contained 2.7 ppm.

In seven Rock Island redhorse, PCB residues averaged 2.8 ppm. In nine specimens from St. Martin Island, mean concentration was 3.2 ppm.

Rainbow trout were caught only near Michigan City and Gills Rock. The Michigan City rainbow trout had 12.0 ppm PCB's, whereas those from Gills Rock averaged only 8.8 ppm.

Concentrations of PCB's in white suckers and smelt were generally between 2 and 4 ppm, although the average concentration was 6.0 ppm in the three white suckers from Saugatuck on October 15 and 10.6 ppm in the six from Michigan City the same day. Except for whitefish caught at Grand Haven and Michigan City, the PCB concentration in whitefish was less than 3.1 ppm.

DDT AND ANALOGS

Concentrations of *p,p'*-DDT, *o,p'*-DDT, *p,p'*-TDE, and *p,p'*-DDE are presented in Table 3 along with the total DDT and percentage of fish that contained residues above the 5ppm action level established by FDA (*1*). Total DDT in alewives ranged from 1.6 ppm near Waukegan to 5.0 ppm near the Manitou Islands. There was no trend in the variations according to region. A brown trout from Michigan City contained 8.4 ppm total DDT, whereas those from Sheboygan and Gills Rock averaged 4.4 ppm. Except for the carp from Michigan City, which averaged 4.6 ppm total DDT, average concentrations in Lake Michigan carp were 1.0 ppm or less.

Total DDT in bloaters ranged from 3.8 ppm at Frankfort and St. Martin Island to 6.2 ppm at Sheboygan. There are no trends for DDT in chubs (Table 3). Except for eight coho salmon caught near Michigan City in the spring, which averaged 1.6 ppm total DDT, total DDT in this species varied little throughout the lake. Mean concentrations ranged between 6.5 and 8.8 ppm.

Lake trout from Michigan City averaged 14.9 ppm total DDT on September 8, 1971; those caught October 15, 1971, averaged only 7.3 ppm. The discrepancy is likely due to size differences. For example, the lake trout caught near Milwaukee in September also contained a mean concentration of approximately 15 ppm; however, the smaller trout caught near Milwaukee in October averaged only 4.2 ppm total DDT. DDT concentrations in lake trout from northern areas of the lake were less than 8 ppm; approximately 60-70 percent of the lake trout contained over 5 ppm total DDT.

Yellow perch from Pensaukee Bar in lower Green Bay had the lowest DDT content, 0.5 ppm; perch from other areas contained between 1.3 and 4.5 ppm total DDT. None of the perch contained more than 5 ppm total DDT.

Concentration of DDT in smelt, whitefish, and white suckers averaged approximately 1-2 ppm, although white suckers from Michigan City averaged 4.6 ppm total DDT.

Summary

Concentration of PCB's ranged from less than 2 ppm in small fish with low lipid content to over 20 ppm in larger fish with higher lipid content. The concentration of PCB's in Lake Michigan coho salmon is two to three times greater than in coho from Lake Huron, approximately 1.5 times greater than in Lake Ontario coho salmon, and approximately 10 times greater than in coho from Lakes Erie and Superior. Essentially 100 percent of large salmon and trout, both popular food sources, and 50-80 percent of bloaters from Lake Michigan contain PCB concentrations greater than the 5 ppm tolerance level set by FDA. Additional monitoring of this watershed is needed to determine whether tissue concentrations will reflect restrictions in domestic PCB sales and possible decreases in PCB usage in the watershed even though U.S. production of Aroclor 1254 has remained essentially the same as in 1969 (*24*).

Acknowledgments

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GENERAL

Distribution of Organochlorine Pesticides in an Agricultural Environment, Holland Marsh, Ontario—1970-72 [1]

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ABSTRACT

Analysis of organochlorine pesticides in soil, fish, and human blood samples from Holland Marsh, Ontario, indicates that although total DDT is present in detectable amounts, it does not constitute a hazard to human health and longevity. Among soils tested, residues were highest in surface samples. DDT levels in human blood samples were similar to those in U.S. and British studies.

Introduction

Holland Marsh, a 7,500-acre area devoted primarily to intense vegetable farming, is located 30 miles north of Toronto, Ontario. It is 7 miles long, 1-3 miles wide, and cultivated by 400 farmers. Soil is classified as peat muck and the average farm size is 25-30 acres. The marsh is served by eight cooperative packing houses which process 90 percent of the crop. Produce is then delivered to Toronto and Hamilton, Ontario; Detroit, Mich.; and areas of upper New York State including Buffalo and Rochester.

Aldrin, dieldrin, and DDT and its metabolites have been applied to soil and crops for the past 40 years. It is proposed that this survey of residues in the Holland Marsh ecosystem form a basis from which the ultimate fate of DDT residues in agricultural environments of southern Ontario may be determined. This study was commenced in 1970, 6 months after use of DDT was banned in Ontario.

Materials and Methods

Blood samples were taken from farm workers and packing house employees of both sexes. Ten-ml blood samples were collected in glass tubes containing potassium oxilate as an anticoagulant. Blood was collected in June (217 samples) and September (108 samples), the commencement and the end of the most active growing period.

Four farms situated along the north-south axis of the marsh were randomly selected for monitoring. Farm size and agricultural history are listed in Table 1. The four farms sampled were larger than average for the marsh, enhancing authors' opportunities for a large sampling area, personal interviews with each farmer, and accurate detailed history of the farm. Soil samples were collected during late spring from six sites randomly selected on each farm. Individual samples were taken from the soil surface, composite samples were taken from 0-7.5 cm deep, and five 7.5-cm cores were sampled in one location to a total depth of 45 cm on each farm. Sampling sites are shown in Figure 1.

TABLE 1. *History of farms sampled for DDT and related compounds, Southern Ontario—1970-72*

Farm	Acres Size,	Approximate Age, Year [1]	Soil Description	Crops Grown
1	135	20	Deep woody muck soil near canal but also sphagnum muck at north end. Very wet below 22.5 cm	Lettuce Celery Onions Carrots Potatoes Parsnips
2	180	28	Deep muck-peat soil. Little wood	Lettuce Carrots Celery Onions
3	30	30	Half is shallow muck with heavy clay underneath. Half is mineral soil with heavy clay underneath	Carrots Cauliflower Cauliflower Cabbage
4	100	10	Deep, wet muck soil. Very woody in places	Carrots Onions Lettuce

[1] Age of farm implies period of time land has been cultivated since first homesteaded.

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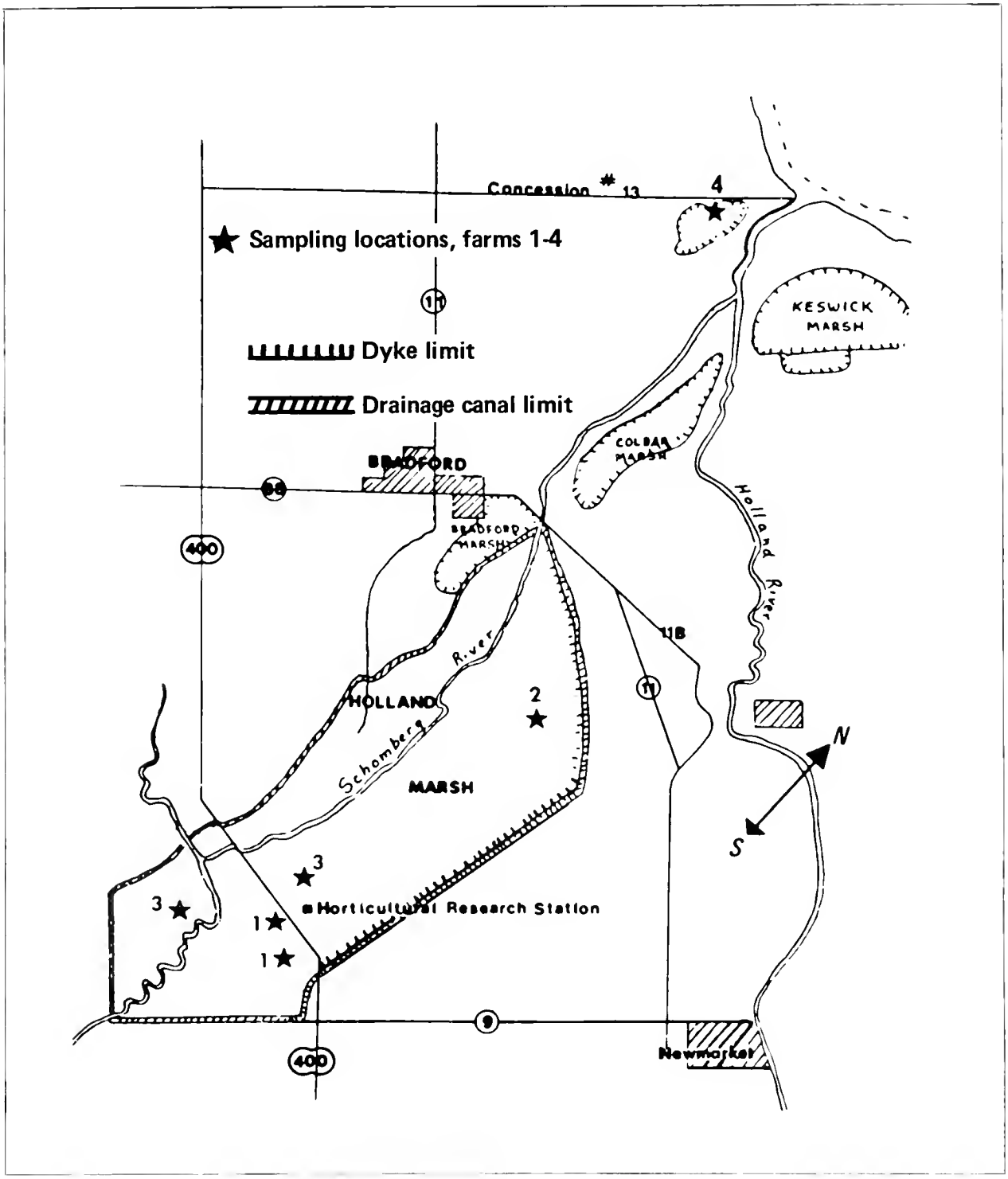

FIGURE 1. *Four farms in Holland Marsh, Ontario, sampled for DDT and related compounds*

Forty-eight fish were obtained by gill net or hook and line from streams throughout the marsh. Three ml whole blood was extracted with 10 ml acetonitrile using a Niagara shaker, 25 ml distilled water was added to the acetonitrile extract, pesticides were partitioned into hexane, and the hexane was concentrated to dryness with a rotary vacuum evaporator. The residue was redissolved in 2 ml hexane and used for subsequent gas-

liquid chromatographic (GLC) analysis. A Varian model 2100 gas chromatograph equipped with 250-mCi tritium electron-capture detectors was used. Columns measuring 1.8 by 4 mm ID were packed with 4 percent SE-30 + 6 percent QF-1 on 100-200-mesh chromosorb W. Average recovery rates for DDT, DDD, and DDE were 78, 82, and 79 percent, respectively.

Ten-g samples of fish and soil were mixed with 10 g anhydrous sodium sulfate and extracted by Soxhlet. Acetonitrile extracts were evaporated to approximately 5 ml, 50 ml sodium chloride solution was added, and the aqueous mixture was extracted three times with 50 ml redistilled hexane. The hexane extract was then evaporated to 10 ml and placed on top of a column containing a mixture of florisil and Celite in a 4:1 ratio by weight. The entire column was eluted with 200 ml of 6 percent ether in hexane and the eluate was evaporated to dryness with a rotary vacuum evaporator. The residue was redissolved in 4 ml hexane and used for subsequent GLC analysis. Average recovery rates for DDT, DDD, and DDE were 93, 93, and 91 percent, respectively. Results have been corrected for recovery. Sensitivity was 0.001 ppm for DDT, 0.0005 ppm for DDD, and 0.0001 ppm for DDE. Total DDT is calculated by adding DDT and the equivalent values for DDE (1.1148) and DDD (1.1076). Total DDT concentrations in human blood samples are listed in Table 2.

TABLE 2. *Total DDT in human blood samples, Holland Marsh, Ontario—1970-72*

	No. samples	Total DDT, ppm		
		Mean ± standard error	Median	Range, ppm
Whole group	356	0.016 ± 0.001	0.011	0.011-0.084
Farmers	92	0.019 ± 0.002	0.013	0.005-0.084
Packers and Others	264	0.014 ± 0.001	0.011	0.001-0.077

TABLE 3. *Hemoglobin in human blood, Holland Marsh, Ontario—1970-72*

	Sex	No. Samples	Mean ± Standard Error
Whole group	M	230	15.7 ± 0.1
	F	126	14.2 ± 0.2
Farmers	M	92	15.5 ± 0.2
Packers and others	M	138	16.1 ± 0.1
	F	126	13.8 ± 0.2

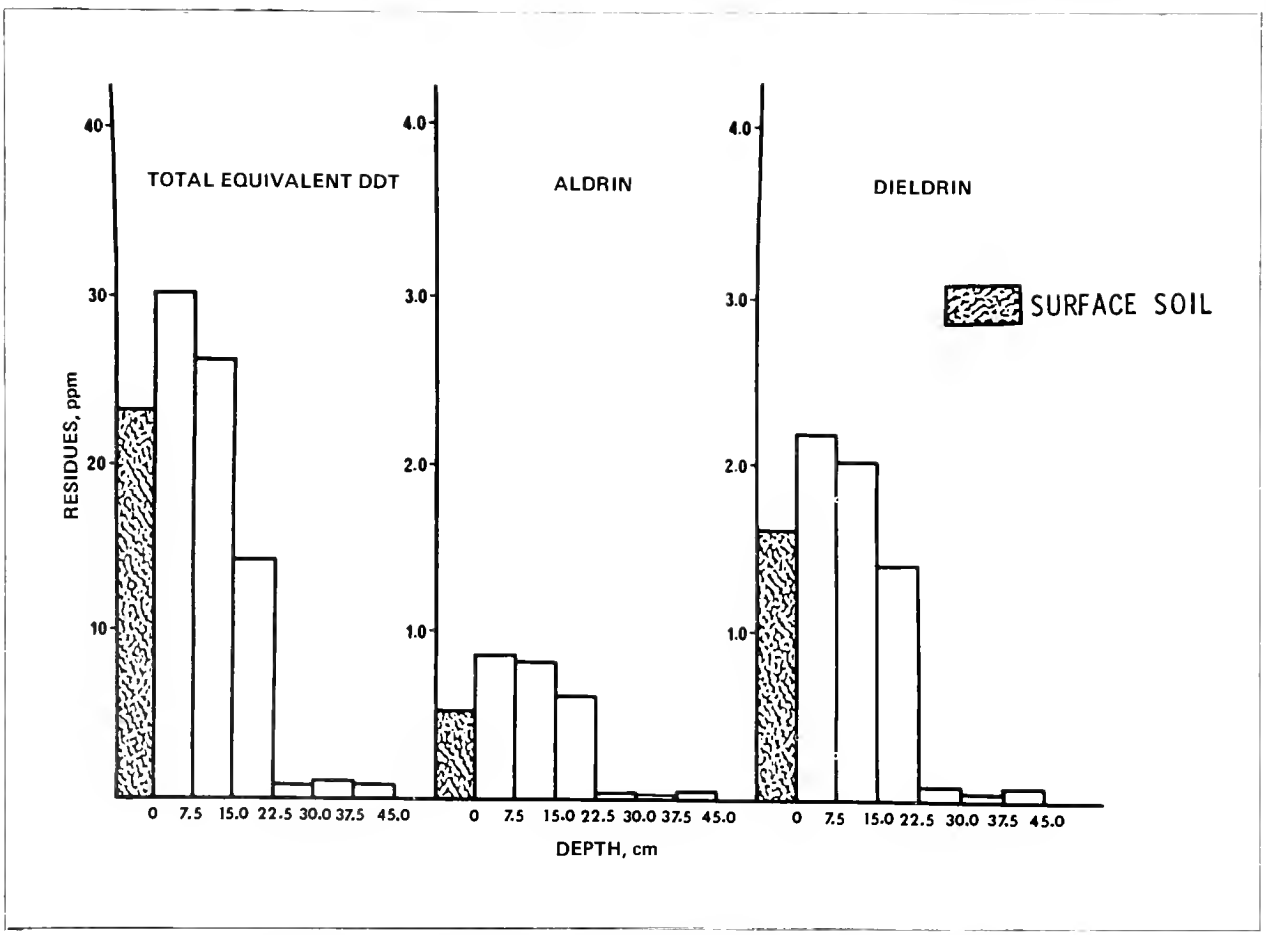

FIGURE 2. *Concentrations of organochlorine pesticide residues by soil depth*

TABLE 4. *Organochlorine pesticide residues in soil samples from four farms, Holland Marsh, Ontario—1970-72*

Depth, cm	No. Samples	Residues, ppm Aldrin	Dieldrin	p,p'-DDE	DDD	p,p'-DDT	Total DDT
Surface	36	0.51	1.61	1.26	0.79	21.13	23.27
0- 7.5	18	0.86	2.19	1.64	1.02	27.41	30.38
7.5-15.0	18	0.78	2.03	1.49	1.07	23.49	26.38
15.0-22.5	18	0.62	1.40	0.86	0.85	12.35	14.25
22.5-30.0	18	0.03	0.08	0.07	0.02	0.73	0.83
30.0-37.5	18	0.02	0.06	0.08	0.03	0.85	0.97
37.5-45.0	18	0.04	0.08	0.08	0.03	0.82	0.95

Results and Discussion

Total DDT levels in human blood from Holland Marsh are similar to those given by Dale (*1*) for the general population in the United States (0.019 ppm) and by Robinson (*2*) for the general population in England (0.013 ppm). Marchand et al. (*3*) and Mastromatteo (*4*) have discussed the possibility of blood dyscrasias arising from the widespread use of chlorinated hydrocarbon pesticides. In view of these hypotheses, hemoglobin in all samples was analyzed using cyanomethemoglobin. Values derived (Table 3) were within clinically acceptable limits for both men and women and did not indicate blood dyscrasia.

Results of all human blood analyses were separated by month of sampling. Median values of total DDT from these two periods (0.013 and 0.011 ppm, respectively) were not significantly different. Quartiles around the medians are 0.010, 0.015, 0.010, and 0.012, respectively.

Samples from packing house employees had a median value of 0.011 ppm; those from the farmers had a median value of 0.013 ppm. As in the study by Wassermann et al. (*5*), people over 40 years of age had higher organochlorine pesticide residues than had those in younger age groups.

Mean residue levels of organochlorine soil samples are listed by farm and sample depth in Table 4 and illustrated in Figure 2. Most compounds detected are concentrated in the first 7.5 cm of soil, a distribution profile similar to that in soil of Norfolk County, Ontario (*6*). Similar results have also been obtained by Albright et al. in Alabama soils (*7*). Organochlorines are subject to decomposition by weathering and normal tillage. It is likely that total DDT concentrations in soil will diminish because DDT is no longer used in Ontario.

Fish samples had lower total DDT levels (Table 5) than those in similar species collected from other areas where DDT has been used extensively, such as Norfolk County, Ontario. Holland Marsh fish had higher DDT levels than fish taken recently from the base of the Bruce Peninsula, an unsettled area in Lake Huron.

The total DDT equivalent has been determined in various ecological systems in the Holland Marsh region. Results indicate that no serious health hazard is associated with total DDT concentrations present.

TABLE 5. *Total DDT in fish muscle, Holland Marsh, Ontario—1970-72*

Species		No. Samples	Mean Total DDT, ppm
Common Name	Scientific Name		
Brown bullhead	*Ictalurus nebulosus*	13	0.56
Bowfin	*Amia calva*	1	0.18
Carp	*Cyprinus carpio*	5	0.75
Goldfish	*Carassius auratus*	1	0.38
Golden shiner	*Notemigonus crysoleucas*	7	0.54
Yellow perch	*Perca flavescens*	5	0.39
Northern pike	*Esox lucius*	3	0.27
Rock bass	*Ambloplites rupestris*	2	0.71
Smallmouth bass	*Micropterus dolomieui*	1	0.73
White sucker	*Catostomus commersoni*	5	0.53
Sunfish (Pumpkinseed)	*Lepomis gibbosus*	15	0.46

NOTE: Fish were collected from ponds, streams, and rivers throughout the marsh.

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Organochlorine Pesticide Residues in a Farming Area, Nova Scotia—1972-73 [1,2]

B. G. Burns, M. E. Peach, and D. A. Stiles

ABSTRACT

Soil, silt, and water samples from the Habitant Creek watershed, Nova Scotia, a tobacco-growing area, have been monitored for organochlorine insecticides. Most samples contain measurable quantities of many persistent pesticides used in farming during the past decade. Sediment levels indicate that residues settle in sluggish parts of the stream. Drainage ditches show highest residual content caused in part by mass transport of soil in runoff. Residue content of water samples is normally one-tenth to one-hundredth that of silt, but is much higher during periods of heavy runoff. Levels vary with the seasons and are highest in the fall, decrease through the spring and summer, and are lowest in the winter. Although samples of well water taken fairly close to the stream showed virtually no residual content, a natural drainage reservoir had a pesticide content similar to that in the stream.

Introduction

In recent years the use of organochlorine insecticides in Canada has come under increasing scrutiny because of their long-term persistence. Although their role as general agricultural insecticides has diminished over the past 5 years, they were, until the early 1970's, used extensively to control infestation in tobacco.

Several reports (*1-5*) have appeared on the long-term persistence of organochlorine insecticides in a variety of settings, most of which were experimental plots. Although Harris (*2,6,7*) has extensively studied organochlorine residues in natural agricultural settings in southwestern Ontario, such work has generally received little attention.

During the past few years, the chemistry department at Acadia University has been investigating organochlorine pesticide residues in the Habitant Creek watershed of Nova Scotia. This region, approximately 10 square miles, is located in the Annapolis Valley and supports a variety of agriculture including tobacco farming. Soils in the agricultural part of the watershed are predominantly loam.

Sampling Procedures

Habitant Creek has both a tidal and a nontidal portion separated by an aboideau. This study deals with the nontidal section only and more specifically with the two main tributaries, Sleepy Hollow Brook and North Brook, which directly border farmland. Sampling locations are shown in Figure 1.

SILT

Samples were collected from readily accessible points along the banks and bed of the stream, natural drainage ditches, and other special areas such as the exit from a reservoir. Streambed samples were taken at a depth of 5-10 cm with a ladlelike device having a total volume of about 12 ml. Samples taken from stream banks and dry land were collected as soil cores of 2.5-cm diameter and 25-cm depth. Generally, at least three samples from the same site were thoroughly mixed prior to storage at 1.5° C.

WATER

Water samples were collected in 25-liter glass containers 1 m from the bottom of the stream. Because the waterway is relatively narrow (< 3 m) at all locations except site 30, no attempt was made to obtain vertical or horizontal profiles. However, it was felt necessary to ensure that all samples represented the stream as a whole rather

[1] Portions of this paper presented at the Third International Congress of Pesticide Chemistry, Helsinki, Finland, July 1974.

[2] Acadia University, Wolfville, Nova Scotia, Canada B0P 1X0. Study supported in part by Agriculture Canada Contract EMR 7103.

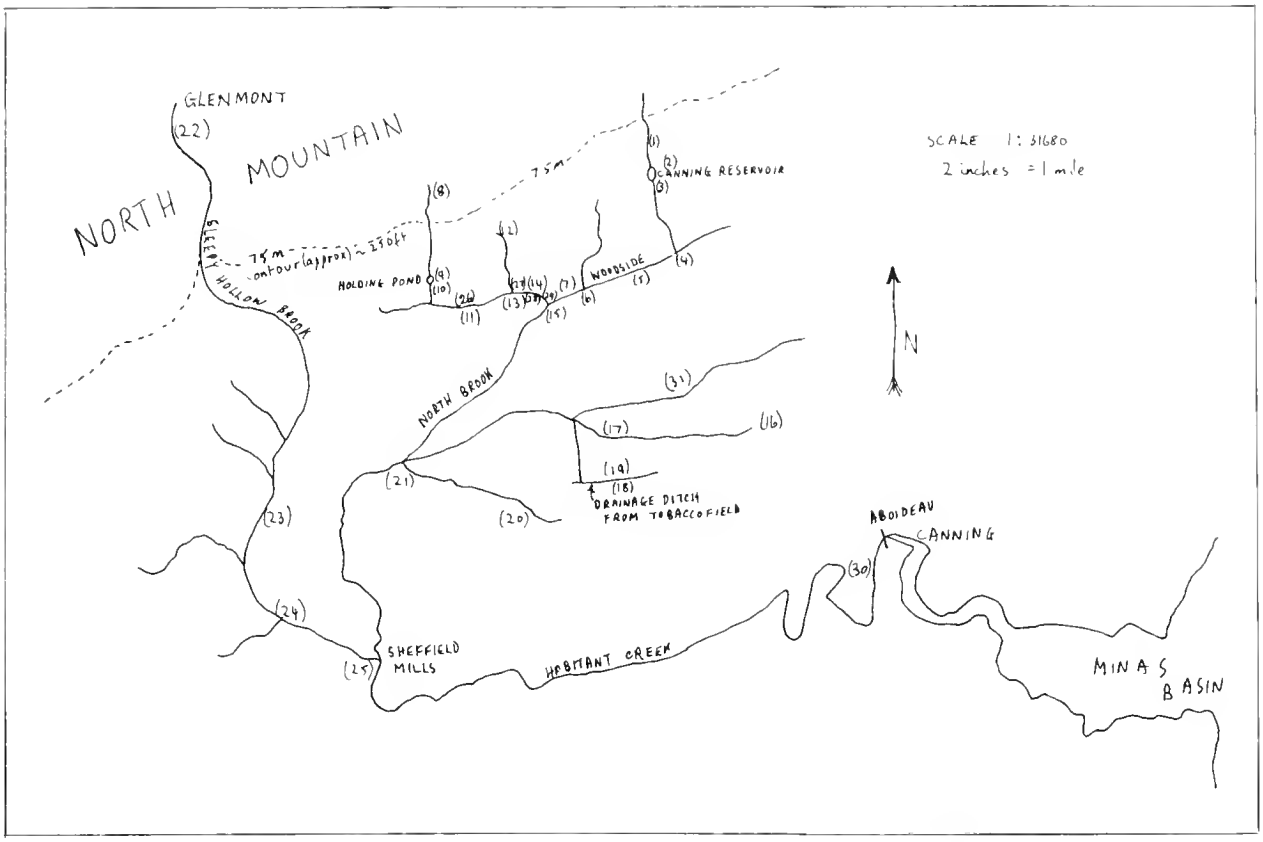

FIGURE 1. *Habitant Creek drainage system showing sampling locations*

than localized pockets. Consequently, three samples were collected at each location from positions as close as possible to the center of the stream. These were combined for analysis.

Analytical Procedures

Organochlorine insecticides were extracted from previously moistened silt samples according to the method of Peach et al. (*8*). Water samples were filtered through glass wool and extracted by the procedure of Kahn and Wayman (*9*). The combined water extracts were then cleaned in standard fashion (*8*).

Residues were identified by gas-liquid chromatography using the following operating parameters:

Gas chromatograph	Hewlett-Packard F and M model 700
Column	pyrex 1.22 m by 0.73 cm, packed with 3 percent OV-17 on acid-washed chromosorb-W, 60–80 mesh, or 1.83 m by 0.73 cm, packed with 3.8 percent UCW-98 on acid-washed chromosorb-W, 60–80 mesh
Detector	electron-capture, pulsed at 50 μs
Temperature:	column 190° C detector 205° C
Purge carrier gas	95 percent argon / 5 percent methane Linde, dried by passing through molecular sieve
Flow rate	purge gas 40 ml/min carrier gas 30 ml/min
Attenuation	50 by 1

Peaks were identified by comparing their retention times with those of analytically pure standards applied to the above columns. Quantification was achieved by comparing peak areas. Calibration curves for each insecticide were prepared daily using analytical standards supplied by Montrose Chemical Corporation, Torrance, Calif.; Shell Canada Limited, Toronto, Ontario; and Velsicol Corporation, Chicago, Ill.

Percent recoveries ranged from 65 to just over 100 percent. Residue levels in soil and water samples were corrected for recovery.

Results and Discussion

The first series of samples was collected during the spring and early summer of 1972, mostly in the form of sediment from streambeds (Table 1). The sample from site 19 was taken from an uncultivated piece of land directly across the road from a drainage ditch serving tobacco fields. Most samples contained measurable quantities of commonly used organochlorine insecticides and their breakdown products.

Most frequently found were the two isomers of DDT in quantities which might be expected from a typical agricultural setting (*2*). Other residues were more localized

but difficult to link with particular field applications because these had been many and varied over a considerable period of time.

Highest residue levels were detected in a sample taken directly from site 18, the drainage ditch of a field on which tobacco had grown for 3 years. However, a sample taken just across the road at site 19, where little surface erosion could have occurred, had the lowest residues in the studied area. Samples were also collected during the summer of 1973 from places where natural drainage ditches led into the creek system. Results of these analyses are shown in Table 2.

Residue concentrations decrease in streambeds at points where water has moved slowly for some time. The exit to the holding pond (site 10) and the exit to Canning Reservoir (site 3) are the most obvious examples of sites where no residue was detected in 1972 or 1973.

Results also agree with water analyses conducted at two other drainage ditches where samples were collected during heavy prolonged rainshowers and about 3 days later (Table 3). Soil, especially the sandy loam of the Habitant Creek watershed, erodes during shower activity. Although the eroded soil was filtered off before water analyses were undertaken, the water still retained a substantial amount of insecticide. After the shower, the soil settled once more and aqueous pesticide concentrations reverted to more usual levels.

Water analyses have also been conducted on aqueous samples collected from several sites during different seasons. Although it was impossible to sample at some sites during the summer and winter because of too low a water flow or too much ice, overall results clearly show maximum pesticide concentration during fall and spring when rainfall is highest and the ground is most subject to erosion (Table 4).

Finally, samples of artesian water were taken from wells on properties bordering North Brook. Residue levels of water samples taken directly from the holding pond and the natural drainage reservoirs serving the towns of Canning and Wolfville are shown in Table 5. Artesian water contains virtually no residue, but wells depending on surface runoff have concentrations comparable to those of streams within the watershed. Although the Wolfville reservoir is not fed from the Habitant Creek system, analyses show that it has an organochlorine content similar to that of the creek.

TABLE 1. *Organochlorine insecticide residues in streambed sediments, Habitant Creek, Nova Scotia—1972*

Collection Site	Residues, ppb											
	γ-BHC	Heptachlor	Aldrin	Heptachlor Epoxide	Nonachlor	α-Chlordane	γ-Chlordane	Dieldrin	Endrin	*o,p'*-DDT	*p,p'*-DDT	Methoxychlor
1	7.9	0.0	5.3	0.0	6.2	42.2	2.5	3.0	5.1	0.9	154.0	0.0
2	11.6	0.0	42.0	0.0	5.0	38.0	0.0	6.0	5.6	22.0	274.0	0.0
3	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
4	1.5	5.0	18.0	0.0	10.0	28.0	0.0	6.5	26.6	19.0	109.0	0.0
5	2.6	4.8	7.4	0.0	1.2	12.0	17.0	0.0	36.0	9.1	572.0	0.0
6	6.6	9.0	2.7	0.0	0.0	8.0	9.5	0.0	28.0	27.0	28.0	0.0
7	14.4	12.0	11.0	0.0	0.0	22.0	9.0	0.0	12.0	16.0	46.0	0.0
8	79.5	0.0	7.1	0.0	0.0	4.0	0.7	0.0	13.8	223.0	74.0	0.0
9	0.0	11.5	37.4	1.2	4.6	6.0	0.7	3.2	8.6	7.9	20.5	0.0
10	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
11	0.0	0.0	21.0	0.0	13.0	664.0	50.0	86.0	309.0	122.0	79.0	0.0
12	89.0	9.0	1.7	0.3	0.0	0.9	1.2	13.4	39.4	45.7	140.0	0.0
13	64.5	17.9	103.0	6.5	12.3	39.0	17.4	0.0	12.5	80.0	10.5	0.0
14	126.0	0.0	36.0	0.0	36.0	6.7	5.1	0.0	21.3	130.0	47.0	0.0
15	3.4	15.0	0.0	0.0	0.2	85.0	0.0	0.0	1.5	25.0	101.0	0.0
16	0.0	0.0	3.5	0.0	0.0	136.0	47.0	0.0	22.0	49.0	22.0	0.0
17	34.0	15.0	0.0	0.0	0.2	0.9	0.0	0.0	1.5	25.0	101.0	0.0
18	0.0	174.0	83.5	30.0	83.0	306.0	0.0	0.0	923.0	261.0	603.0	0.0
19	36.3	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
20	0.0	0.0	8.6	0.0	15.0	9.2	2.1	0.0	145.0	123.0	340.0	0.0
21	0.0	85.0	0.0	30.0	0.0	38.0	40.0	0.0	0.0	64.5	40.0	0.0
22	0.0	0.0	0.0	0.0	0.0	8.0	0.0	0.0	0.0	64.5	40.0	0.0
23	0.0	104.0	0.0	11.5	0.0	120.0	51.0	0.0	750.0	261.0	110.0	0.0
24	0.0	29.5	368.0	0.0	0.0	285.0	0.0	3.8	46.0	4.2	22.5	0.0
25	10.0	11.3	11.3	0.0	0.0	0.0	0.0	0.0	5.5	4.0	263.0	43.0

TABLE 2. *Organochlorine insecticide residues in sediments of natural drainage ditches entering Habitant Creek system, 1973*

Site	Residues, ppm											
	γ-BHC	Heptachlor	Aldrin	Heptachlor Epoxide	Nonachlor	α-Chlordane	γ-Chlordane	Dieldrin	Endrin	*o,p'*-DDT	*p,p'*-DDT	Methoxychlor
26	0.00	0.67	0.53	0.00	0.00	0.75	0.00	5.95	0.67	0.83	3.75	0.00
27	0.00	0.00	0.00	0.00	0.00	0.00	0.00	5.95	2.68	6.67	6.25	0.00
28	0.00	4.76	2.22	17.30	0.94	0.19	0.31	13.75	0.38	2.75	4.83	0.00
29	0.00	2.67	1.60	0.40	0.00	0.44	0.00	1.19	0.27	2.33	7.00	0.00

TABLE 3. *Organochlorine insecticide residues in drainage ditch water, Habitant Creek Watershed—1972*

Site	Residues, ppb											
	γ-BHC	Hepta-chlor	Aldrin	Hepta-chlor Epoxide	Nona-chlor	α-Chlor-dane	γ-Chlor-dane	Dieldrin	Endrin	*o,p'*-DDT	*p,p'*-DDT	Me-thoxy-chlor
	During Thunderstorm											
18	0.08	0.38	0.33	1.04	0.47	0.46	0.42	0.00	1.07	0.49	0.45	0.05
Near site 6	0.06	0.00	0.02	0.00	0.00	0.45	0.04	0.00	0.31	0.56	0.64	0.02
	3 Days After Thunderstorm											
18	0.00	0.02	0.00	0.00	0.02	0.02	0.00	0.05	0.06	0.01	0.03	0.00
Near site 6	0.00	0.00	0.01	0.00	0.00	0.02	0.00	0.02	0.03	0.01	0.03	0.00

TABLE 4. *Organochlorine insecticide residues in water, Habitant Creek—1972*

Site, Date	Residues, ppb											
	γ-BHC	Hepta-chlor	Aldrin	Hepta-chlor Epoxide	Nona-chlor	α-Chlor-dane	γ-Chlor-dane	Dieldrin	Endrin	*o,p'*-DDT	*p,p'*-DDT	Me-thoxy-chlor
22												
Spring	0.00	0.00	0.01	0.00	0.00	0.01	0.00	0.01	0.03	0.23	0.36	0.01
Summer	—	—	—	—	—	—	—	—	—	—	—	—
Fall	0.00	0.01	0.01	0.00	0.00	0.00	0.00	0.04	0.04	0.25	0.35	0.04
Winter	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
23												
Spring	0.00	0.10	0.55	0.43	0.41	3.72	0.00	0.29	0.12	0.15	0.15	0.09
Summer	0.00	0.36	0.42	0.05	0.08	0.56	0.00	0.47	0.01	0.18	0.18	0.00
Fall	0.11	0.46	0.61	0.86	1.67	2.41	0.30	1.12	0.73	0.36	1.49	0.09
Winter	0.01	0.00	0.00	0.00	0.02	0.05	0.00	0.00	0.01	0.05	0.08	0.00
24												
Spring	0.01	0.02	0.02	0.00	0.00	0.38	0.00	0.00	0.00	0.00	0.03	0.00
Summer	—	—	—	—	—	—	—	—	—	—	—	—
Fall	0.01	0.03	0.01	0.01	0.01	0.43	0.02	0.00	0.00	0.00	0.03	0.00
Winter	—	—	—	—	—	—	—	—	—	—	—	—
25												
Spring	0.01	0.26	0.03	0.02	0.04	0.01	0.00	0.04	0.03	0.05	0.05	0.00
Summer	—	—	—	—	—	—	—	—	—	—	—	—
Fall	0.02	0.08	0.12	0.20	0.67	0.25	0.08	0.03	0.04	0.04	0.09	0.00
Winter	0.03	0.00	0.00	0.03	0.03	0.07	0.00	0.05	0.00	0.02	0.06	0.00
30												
Spring	0.00	0.09	0.16	0.16	0.03	0.04	0.00	0.03	0.02	2.32	0.36	0.00
Summer	0.06	0.05	0.04	0.02	0.03	0.12	0.02	0.01	0.03	0.04	0.12	0.00
Fall	0.03	0.42	0.66	5.14	7.83	16.94	4.13	11.80	4.61	1.40	0.39	0.00
Winter	—	—	—	—	—	—	—	—	—	—	—	—
31												
Spring	0.01	0.02	0.01	0.01	0.00	0.01	0.00	0.01	0.03	0.05	0.01	0.00
Summer	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.01	0.11	0.01	0.00	0.00
Fall	0.01	0.03	0.01	0.01	0.01	0.13	0.00	0.01	0.04	0.05	0.10	0.00
Winter	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
21												
Spring	0.00	0.02	0.01	0.00	0.02	0.02	0.00	0.05	0.06	0.01	0.03	0.00
Summer	0.00	0.00	0.00	0.00	0.01	0.01	0.00	0.03	0.05	0.01	0.02	0.00
Fall	0.00	0.35	0.67	6.10	6.10	31.30	17.89	10.48	18.46	28.38	1.68	0.00
Winter	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00

NOTE: — = no sample taken.

TABLE 5. *Organochlorine insecticide residues in waters within and outside Habitant Creek watershed, 1972-73*

Site	Residues, ppb											
	γ-BHC	Hepta-chlor	Aldrin	Hepta-chlor Epoxide	Nona-chlor	α-Chlor-dane	γ-Chlor-dane	Dieldrin	Endrin	*o,p'*-DDT	*p,p'*-DDT	Me-thoxy-chlor
Artesian Wells												
1	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.01	0.00	0.00	0.01	0.00
2	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
3	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
4	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Holding Pond	0.04	0.08	0.03	0.01	0.05	0.41	0.00	0.06	0.04	0.01	0.28	0.06
Canning Reservoir	0.02	0.05	0.04	0.08	0.21	0.86	0.27	0.22	0.16	0.09	0.30	0.00
Wolfville Reservoir	0.07	0.07	0.04	0.05	0.08	0.23	0.08	0.20	0.21	0.45	0.37	0.00

NOTE: Only the holding pond and Canning Reservoir are fed from Habitant Creek system.

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Chlorinated Hydrocarbon Pesticides and Mercury in Coastal Biota, Puerto Rico and the U.S. Virgin Islands—1972-74 [1]

Robert J. Reimold [2]

ABSTRACT

Baseline levels of mercury and chlorinated hydrocarbons were determined for Caribbean coastal biota as part of the U.S. Environmental Protection Agency estuarine monitoring program. Forty-one percent of the 150 environmental samples taken had significant levels of these compounds.

Concentrations of chlorinated hydrocarbons suggest spatial and temporal variations within the plant or animal. In some cases residues in biota could be related to the land-use practices in the sampled watershed.

Introduction

The presence of chlorinated hydrocarbons in continental U.S. marine and estuarine organisms has been routinely monitored since 1965 (*1, 2*). There is, however, a paucity of data concerning concentrations of these chlorinated hydrocarbons in estuarine and marine fauna and flora from the Caribbean (*3*).

As part of the estuarine monitoring program of the U.S. Environmental Protection Agency (EPA), a biannual survey of selected Caribbean islands was initiated in October 1972. The purpose of this paper is to report baseline concentrations including negative results in selected environmental samples collected from U.S. territories in the Caribbean.

Methods

The study area includes Puerto Rico and the U.S. Virgin Islands of St. John, St. Thomas, and St. Croix. Collection locations for each of the four island areas are identified in Figures 1 and 2. At each location, samples were collected within 1 km of the edge of shore. Sites were selected in watersheds which respond quickly to rainfall and produce runoff which might contribute pollutants to coastal biota.

Samples were collected by seine, trap, hook and line, or by hand during fall 1972, spring 1973, fall 1973, and spring 1974. They were immediately placed on ice in aluminum foil packets. Within 4 hours of collection, samples were processed for analysis according to previously developed techniques (*4,5*). Operating parameters of the gas-liquid chromatographic (GLC) techniques were:

Column:	glass, 5 ft by 18 in., packed with 3 percent DC-200 on 80/100 mesh Gas-Chrom Q
Temperatures:	Oven 190° C Injector 210° C Detector 210° C
Carrier Gas:	Prepurified nitrogen at a flow rate of 40 ml/min. Three columns of different polarity were used for confirmation.

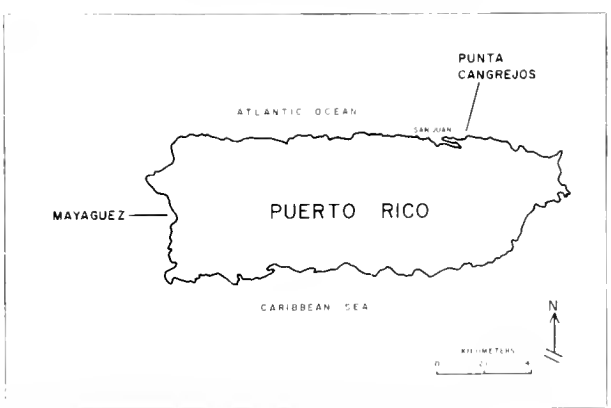

FIGURE 1. *Collection sites for coastal biota, Puerto Rico*

[1] Contribution No. 286, Marine Institute, University of Georgia, Sapelo Island, Ga. 31327. Project funded in part by U.S. EPA Contract 68-02-1254.

[2] Marine Resources Extension Center, University of Georgia, P.O. Box 517, Brunswick, Ga. 31520.

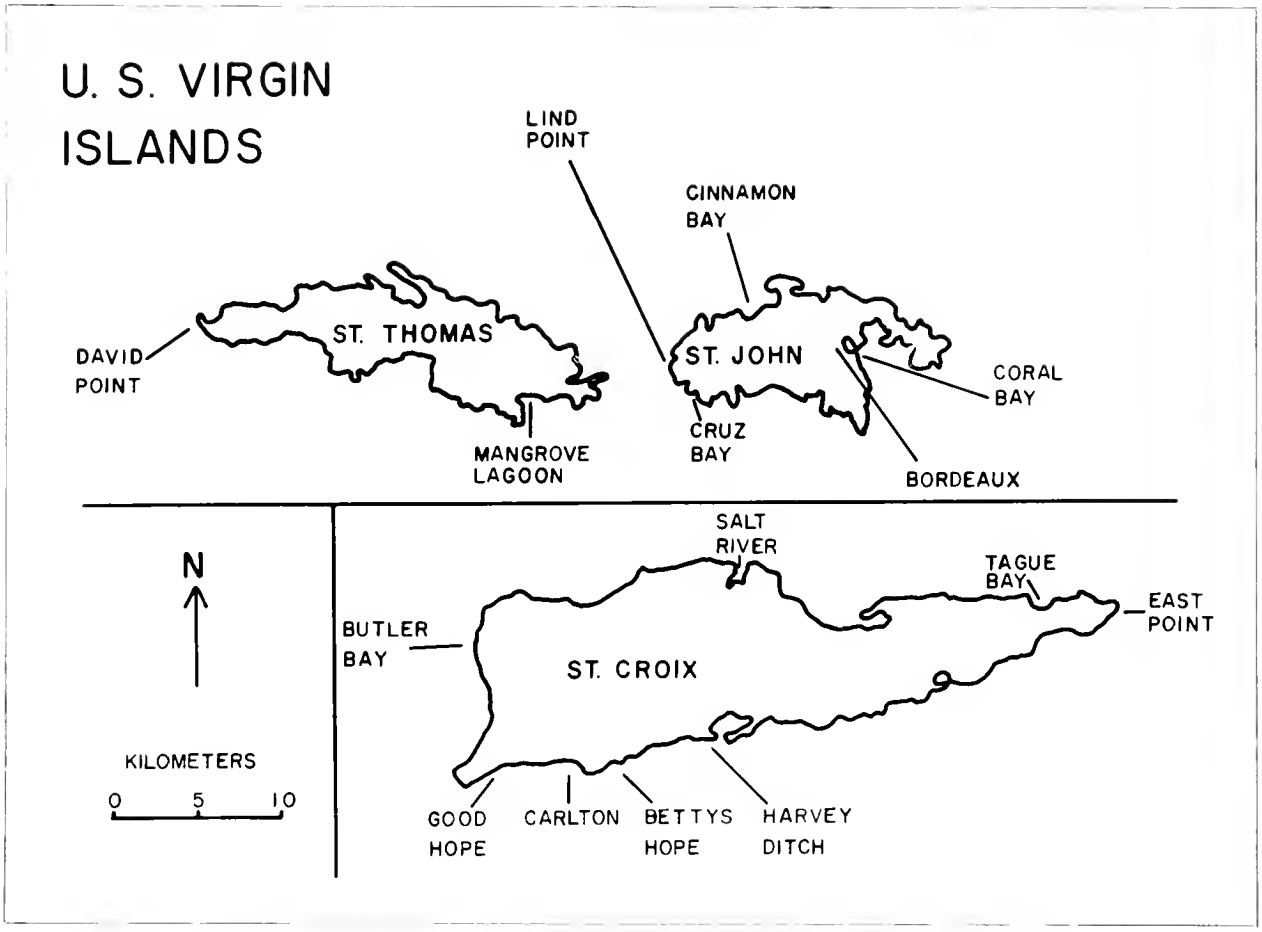

FIGURE 2. *Collection sites: St. Croix, St. Thomas, and St. John, U.S. Virgin Islands*

Analyses were performed by the EPA Pesticide Monitoring Laboratory, Bay St. Louis, Miss., and by the Marine Institute Laboratory, University of Georgia, Sapelo Island. In an earlier monitoring program for chlorinated hydrocarbon pesticides, the two laboratories synchronized methodologies and analyzed split samples. Results from this study were not significantly different.

Samples processed by the EPA laboratory were analyzed using Butler's technique (*2*). Specific chlorinated hydrocarbons determined were DDT, DDE, TDE, dieldrin, and polychlorinated biphenyls (PCB's). The PCB's were separated from pesticides and identified as Aroclor 1254 by matching chromatograms of field samples with chromatograms of standard Aroclor samples. All concentrations are reported as μg/kg or ppb on a whole-body, wet-weight basis. Relative recovery from the samples was between 85 and 90 percent. Data are not corrected for recovery. Concentrations less than 5 ppb are not considered in this study.

All analyses for mercury were conducted by the EPA laboratory using the techniques of Uthe et al. (*6*) and Brandenberger and Bader (*7,8*). These results are also expressed in μg/kg or ppb on a whole-body, wet-weight basis. Mercury concentrations less than 0.02 μg/kg are not considered.

Results

Of 150 environmental samples collected and analyzed, 41 percent had significant concentrations (> 5 ppb) of mercury or chlorinated hydrocarbons (Table 1). Table 2 lists scientific names of the biota and summarizes sample collection data.

Low concentrations of dieldrin were found in red mangrove leaves collected from St. Croix and St. John. There were also very low concentrations of dieldrin in a Nassau grouper and a soldier crab, both from St. John. Occurrence of dieldrin in St. John samples from the Coral Bay coincides with the presence of dieldrin in well and cistern water from a church at the bay (*9*). Cistern water sampled in 1970 contained 0.01 ppb dieldrin.

TABLE 1. *Chlorinated hydrocarbon concentrations in biota, U.S. Virgin Islands and Puerto Rico, 1972-74*

Date	Location	Common Name	Residues, ppb					
			Dieldrin	DDT	DDE	TDE	PCB's	Mercury
Fall '72	Mayaguez PR	Snook		157			162	
Spring '73	Mayaguez PR	Great barracuda		69	103			968
Spring '73	Mayaguez PR	Red drum						114
Fall '73	Mayaguez PR	Bluestriped grunt						70
Spring '74	Mayaguez PR	Yellowfin mojarra					399	
Spring '74	Mayaguez PR	Barbu					157	824
Fall '72	Punta Cangrejos PR	West Indian sardine		39		25	201	
Spring '73	Punta Cangrejos PR	West Indian sardine					416	271
Spring '73	Punta Cangrejos PR	Atlantic spadefish					240	194
Spring '73	Punta Cangrejos PR	Red mangrove						40
Spring '73	Punta Cangrejos PR	Great barracuda		69	103			968
Fall '73	Punta Cangrejos PR	Yellowfin mojarra						87
Spring '74	Punta Cangrejos PR	Striped mullet					579	
Spring '74	Punta Cangrejos PR	Silver jenny					89	
Spring '74	Punta Cangrejos PR	Red mangrove					68	80
Spring '74	Punta Cangrejos PR	Fiddler crab		<10	12	<10		
Fall '72	David Point STT	Red grouper					133	
Spring '73	David Point STT	Queen triggerfish						400
Spring '73	David Point STT	Red snapper						736
Fall '73	David Point STT	Queen triggerfish						822
Fall '73	David Point STT	Rock hind						290
Spring '74	David Point STT	Rock hind						304
Spring '74	David Point STT	Gray snapper						700
Spring '74	Mangrove Lagoon STT	Red mangrove					64	20
Fall '72	Cruz Bay STJ	Soldier crab		36	44	14		
Fall '72	Cruz Bay STJ	Red mangrove					129	
Fall '73	Cruz Bay STJ	Rock hind						40
Fall '72	Cinnamon Bay STJ	Mongoose (liver only)		22	47	11		
Fall '72	Coral Bay STJ	Soldier crab		43	132	14		
Fall '72	Coral Bay STJ	Red mangrove	21					
Fall '72	Coral Bay STJ	Turtle grass					40	
Fall '72	Coral Bay STJ	Nassau grouper	<10					
Spring '73	Coral Bay STJ	West Indian sardine					719	
Spring '73	Coral Bay STJ	Mangrove oysters						58
Spring '73	Coral Bay STJ	Schoolmaster						155
Spring '73	Coral Bay STJ	Porcupine fish						78
Fall '73	Coral Bay STJ	Red mangrove						50
Spring '74	Coral Bay STJ	Mangrove oysters					110	
Fall '73	Bordeaux STJ	Soldier crab	<10	30	112			
Fall '73	Bordeaux STJ	Soldier crab		758	17508			
Fall '73	Lind Point STJ	Soldier crab			21			
Fall '72	East End Point STX	Jewfish					495	
Fall '73	East End Point STX	Yellowtail snapper						83
Fall '73	East End Point STX	Ocean surgeon						25
Fall '73	East End Point STX	Queen triggerfish						75
Fall '72	Harvey Ditch STX	Red mangrove					181	
Fall '72	Harvey Ditch STX	Red mangrove					181	
Spring '73	Harvey Ditch STX	Red mangrove						38
Spring '74	Harvey Ditch STX	Striped mullet					809	
Spring '74	Harvey Ditch STX	French grunt					467	
Spring '74	Harvey Ditch STX	Spotted pink shrimp					4630	
Spring '74	Harvey Ditch STX	Fiddler crabs	<10				8624	
Spring '74	Harvey Ditch STX	Striped mullet					5391	
Fall '72	Bettys Hope STX	Red mangrove					132	
Fall '72	Bettys Hope STX	Checkered puffer					1817	
Fall '72	Carleton STX	Red mangrove					61	
Spring '73	Carleton STX	Red mangrove	11					
Fall '72	Good Hope STX	Fish doctor					166	
Fall '72	Butler Bay STX	Great barracuda					129	
Spring '73	Salt River STX	Mangrove oysters						39
Spring '73	Tague Bay STX	Great barracuda						271

NOTE: All residues are given on a whole-fish, wet-weight basis.
PR = Puerto Rico, STJ = St. John, STT = St. Thomas, STX = St. Croix.
Blank spaces indicate no residues detected.

DDT and DDE were found in mongoose liver collected from Cinnamon Bay, St. John, and soldier crabs collected at Coral Bay and nearby Bordeaux on St. John. Earlier studies of the cistern water and sediments at these sites did not reveal DDT or DDE (*9*), although they reported 0.14 ppm DDE in sediment of a cistern at Coral Bay.

DDT and DDE were found in East Indian sardines, snook, and great barracuda from Mayaquez, P.R. In the great barracuda, there were 69 μg/kg DDT and 103 μg/kg DDE on a whole-fish basis. Giam et al. (*3*) sampled great barracuda east of the Yucatan peninsula and detected 8 μg/kg DDT in the muscle and 42 μg/kg DDT in the liver.

TDE was found only in soldier crabs (14 μg/kg) and mongoose liver (11 μg/kg) from Cruz, Coral, and Cinnamon Bays, St. John. Earlier research efforts (*9*) did not reveal TDE at these sites.

Aroclor 1254, the only PCB compound identified, was found in West Indian sardines collected from Mayaguez,

P.R. (201 μg/kg), Punta Cangrejos, P.R. (416 μg/kg), and Coral Bay, St. John (719 μg/kg). This compound also appeared in red mangrove leaves from Cruz Bay, St. John (129 μg/kg); and from Harvey Ditch (181 μg/kg), Bettys Hope (132 μg/kg), and Carleton (61 μg/kg), all in St. Croix. Aroclor 1254 was also detected in several other fish (Table 1) including a great barracuda from Butler Bay, St. Croix (129 μg/kg), and striped mullet (5,391 μg/kg) and fiddler crabs (8,624 μg/kg) from Harvey Ditch, St. Croix. This is a considerably greater concentration of Aroclor 1254 than that reported in a great barracuda collected by Giam et al. (*3*), which had 9 μg/kg in the muscle and 57 μg/kg in the liver.

TABLE 2. *Genera, species, and common names of biota sampled, U.S. Virgin Islands and Puerto Rico, fall 1972—spring 1974*

Species	PR	STJ	STT	STX
PLANTS				
Red mangrove (*Rhizophora mangle*)	X	X	X	X
Turtle grass (*Thalassia testudinum*)		X		
INVERTEBRATES				
Spotted pink shrimp (*Penaeus brasiliensis*)				X
Fiddler crab (*Uca pugilator*)	X			X
Soldier crab (*Coenobita clypeatus*)		X		
Pacific oysters[1] (*Crassostrea gigas*)				X
Mangrove oysters (*Crassostrea rhizophorae*)		X		X
Scallops[1] (*Argopecten irradians*)				X
FISH				
Ocean surgeon (*Acanthurus bahianus*)				X
Spotted eagle ray (*Aetobatus narinari*)				X
Queen triggerfish (*Balistes vetula*)			X	X
Bar jack (*Caranx ruber*)				X
Snook (*Centroponus undecimalis*)	X			
Atlantic spadefish (*Chaetodipterus faber*)	X			
Banded butterflyfish (*Chaetodon striatus*)				X
Porcupinefish (*Diodon hystrix*)		X		
Rock hind (*Epinephelus adscensionis*)	X	X	X	X
Jewfish (*Epinephelus itajara*)				X
Red grouper (*Epinephelus morio*)			X	
Nassau grouper (*Epinephelus striatus*)			X	X
Silver jenny (*Eucinostomus gula*)	X			
Yellowfin mojarra (*Gerres cinereus*)	X			X
Fish doctor (*Gymnelis viridis*)				X
Margate (*Haemulon album*)				X
French grunt (*Haemulon flavolineatum*)				X
White grunt (*Haemulon plumieri*)				X
Bluestriped grunt (*Haemulon sciurus*)	X	X		
Schoolmaster (*Lutjanus apodus*)	X	X		X
Red snapper (*Lutjanus campechanus*)			X	
Sand tilefish (*Malacanthus plumieri*)				X
Striped mullet (*Mugil cephalus*)	X			X
White mullet (*Mugil curema*)	X			
Yellowtail snapper (*Ocyurus chrysurus*)				X
Barbu (*Polydactylus virginicus*)	X			
Spotted goatfish (*Pseudupeneus maculatus*)		X		
West Indian sardine (*Sardinella sardina*)	X			
Striped parrotfish (*Scarus croicensis*)	X			
Red drum (*Sciaenops ocellata*)	X			
Redtail parrotfish (*Sparisoma chrysopterum*)				X
Stoplight parrotfish (*Sparisoma viride*)		X	X	X
Checkered puffer (*Sphoeroides testudineus*)				X
Great barracuda (*Sphyraena barracuda*)	X			X
MAMMALS				
Mongoose (*Herpestes javanicus*)				X

NOTE: PR = Puerto Rico, STT = St. Thomas, STJ = St. John, STX = St. Croix.

[1] Sample obtained from artificial upwelling mariculture project, Lamont-Doherty Geological Observatory, Columbia University.

The highest concentration of mercury, 968 μg/kg, was found in a great barracuda collected near Mayaguez, P.R., in spring 1973. It was also detected in the red snapper (400 μg/kg) collected at David Point, St. Thomas. Mercury also occurred in the red mangrove from Punta Cangrejos, P.R. (40 μg/kg) and from Harvey Ditch, St. Croix (38 μg/kg); and in other components low in the food chain, such as mangrove oysters from Coral Bay, St. John (58 μg/kg), and from Salt River, St. Croix (39 μg/kg).

Discussion

The author's findings supplement information recently published by Giam et al. (*3*) and Lenon et al. (*9*). In all three studies, concentrations of chlorinated hydrocarbons suggest spatial and temporal variation within the same plant or animal.

In some instances, residues in the biota could be related to the land-use practices in the watershed. At Coral Bay, St. John, the Virgin Islands Department of Health had employed both DDT and dieldrin in an insect control program. Lenon et al. (*9*) reported both DDT and dieldrin in cistern water at Coral Bay. As shown in Table 1 of the present study, dieldrin and DDT were found in measurable concentrations in fauna collected from Coral Bay.

In another instance illustrated in Table 1 and Figure 2, Aroclor 1254 was found in red mangroves on the south side of St. Croix. Residues in samples collected westward along the ocean shore during fall 1972 declined from the first measured concentration, 181 μg/kg at Harvey Ditch, to 132 μg/kg at Bettys Hope and 61 μg/kg at Carleton. By spring 1974, Aroclor 1254 had trophically magnified to levels of 8,624 μg/kg in the fiddler crabs and 5,391 μg/kg in striped mullet, both potential detrivores. The source of this PCB compound is not known. One might speculate that it is local, considering that residues are found at such low trophic levels in the primary producers and detrivores.

It is not yet possible to determine whether the detected measured pollutants are increasing, decreasing, or maintaining status quo. Data in this study do establish baseline conditions for future comparisons in these relatively uncontaminated areas of Puerto Rico and the U.S. Virgin Islands.

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Total Mercury in Water, Sediment, and Selected Aquatic Organisms, Carson River, Nevada—1972 [1]

Robert T. Richins [2] and Arthur C. Risser, Jr.[3]

ABSTRACT

A 1971-72 study of the Nevada Carson River drainage system by the Geological Survey, U.S. Department of Interior, revealed substantial amounts of mercury from pre-1900 gold and silver milling operations of the Comstock Lode. A monitoring survey was initiated to determine the extent of mercury uptake from corresponding surface water and sediments for seven aquatic species collected from five sampling stations along the watercourse. Total mercury content in fish ranged from 0.02 to 2.72 ppm; highest concentrations occurred in piscivorous white bass (0.50-2.72 ppm) sampled from Lahontan Reservoir. Residue levels appeared to be related to fish size, as demonstrated by highly significant correlations between wet weight and mercury content of five of the six species. Concentrations also appeared to be directly influenced by the species' position on the aquatic food chain. These results indicate that mercury levels in some fish from the Carson River drainage system may exceed the 0.50 ppm maximum concentration considered by the Food and Drug Administration, U.S. Department of Health, Education, and Welfare, to be safe for human consumption.

Introduction

Increased mercury levels in various localized areas, particularly the aquatic environment, are often influenced by people. Their use of mercury has threatened bird populations in Sweden (*1*) and contaminated lakes and rivers in some areas of the United States, rendering fish unsafe for consumption (*2*). Consequences of exposure to such acute concentrations are evident in reports from Minamata and Niigata, Japan (*3,4*).

Natural sources also contribute to mercury contamination (*5*). Levels of naturally occurring mercury as high as 1,200 ppb have been reported in air over heavy ore deposits (*6*). It has been estimated that the earth receives approximately 100,000 tons of mercury annually from precipitation. This compares to the yearly human production of about 10,000 tons (*7*).

Since the first century B.C. elemental mercury has been used to extract gold and silver from their ores by amalgamation (*8*). Thus when the Nevada Comstock Lode was discovered in the spring of 1859 near Virginia City, Nev. (*9*), large amounts of the liquid metal were imported to 75 gold-milling sites in the area. In 1869 railroad lines connected Virginia City with the 12 millsites along the Carson River in the Brunswick Canyon area. After this link was completed nearly all milling in the Comstock Lode was carried out at these sites because water power was available (*10*).

The Patio process, which employed an average charge of 1:10 quicksilver (mercury) to the weight of the ore (*9*), was used for extraction (*11*). Though records are incomplete, Hatch and Ott's estimates of total mercury lost during the 30-year peak of the Comstock (1865-1895) are as high as 200,000 flasks, or approximately 15,000,000 lb (*12*). These authors also make further reference to the recovery of quicksilver from tailings at the Douglas Mill in Six-Mile Canyon below Virginia City. Here, using cyanide and flotation methods which had first been perfected for extracting gold and silver, the site's tailings were refined around 1906. Between 1906 and 1914 the operation recovered over 1,000 flasks of mercury.

Until the last decade it was generally accepted that metallic mercury settled to the bottom of a body of water, posing no threat to the aquatic environment. Westoo (*13*), however, reported that 90 percent of the

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mercury in tissues of Swedish fish was present as methylmercury, an organic form highly toxic to wildlife and people. Johnels et al. (*14*) subsequently published the opinion that methylmercury could be created anaerobically by bacterial action in bottom sediments. This theory was verified by Jernelov and Jensen (*15*).

A 1971 study by the Geological Survey, U.S. Department of Interior, on surface water and sediments from the streams, canals, drains, and lakes in and below Brunswick Canyon, reported that substantial amounts of mercury from pre-1900 milling activity had entered the Carson River drainage system. Total mercury levels as high as 20.0 ppm were reported for bottom-sediment samples collected near the upstream end of Lahontan Reservoir; the highest level in sediment from the Carson River near Fort Churchill was 11.0 ppm. Attention immediately focused on the accumulation of mercury by domestic plants and animals raised in the area. A study was undertaken in 1971 by the College of Agriculture Extension Service, University of Nevada, Reno (*16*).

Equally important was the determination of mercury levels in tissues of native fish populations because aquatic organisms are known to concentrate mercury (*17-18*). Although numerous studies on mercury levels in fish of contaminated areas exist (*19-21*), data for the Carson River system were sparse and inconclusive (*22*). Previous work was concerned with data collected only from Lahontan Reservoir, a project completed in 1915 by the U.S. Department of Interior—Reclamation Service (predecessor of the Bureau of Reclamation). No references to fish size or weight had been published, nor had any attempt been made to correlate mercury levels in sediment with those in fish. Thus the present study was undertaken to ascertain total mercury levels for water and accompanying sediment, the relation between individual fish species and mercury levels, and the effect of fish weight on individual mercury concentrations in the Carson River drainage system.

The Carson River flows in a northeasterly direction from its origin in the Blue Lake area, Alpine County, Calif. (elevation 3,176 m). From the convergence of the east and west forks between Genoa and Minden, Nev., the river drops approximately 243 m to its termination at the Carson sink located 12.5 km north of Fallon, Nev. (elevation 1,173 m). Flow rates range from an average monthly high of 320 m^3/sec during maximum discharge in May, to an average monthly low of 4 m^3/sec in August (*23*). Bottom sediment ranges from coarse sand to clay, with turbidity and alkalinity generally increasing as the stream nears Lahontan Reservoir 10 km west of Fallon (*24*).

Initially, a 22-km stretch of the Carson River drainage system between New Empire, Nev., and Lahontan Reservoir was chosen for sampling. On the basis of presumed total mercury content of bottom sediment from pre-1900 ore milling, five collecting sites were designated representative of mercury content increasing progressively downstream. Areas were chosen for sampling on the basis of accessibility and previous data (*23*).

Sampling sites are shown in Figure 1. Site 1 was located 2.5 km east of Carson City, Nev., at the Brunswick Canyon Bridge. River width was approximately 24 m; the bed sloped to a maximum depth of 1.25 m. Water was moderately turbid and the bottom substrate was composed of materials ranging from very coarse sand to silt. Protective rock cover was generally poor and aquatic vegetation was sparse. This site represented an uncontaminated area above the 12 millsites associated with the drainage system, showing no evidence of previous milling activity.

Site 2 was located 5 km east of Carson City in Brunswick Canyon. It was immediately adjacent to the Eureka millsite, approximately 3 km below site 1. The watercourse at this station narrowed markedly to about 18 m as the river cut through the steep canyon. Depth increased from less than 1 m to a maximum of 2.12 m and bottom sediment was characterized by rock rubble. The current was considerably faster than it was upstream because of the river's decreased width and increased elevation decline. Jutting rock formations provided maximum shelter for fish and other aquatic organisms. Tailings from three Comstock milling operations extended to the water's edge. This area had been directly contaminated by pre-1900 milling activities.

Station 3 was located 1.25 km below Dayton, Nev., at the river's maximum width of 45.5 m. Depth varied from 1 to 2 m, channeling was prevalent, and turbidity generally increased as the waterflow slowed to a minimum for the four sampling sites. The bottom substrate was composed of sand ranging from coarse to very fine, with a brownish top coating of organic material. Although rock rubble was scarce, rooted vegetation was heavy and supplied adequate protective cover for aquatic organisms. Irrigation diversions for agriculture became numerous downstream from this site. No evidence of milling activity was observed near station 3 although a sand and gravel operation was located approximately 0.6 km upstream.

Site 4 was located 10 km east of Dayton midway between Break-A-Heart Ranch Number 1 and Break-A-Heart Ranch Number 2. The site was situated in the center of farmland and was characterized by numerous irrigation diversions. The river widened to approximately 24.2 m and reached a maximum depth of 2 m. The bottom substrate was mostly fine sand with little rock rubble. Banks were steep and channeled. No rooted vegetation was observed although flow was calm and turbidity moderate. This area represents a section of the river indirectly contaminated by milling operations.

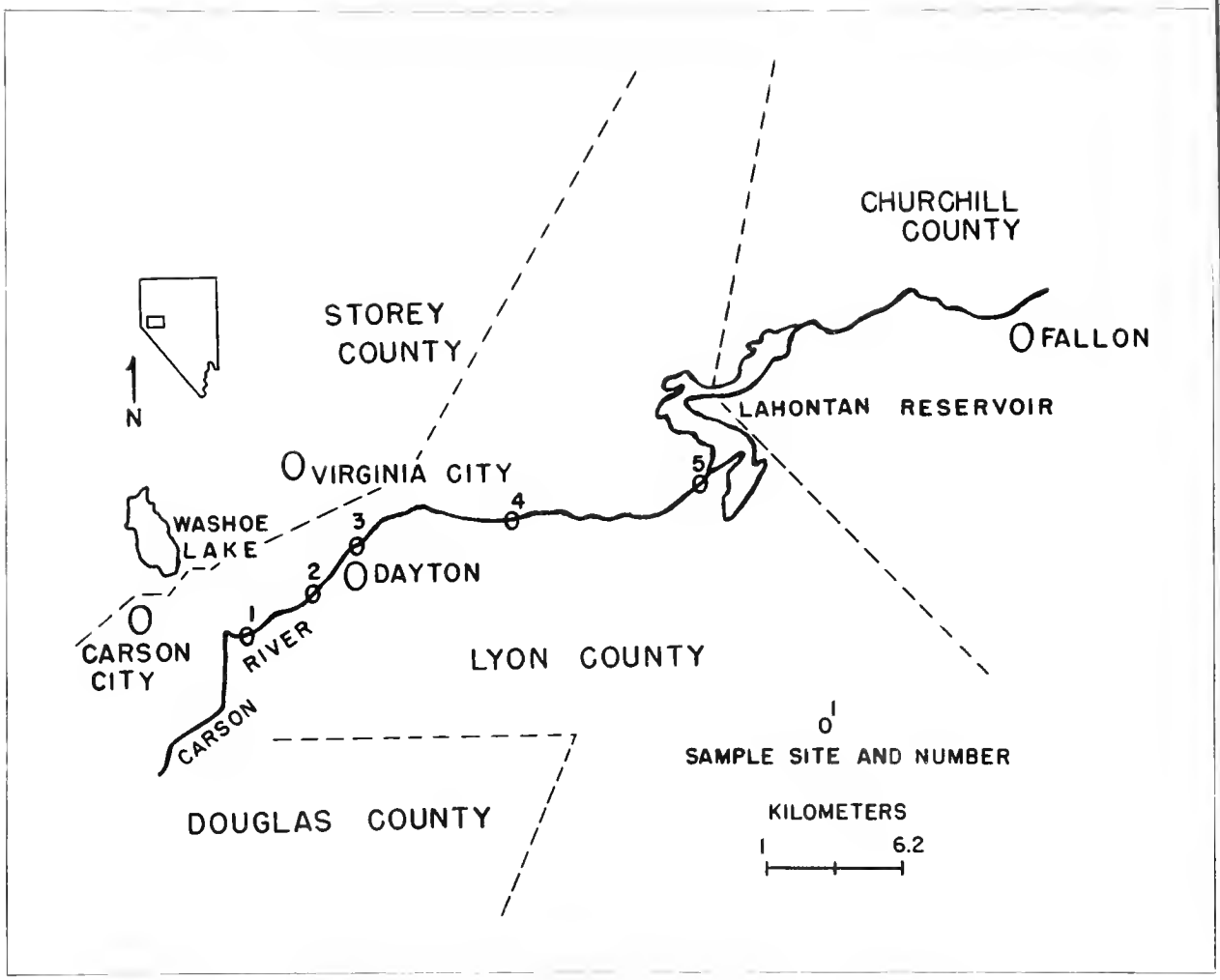

FIGURE 1. *Mercury sampling locations, Carson River, Lyon County, Nevada—1972*

Sampling site 5 was located at the upstream end of Lahontan Reservoir, which is located approximately 10 km west of Fallon, and is 10.5 km long. At conservation level during an average water year (under normal rainfall conditions), Lahontan impounds some 293,000 acre-feet of water, reaching depths in excess of 30 m (*24*). Bottom sediment is composed of clay, silt, and some fine organic material. This site represents a location remote from early milling operations.

Materials and Methods

SAMPLING

Samples of fish including crayfish were collected by electrofishing from the four Carson River sites during the months of July through October 1972, with a dual-electrode shocking apparatus. The electrical source was a 115-volt AC Briggs and Stratton gasoline-powered generator.

Each sampling effort consisted of a run between two predetermined points at the particular collecting site. Stunned fish were retrieved with a long-handled dip net. Emphasis was placed on collecting the largest fish of as many species as possible from each site.

The electrofishing gear was effective for the river collections but proved inadequate at the reservoir. Sampling at this site consisted of individual angler catch trolling and bankfishing; species numbers and size of fish varied uncontrollably.

Samples were labeled according to wet weight, species identification, and date and site of collection. They were preserved by freezing in water-filled polyethylene bags.

Bottom sediment samples collected in July 1972 from the four river sites consisted of composites of the uppermost 2.5-7.6 cm of fine-grained sediment from the right bank of the river. Samples for the Lahontan station were obtained in the shallows near the upstream end of the reservoir. All sediments were collected in acid-rinsed quart jars, characterized by sediment type, and labeled according to location. Unfiltered samples were preserved by acidification with 10 ml 1:1 distilled

water:nitric acid of low mercury content, and refrigerated until analysis (*25*).

Special attention was given to the stream flow rate during the sampling period because total mercury content of sediment and surface waters is related to stream discharge (*23*). Flow rates were supplied by the Geological Survey office in Carson City.

Surface water samples were also collected in July. Five dipped samples were taken across the stream from each site at a depth of approximately 15 cm, placed in acid-rinsed quart jars, dated, and preserved for future analysis by acidification with 10 ml 1:1 distilled water:nitric acid. Samples were then refrigerated. Water aliquots were not filtered because they were to be tested primarily for total mercury content.

Analytical Procedures

Cold vapor, flameless atomic absorption was selected as the analytical technique. Design samples were analyzed in triplicate with a Beckman Atomic Absorption System/Beckman model DB-G grating spectrophotometer, and reported as mean values. If sample variation between any duplicate set exceeded 5 percent, analyses for that set were repeated.

General procedures for fish samples followed those of Hatch and Ott (*26*), as modified by Uthe et al. (*27*) and Armstrong and Uthe (*28*). A 0.1-0.5-g sample of flesh taken from the trunk region below the dorsal fin and above the lateral line was dissolved in a 250-ml flask with 5 ml of a 4:1 solution of concentrated sulfuric acid : nitric acid and was oxidized with 15 ml 6 percent $KMnO_4$ and 2 ml 6 percent $K_2S_2O_8$ after cooling. Excess permanganate was reduced with a 30 percent H_2O_2 solution and the sample was made to 100 ml with distilled water. The sample was further reduced with 4 ml 10 percent $SnCl_2$ and aerated through the atomic absorption apparatus. Recovery studies of spiked fish samples averaged 92.7 percent with a sensitivity of 0.02 ppm. Standard deviations were 0.040 for samples analyzed at the 0.05 ppm spike level and ± 0.050 for tissues containing 0.5 ppm total mercury.

For sediment analysis, a 0.5-g sample was digested with 2 ml of the sulfuric acid : nitric acid solution and permitted to stand for 5 hours. After cooling, an oxidation-reduction procedure identical to that employed for fish tissues was followed. Recoveries for seeded sediment samples averaged 89.4 percent, with standard deviations of ± 0.041 at 0.05 ppm and ± 0.068 at 0.5 ppm.

A modified version of the Federal Water Quality Administration provisional method (*25*) was employed for water analysis. Samples consisted of unfiltered 50-ml aliquots digested for 5 hours with 5 ml of the sulfuric acid:nitric acid solution. After cooling, the portions were oxidized with 1 ml of a 6 percent $KMnO_4$ solution and 2 ml of a 6 percent $K_2S_2O_8$ solution. Samples were then reduced with a 10 percent hydroxylamine hydrochloride solution and 4 ml of a 10 percent $SnCl_2$. Recoveries averaged 94.1 percent with a sensitivity of ± 0.065 at the 0.2 ppb level and ± 0.040 at the 2.0 ppb level.

Results

Total mercury levels in surface waters of the drainage system are listed in Table 1. Values shown were not corrected for recovery. Based on triplicate analyses of unfiltered samples collected during a mean stream flow of 10.1 m^3/sec, results for the Brunswick Canyon Bridge, Eureka Mill, and Dayton Bridge collecting stations showed mean total mercury concentrations of less than 0.20 ppb, the minimum detectable level for water.

TABLE 1. *Total mercury levels in surface water, Carson River, Nevada—July 18, 1972*

Site No.	Source	Total Hg, ppb
1	Carson River, Brunswick Canyon Bridge, 2.5 km east of Carson City	<0.20
2	Carson River, Eureka Millsite, 5 km east of Carson City	<0.20
3	Carson River, Dayton, 1.25 km below Dayton Bridge	<0.20
4	Carson River, 10 km east of Dayton, below Break-A-Heart Ranch No. 1	0.87
5	Lahontan Reservoir, Lyon County, at upstream shallows	2.10

NOTE: Concentrations based on average of triplicate analysis of unfiltered samples. If no absorbance was detected, Hg level was recorded as <0.20 ppb, minimum detectable level in water.

Levels in water from the two downstream sites increased as the river neared Lahontan Reservoir. At site 4 levels averaged 0.87 ppb. Site 5 levels suggested an accumulation of mercury by surface water: mean total mercury level based on triplicate analysis reached 2.10 ppb. The Food and Drug Administration (FDA), U.S. Department of Health, Education, and Welfare, considers 5.0 ppb to be the maximum level acceptable in drinking water (*8*). Although normal background levels for unpolluted surface waters vary widely and are affected by many parameters, the 2.10 ppb concentration at the Lahontan site was well above the 0.03 ppb level presumed to be the mean natural mercury content for uncontaminated waters (*8*).

Total mercury levels of sampled bottom sediment are shown in Table 2; they are not corrected for recovery. Based on triplicate analysis of unfiltered samples collected during a mean discharge flow of 10.1 m^3/sec on July 18, 1972, levels at the five stations also suggested that mercury content increased as water flowed downstream farther from previous milling activity. Mercury concentrations at Brunswick Canyon Bridge, site 1, ranged from 0.111 to 0.130 ppm with a mean level of 0.122 ppm. Corresponding levels of total mercury at the Eureka millsite, site 2, were as high as 0.447 ppm and averaged 0.349 ppm.

TABLE 2. *Total mercury in fine-grained sediment, Carson River and Lahontan Reservoir, Nevada—July 18, 1972*

Site No.[1]	Total Hg, ppm	Source	Description
1	0.122	Off right bank, 25 m below bridge	Dark brown silt and clay
2	0.349	Off right bank, 5 m below millsite	Coarse silt and sand
3	0.209	Off right bank, 0.6 km below Dayton Bridge	Dark brown clay
4	0.722	Off right bank, 100 m below Break-A-Heart Ranch No. 1	Silt and clay
5	1.345	10 m off bank below water surface	Dark brown silt and clay

NOTE: All samples represent the top 2.5-7.6 cm sediment. Concentrations based on average of triplicate analysis of unfiltered samples.
[1] See Table 1 for specific site locations.

An exception to the trend of mercury levels increasing in a downstream direction was observed at site 3. Here the mean level was only 0.209 ppm. Although stream flow decreased at this site, no apparent cause for this decline was observed.

Total mercury levels at site 4 were markedly higher than those observed at Dayton. Concentrations averaged 0.722 ppm for the three samples analyzed. Levels of mercury at Lahontan averaged 1.345 ppm. Such information implies that variations in mercury distribution in sediment along the river are caused by the washing action of local currents, which progressively enrich the mercury content of bottom sediments in a downstream direction.

Six species of fish and one species of crustacean were collected between July and October 1972 (Table 3) when mean stream discharge was 13.4 cm. Wet weight, average mercury concentration, standard deviation, and total mercury range were recorded for the species at each site in Tables 4-8. Residues were not corrected for recovery.

TABLE 3. *Aquatic organisms sampled for mercury content, Carson River drainage system—July-October 1972*

Species	Site No.[1]
Golden shiner (*Notemigonus crysoleucras*)	1-4
Crayfish (*Pacificastacus liniusculus*)	1-4
Tahoe sucker (*Catostomus tahoensis*)	1-4
Carp (*Cyprinus carpio*)	1-5
White bass (*Morone chrysops*)	5
White catfish (*Ictalurus catus*)	5
Brown bullhead (*Ictalurus nebulosus*)	5

[1] See Table 1 for specific site locations.

As was the case for water and sediment samples, total mercury concentrations for individual aquatic species increased as the river approached Lahontan Reservoir. Table 4 shows mercury concentrations in organisms collected at the Brunswick Canyon Bridge. Mercury concentrations ranged from 0.020 to 0.520 ppm for the 24 samples collected; 12.5 percent exceeded 0.50 ppm. Highest levels were present in carp, which had an average level of 0.258 ppm total mercury. Levels in crayfish ranged from 0.100 to 0.520 ppm; two of the five samples had residues in excess of 0.50 ppm. Mean total mercury contents for the golden shiner and the sucker were notably low, averaging 0.183 and 0.189 ppm, respectively. Only three samples analyzed from this site contained less than 0.020 ppm total mercury.

A paired t-test showed no significant difference between mean total mercury concentrations. Wet-weight range and sample size of individual species collected at this site were lower than those of species from other stations.

Mean total mercury levels of organisms from the Eureka Millsite are presented in Table 5. Residues were consistently higher than at the Brunswick Bridge in all species except golden shiners. Likewise, mean wet weights of all species except the shiner were consistently higher. The greatest increase in mercury concentrations appeared in carp: five of eight specimens ranging from 1.02 to 411.20 g had wet weights exceeding 0.50 ppm. Levels in crayfish averaged 0.435 ppm total mercury with a range of 0.114 to 0.732 ppm. Suckers at this site demonstrated slightly higher levels of mercury than at Brunswick Bridge. Overall, 16.2 percent of the samples contained residues in excess of 0.50 ppm total mercury; 10.8 percent represented levels less than 0.02 ppm, the minimum detectable concentration for fish.

At the Eureka site mercury levels in carp were significantly greater than in golden shiners and suckers ($p < 0.01$). Differences between residues found in all other species comparisons were insignificant.

At the Dayton collecting station residues in shiners decreased appreciably (Table 6) and had a mean mercury concentration of 0.097 ppm, the lowest recorded mean level of any species at any site. Mercury content in crayfish and suckers also dropped. Concentrations averaged 0.105 and 0.103 ppm, respectively. Levels in carp, however, remained relatively high. Of eight carp specimens analyzed, levels in six exceeded 0.50 ppm.

A t-test comparison of levels present at the Dayton site demonstrated no significant difference in mercury levels accumulated by shiners, crayfish, and suckers. Mercury concentrations in carp, however, were significantly greater ($p < 0.01$), averaging five times more total mercury than the other three species.

Table 7 demonstrates corresponding mercury levels in fish tissue samples from site 4. Although one would have expected mercury concentrations to decrease somewhat proportionately with distance from milling sites, levels actually increased substantially. Of particular interest were concentrations found in crayfish. Ranging

from 0.534 to 0.969 ppm, mercury content in all six specimens exceeded the FDA 0.50 ppm tolerance level. Higher residues averaging 0.524 ppm were also found in sucker tissues. Although wet weights for this species were considerably greater than those for suckers at any of the previous sites, the wet-weight range for crayfish at this station was relatively small. Mercury levels in shiners were consistent with those at the other river sites, ranging up to 0.318 ppm. Concentrations for carp also remained rather constant although there was a high individual total mercury level of 1.360 ppm. Of the 37 samples collected at site 4, 45.9 percent contained total mercury concentrations in excess of 0.50 ppm. This represents the highest levels found in fish tissue at any of the four collection sites along the Carson River.

Mean total mercury levels in crayfish, suckers, and carp were significantly greater than those in shiners at this station ($p < 0.05$). Concentrations in crayfish were also significantly greater than those in suckers ($p < 0.05$). Residue variances between crayfish and carp did not differ significantly from those between suckers and carp.

Total mercury levels for aquatic species collected from Lahontan Reservoir are shown in Table 8. Wet weights of all species were greater than those of samples taken from the four river sites. Likewise, mercury content in sample tissues was higher. Highest concentrations were observed in white bass in which levels ranged from 0.501 to 2.720 ppm. Of eight specimens analyzed, all contained residues exceeding 0.50 ppm. White catfish had a mean total mercury content of 0.394 ppm. Levels in carp analyzed from this site were also high. One specimen contained 1.087 ppm total mercury. Every sample from the reservoir contained mercury residues above 0.020 ppm; 62.5 percent exceeded 0.50 ppm.

TABLE 4. *Total mercury residues in aquatic organisms, Brunswick Canyon Bridge, Carson River, Nevada (site 1)—1972*

Species	No. Fish in Sample	Mean Wet Weight, g (±S.D.)	Wet Weight Range, g	Mean Total Hg, ppm (±S.D.)	Total Hg, ppm	Positive Samples, % [1]	Samples (%) Over 0.50 ppm
Shiners	6	6.66(±3.33)	2.50-10.50	0.183(±0.157)	0.020-0.356	67.0	0.0
Crayfish	5	13.98(±4.09)	9.60-20.05	0.211(±0.176)	0.100-0.520	100.0	40.0
Suckers	7	50.07(±36.93)	7.22-105.33	0.189(±0.118)	0.020-0.333	85.7	0.0
Carp	6	73.58(±76.19)	8.29-182.30	0.258(±0.180)	0.069-0.503	100.0	16.6

[1] Samples considered positive if total mercury residue exceeded 0.020 ppm, minimum detectable level in fish.

TABLE 5. *Total mercury residues in aquatic organisms, Eureka millsite, Nevada (site 2)—1972*

Species	No. Fish in Sample	Mean Wet Weight, g (±S.D.)	Wet Weight Range, g	Mean Total Hg, ppm (±S.D.)	Total Hg, ppm	Positive Samples, % [1]	Samples (%) Over 0.50 ppm
Shiners	10	5.19(±3.14)	1.75-10.53	0.172(±0.128)	0.020-0.353	80.0	0.0
Crayfish	5	29.59(±13.92)	10.45-42.50	0.435(±0.278)	0.114-0.732	100.0	20.0
Suckers	14	77.88(±53.50)	5.10-178.40	0.222(±0.104)	0.122-0.476	100.0	0.0
Carp	8	158.58(±207.21)	1.02-411.20	0.637(±0.367)	0.020-0.919	75.0	62.5

[1] Samples considered positive if total mercury residue exceeded 0.020 ppm, minimum detectable level in fish.

TABLE 6. *Total mercury residues in aquatic organisms, Dayton, Nevada (site 3)—1972*

Species	No. Fish in Sample	Mean Wet Weight, g (±S.D.)	Wet Weight Range, g	Mean Total Hg, ppm (±S.D.)	Total Hg, ppm	Positive Samples, % [1]	Samples (%) Over 0.50 ppm
Shiners	10	3.67(±1.25)	1.98-5.20	0.009(±0.069)	0.020-0.170	50.0	0.0
Crayfish	7	15.90(±5.66)	9.55-21.35	0.105(±0.054)	0.020-0.149	85.7	0.0
Suckers	14	42.97(±31.46)	14.95-105.10	0.103(±0.070)	0.033-0.250	100.0	0.0
Carp	8	109.36(±139.48)	1.59-400.20	0.536(±0.113)	0.355-0.650	100.0	75.0

[1] Samples considered positive if total mercury residue exceeded 0.020 ppm, minimum detectable level in fish.

TABLE 7. *Total mercury residues in aquatic organisms, Break-A-Heart Ranch No. 1, Nevada (site 4)—1972*

Species	No. Fish in Sample	Mean Wet Weight, g (±S.D.)	Wet Weight Range, g	Mean Total Hg, ppm (±S.D.)	Total Hg, ppm	Positive Samples, % [1]	Samples (%) Over 0.50 ppm
Shiners	11	2.43(±1.75)	0.87-6.31	0.136(±0.127)	0.020-0.318	54.5	0.0
Crayfish	6	13.24(±3.99)	9.20-20.20	0.756(±0.178)	0.534-0.969	100.0	100.0
Suckers	11	127.29(±69.22)	24.20-210.70	0.524(±0.227)	0.205-0.965	100.0	63.6
Carp	9	95.41(±167.11)	1.40-399.12	0.616(±0.385)	0.020-1.360	88.9	55.5

[1] Samples considered positive if total mercury residue exceeded 0.020 ppm, minimum detectable level in fish.

These data suggest that the elevated mercury levels in fish species sampled from Lahontan are probably due to the presence of fluvial sediment high in mercury content deposited at the upper end of the reservoir.

A statistical comparison showed that mean total mercury concentrations in white bass collected from Lahontan Reservoir were significantly greater than those in white catfish or brown bullhead ($p < 0.01$). No other comparisons of the various species demonstrated major differences in mercury levels although a larger sample size would be desirable for this observation to be considered significant.

A t-test was performed to evaluate variation of mean total mercury contents among species of the four Carson River sites. Results demonstrated several distinct trends. In general, total mercury concentrations in shiners did not vary significantly from site to site. Levels in crayfish collected at site 4, however, were significantly greater than those sampled at the other river sites ($p < 0.01$). Levels in suckers from this area were also significantly greater than those from the other river sites ($p < 0.01$). Residues in the Brunswick Bridge carp samples were significantly less than those in carp collected from downstream sites ($p < 0.05$).

A relationship also appeared between mercury concentrations and species' weight. Further statistical analyses were performed to determine whether there was a positive correlation strong enough to establish weight limits within which safe mercury concentrations could be found. Table 9 presents simple correlation coefficients for mercury versus weight. The relationship was examined for the seven species collected in the study area, although sample sizes for white bass, white catfish, and brown bullhead were too small for accurate prediction.

Several points are noteworthy. Among species, the relation between mercury concentrations and fish weight was not consistent. Within species, there was generally a strong positive correlation between mercury content and fish weight, as indicated by shiner, sucker, carp, brown bullhead, and white bass populations. The absence of such a correlation in white catfish is probably attributable to small sample size and wet-weight range. No such explanation was apparent for crayfish.

Statistical analyses were also performed to determine the relationship between mercury levels in bottom sediments and mean residues in individual fish species at each site (Fig. 2). Data demonstrated no significant correlation between mercury concentrations in shiners and carp and levels of accompanying sediments for the four river sites. There was, however, a significant correlation between mean residue levels in suckers and crayfish and mercury concentrations in bottom sediment at individual collecting stations ($p < 0.10$). Similar analyses for white bass, white catfish, and brown bullhead were not initiated because these species were collected only from Lahontan Reservoir. More individual sampling sites are necessary to insure validity of correlations between mean mercury concentrations in aquatic species and those in respective bottom sediments.

TABLE 8. *Total mercury residues in aquatic organisms, Lahontan Reservoir, Nevada (site 5)—1972*

Species	No. Fish in Sample	Mean Wet Weight, g (±S.D.)	Wet Weight Range, g	Mean Total Hg, ppm (±S.D.)	Total Hg, ppm	Positive Samples, % [1]	Samples (%) Over 0.50 ppm
White bass	8	414.23(±72.79)	320.80-527.20	1.297(±0.845)	0.501-2.720	100.0	100.0
White catfish	5	356.29(±76.73)	280.35-440.11	0.374(±0.227)	0.211-0.769	100.0	20.0
Brown bullhead	6	419.49(±112.54)	300.98-540.20	0.554(±0.394)	0.250-1.083	100.0	33.3
Carp	5	284.17(±126.97)	120.00-392.35	0.743(±0.285)	0.382-1.087	100.0	80.0

[1] Samples considered positive if total mercury residue exceeded 0.020 ppm, minimum detectable level in fish.

TABLE 9. *Analyses for homogeneity of mercury-weight conditions in aquatic organisms, Carson River drainage system, Nevada—1972*

Species	No. Fish in Sample	Mean Hg Content, ppm	Size, g	Correl. Coeff.	p-Value
Shiners	36	0.129	0.87-10.53	0.6818	0.001
Crayfish	23	0.345	9.20-42.50	0.0204	NS
Suckers	45	0.245	5.10-210.70	0.7633	0.001
Carp	36	0.547	1.02-411.20	0.6165	0.001
White bass	8	1.297	320.80-527.20	0.9750	0.001
White catfish	5	0.374	280.35-440.11	0.7746	NS
Brown bullhead	6	0.554	300.98-540.20	0.8971	0.02

NOTE: NS = not significant.

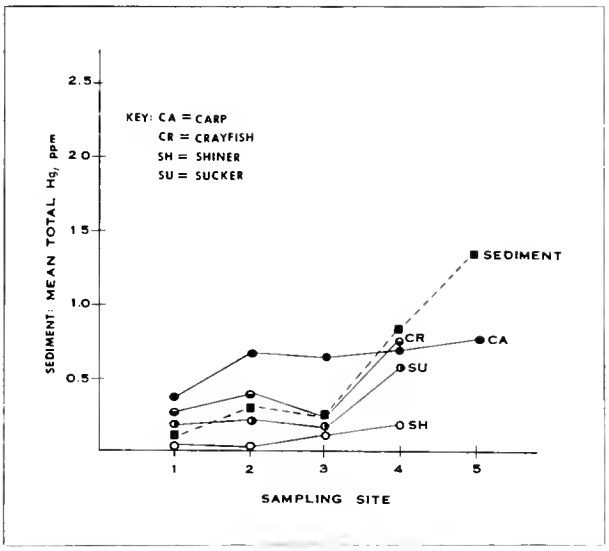

FIGURE 2. *Total mercury in fine-grained bottom sediment and aquatic organisms, Carson River, Nevada—1972*

Discussion

Mercury concentrations in the environment are difficult to assess. Before one declares a water body or organisms present in that water contaminated with mercury waste from people's activities, it is necessary to know the naturally occurring background levels of the metal in both water and organisms. Because the full extent of the mercury problem has only recently become apparent, attempts to establish background levels have been limited. Background data on mercury concentrations in the Carson River consist of surface water and sediment analyses taken upstream from pre-1900 ore milling sites in 1971-72 by the Geological Survey. No previous information exists on baseline levels present in Carson River fish, although random spot samplings of various locations throughout the State were performed by the U.S. Environmental Protection Agency in cooperation with the Nevada State Fish and Game Commission in 1970-71. In general, mercury content for surface water above the Brunswick Canyon area is less than 0.20 ppb (*23*). Total mercury present in corresponding sediments ranges between 0.04 and 0.10 ppm. These concentrations compare with the accepted 0.03 ppb mean natural background level for uncontaminated stream and river waters and the 0.073 ppm mercury content found in uncontaminated stream and river sediments (*8*).

The present study and the Geological Survey findings (*23*) indicate that mercury concentrations in the Carson River drainage system downstream from pre-1900 gold and silver mines far exceed naturally occurring background levels in the river. Apparently total mercury in water and sediment increases in proportion with increased distance downstream from early milling sites. This trend is presumably due to contributions from milling tailings along the river which progressively enrich mercury content downstream, reflecting the flushing action of seasonal runoff. Greatest concentrations are within and immediately upstream from Lahontan Reservoir.

Mercury concentrations in water and sediment are greatly influenced by stream flow because an increase in flow enhances scrubbing action on geological deposits. Samples collected during periods of high discharge generally reflect higher mercury content (*23*). This is evidenced by contrasting values of water and sediment collected from the Carson River by the Geological Survey during a period of high snow runoff in May with those recorded in this study from similar sites during the months of minimum discharge, July and August 1972. Of six surface waters sampled by the Geological Survey, total mercury content ranged from 0.2 to 6.3 ppb. Two samples exceeded the FDA 5.0 ppb tolerance limit for drinking water. Corresponding sediment analyses revealed mercury levels ranging from 9.5 to 20.0 ppm. Concentration in samples from the present study showed total mercury content ranging from 0.20 to 2.10 ppb for water, and from 0.122 to 1.345 ppm for sediment. Extrapolation of these data suggests that mercury content for surface water and sediment can vary markedly, depending on stream discharge. On this basis, it can further be assumed that since maximum discharges during 1971-72 were well below those of many recent years, peak mercury concentrations during the same years were probably also less than those associated with higher flows (*23*).

The ability of aquatic organisms to concentrate mercury above the levels found in their environment is well known (*17,29*). Mechanisms by which fish accumulate organomercury compounds, however, are not fully understood. It is believed that all microorganisms capable of vitamin B^{12} systhesis are also capable of methyl and dimethylmercury synthesis (*30*). Apparently carbon, phosphates, nitrogen, and various trace elements provide these organisms with the food they require to grow and multiply. This food supply in turn determines the size of populations of bacteria and molds present, and thus the rate of organic mercury conversion. The reaction is viewed as a detoxification of the microorganisms' environment at the expense of the fish, and is important because the solubilities of these organomercurials permits the compounds to be directly absorbed in fish by diffusion across the gills (*31*).

Numerous investigators have shown mercury residue in fish tissues to be present as methylmercury. Kamps et al. (*32*) demonstrated that methylmercury comprises 95 percent of the total mercury present in white bass. Westoo has shown mercury in pike to be at least 90 percent methylmercury (*13*). Although a detailed evaluation by the Geological Survey showed most mercury in the water and bottom sediments of the Carson River present as a component of the sulfide or nonmethyl

organic substance (*23*), it became apparent after analyzing some 200 fish samples in the present study that methylmercury conversion was occurring in the system. Results in Table 8 demonstrate mercury concentrations in white bass and brown bullhead collected from Lahontan Reservoir exceeding 2.70 and 1.08 ppm, respectively. Levels for carp and crayfish from the Carson River near site 4 ranged from 0.20 to 1.360 ppm, averaging 0.616 and 0.756 ppm, respectively. These data represent a substantial uptake of mercury from the aquatic environment, the majority of which must be assumed methylmercury. These levels also represent residues which are considerably higher than 0.20 ppm, generally accepted as the naturally occurring background level for most fish (*8*).

As noted earlier, residues varied widely between individual fish within a species. This was particularly evident in carp from site 4, whose individual mercury residues ranged from 0.020 to 1.360 ppm, and in white bass from Lahontan, whose levels varied from 0.501 to 2.720 ppm. This variance appeared to be, in part, a function of fish weight as demonstrated by the highly significant correlations between fish weight and total mercury content shown in Table 9. Similar studies have also shown significant correlations between fork length and total mercury content, and age and mercury accumulation for several species of fish (*32,33*). Neither of these relationships was explored in the present study.

In order to predict weight ranges with a mercury content less than 0.50 ppm, regression analyses were performed on species which reflected highly significant correlation between mercury content and weight. Values for intro-species regressions of total mercury appear in Table 10; estimated regression lines for each of the five species are shown in Figure 3. Extrapolation of these data permits prediction of individual mercury levels within species, providing wet-weight values are given.

For example, it can be predicted that the total mercury content of a carp weighing 200.0 g corresponds to 0.623 ppm. This prediction is reached by direct interpretation from the carp regression line (Fig. 3); or by calculation from the equation $Y = a + b(X)$, substituting the values 0.395 for a, and 1.139×10^{-3} for b (Table 10), and 200.0 g for X. Similar computations show the following practical wet-weight limits below which individuals of the five species can be expected to contain less than 0.500 ppm total mercury: shiner, 18.00 g; sucker, 180.00 g; carp, 100.00 g; brown bullhead, 430.00 g; and white bass, 350.00 g.

Sample sizes for white bass and brown bullhead were too small for accurate prediction. A wider range would also have been desirable because predicted values are likely to fall far outside the sample range. The merit of such predictions might possibly be found by selective fishing; the person fishing could weigh each fish to determine mercury content.

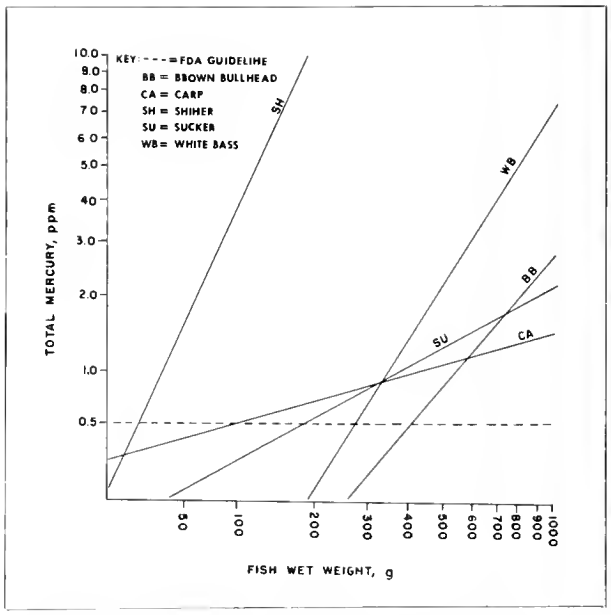

FIGURE 3. *Linear regressions of total mercury content on fish wet weight, Carson River, Nevada—1972*

TABLE 10. *Regression equations for total mercury content versus wet weight in fish, Carson River drainage system, Nevada—1972*

Species	No. Fish in Sample	Total Mercury Content [1]
Shiner	36	$7.623 \times 10^{-3} + 2.955 \times 10^{-2}$(FW)
Sucker	45	$6.290 \times 10^{-3} + 2.416 \times 10^{-3}$(FW)
Carp	36	$0.395 + 1.139 \times 10^{-3}$(FW)
White bass	8	$-3.284 + 1.115 \times 10^{-2}$(FW)
Brown bullhead	6	$-1.121 + 4.016 \times 10^{-3}$(FW)

[1] FW = fish weight, g.

Another conclusion was that mercury levels varied widely between species, indicating marked differences in ability to concentrate mercury (Fig. 4). There is also increasing variance between species and increasing frequency of mean levels exceeding 0.50 ppm total mercury in a downstream direction. These differences are probably explained by variations in feeding activities of the different groups and the accompanying mercury content in surface water and bottom sediments of the respective stations. Levels in golden shiners ranging from 0.097 to 0.183 ppm were consistently lower than concentrations found in other species at each site. McKechnie has shown that algae and plankton are the principal food of shiners when available (*34*). Algae and plankton represent minimum mercury sources because of their position at the base of the food pyramid.

Mean total mercury levels for suckers and crayfish were also consistently low from site to site. In general, mean mercury concentrations in suckers ranged from 0.103 to 0.524 ppm and those for crayfish ranged from 0.105

to 0.756 ppm. The exception for both species was observed at site 4, where t-test comparisons showed mean mercury residues of 0.524 ppm for suckers and 0.756 ppm for crayfish. These were significantly greater than levels in the other species from the site ($p < 0.01$) and mean values for individuals of the same species at the three upstream sites ($p < 0.01$).

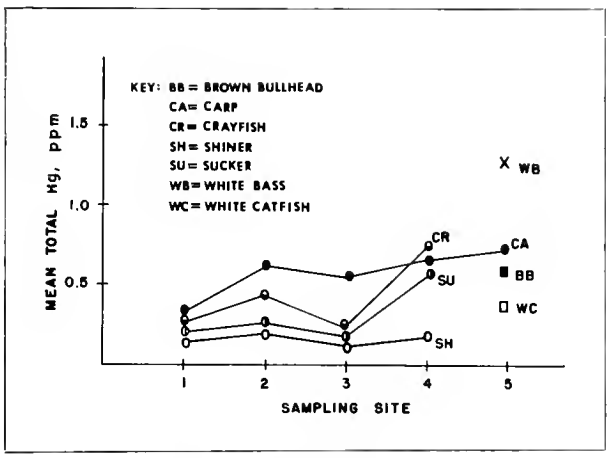

FIGURE 4. *Mean total mercury in aquatic organisms, Carson River, Nevada—1972*

This again reflects feeding activities. Suckers are bottom-dwellers, grazing mainly on green algae, insects, and mollusks (*35*). Crayfish are also bottom-dwellers, feeding on nearly anything that is edible (*24*). Because total mercury content of surface water and sediments was also significantly higher at site 4, and because fish have been shown to absorb mercury compounds directly through their gills and through ingestion of food (*31*), authors had expected tissue levels of bottom-feeders to be higher as well.

Average residues in carp ranged from 0.258 to 0.743 ppm in the five collecting stations. A t-test comparison demonstrated significantly lower levels ($p < 0.01$) in carp taken from the New Empire location above pre-1900 milling activity. Further t-test comparison showed mean mercury concentration in carp significantly higher than in shiners except at site 1 ($p < 0.01$). Mean concentrations varied insignificantly from mean content of other species at individual stations.

Authors made these comparisons with the hope of arriving at a single fish species as an indicator of trends in mercury levels within a station or the entire drainage system over a period of years. Carp, then, represent the species most suitable for such an indicator in the Carson River system: they are present at all five sampling sites; mercury levels within the species do not vary significantly except above milling operations where evidence of natural background concentration exists; and mercury concentrations in carp are similar to those in the other species except shiners.

Carp also reflect an increasing omnivorous diet. Filamentous green algae make up the bulk of their food (*36*); aquatic insects, crustaceans, and small fry are secondary items. Some large carp are even cannibalistic, as demonstrated in downstream sites where most of the large carp were captured by angling with live minnow bait. The species, therefore, provides a good index of mercury accumulation for fish that are both herbivorous and omnivorous.

Because mercury levels in white catfish, brown bullhead, and white bass were determined only for samples collected from Lahontan Reservoir, a comparison of mercury variation among sites was not possible. A t-test comparison of the three species sampled at site 5 showed that mean levels in white bass were significantly higher than in brown bullhead and white catfish ($p < 0.05$). Concentrations of 0.554 ppm in brown bullhead and 0.374 ppm in white catfish varied insignificantly. The differences between mercury levels in the three species can again be explained in terms of feeding habits. White catfish and brown bullhead are omnivorous, feeding near the bottom. Major food items include algae, diatoms, and crustacea; secondary items include insects and other fish (*24*). White bass are primarily piscivorous, consuming a greater volume of fish than all other foods combined (*37*); this habit was reflected in their average total mercury level of 1.297 ppm. Accompanying sediment and water analyses from the reservoir were correspondingly high, undoubtedly influencing mercury uptake by fish.

D'Itri has categorized fish according to their ability to accumulate mercury (*8*). Category I, encompassing predators such as bass and pike, accumulate the highest quantities of mercury. Category II includes such fish as carp and bluegills, which usually contain less mercury. Fish in category III, generally including bottom-feeders such as catfish and suckers, have the least tendency to concentrate mercury. This categorization is corroborated by observations in the present study, especially from Lahontan Reservoir, where mean total mercury content for white bass averaged 1.297 ppm. Category II carp demonstrated a mean content of 0.743 ppm at site 5 although one specimen at this site contained 1.087 ppm. Category III catfish, brown bullhead, averaged 0.554 ppm total mercury at site 5. Results imply biological magnification of mercury among fish or an increase in levels of mercury in fish food organisms at each trophic level of the generalized food chain.

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ERRATA

PESTICIDES MONITORING JOURNAL, Volume 8, Number 4, pp. 247-254. In the paper "Organochlorine Residues in Starlings, 1972," the following corrections are in order:

Page 250

Column 2, line 6, should read, "Residue values of DDT and its metabolites from each station were compared, as were those of dieldrin, for the periods summer-winter 1967-68 versus fall 1968, fall 1968 versus fall 1970, and fall 1970 versus fall 1972."

Table 2, title, should read, "Geometric and arithmetic means of DDT and dieldrin residues in starlings, 1967-72."

Page 251

Column 2, line 1: "periods" should be "period." Column 2, lines 16-17: "metabolic" should be "metabolite."

Page 252

Table 5: footnotes 1 and 2 should be reversed; the former refers to sites and the latter to PCB's.

Page 254

Column 2, line 1, should read: "A metabolite of chlordane, oxychlordane, was found in nearly all samples at very low levels."

Column 2, Literature Cited, reference 1: publication date should be 1969.

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
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
DDMU	1,1'-(Chloroethenylidene)bis(4-chlorobenzene)
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-dimethano-naphthalene
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
HCB	Hexachlorobenzene
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
METHOXYCHLOR	1,1,1-Trichloro-2,2-bis(*p*-methoxyphenyl) ethane
MIREX	Dodecachlorooctahydro-1,3,4-metheno-2H-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
PCB'S (POLYCHLORINATED BIPHENYLS)	Mixtures of chlorinated biphenyl compounds having various percentages of chlorine
TDE	2,2-Bis(*p*-chlorophenyl)-1,1-dichloroethane
THIODAN	See endosulfan.
TOXAPHENE	Chlorinated camphene (67-69% chlorine); product is a mixture of polychlor bicyclic terpenes with chlorinated camphenes predominating.

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

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

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CONTENTS

Volume 9 September 1975 Number 2

PESTICIDES IN PEOPLE

Total Mercury Levels in Selected Human Tissues, Idaho—1973-74 [1,2]

J. Gabica, W. Benson, and M. Loomis

ABSTRACT

Total mercury levels were determined in human tissues taken at autopsy from six hospitals in the three basic geographical areas of Idaho. Of the 242 specimens analyzed, 76 percent contained detectable mercury. Levels were compared with respect to the age, sex, and geographic residence of autopsied individuals. Mean levels detected were 1.04 ppm in kidney tissue, 0.34 ppm in liver, and 0.08 ppm in brain. Mean mercury levels for the three geographical areas were: southeastern Idaho, 0.22 ppm; southwestern Idaho, 0.80 ppm; and northern Idaho, 0.43 ppm. The relatively high means in southwestern Idaho specimens may be related to the preponderance of natural cinnabar deposits in that portion of the State. Mercury levels were higher in women than men for all tissues in both the southwestern and northern areas, but the reverse was true in the southeast. Data were compared with findings of other investigators in an attempt to arrive at background levels of total mercury residues in human tissues.

Introduction

Data on mercury levels in human tissues are limited. Mercury has not been included in most comprehensive studies on trace metals in human tissues. Analytical difficulties may offer a partial explanation for this exclusion (*1, 2*).

Knowledge of background levels of mercury in various human tissues is important because of the possible mutagenic effects or toxic properties of this element and its various compounds. Any use of mercurials as diuretics, antiseptics, cathartics, or pesticides (*3-6*) would presumably contribute to mercury found in various body tissues. Naturally occurring cinnabar ore deposits may be an additional source of exposure in Idaho with its extensive history of mining in which large quantities of metallic mercury were used to extract gold from ore (*7*). Some of this mercury is still present in large quantities in certain locations, especially streambeds throughout the State (*8*).

The present study was intended to be a preliminary screening of a survey of mercury levels in certain tissues of humans and a wide variety of wildlife. Cause of death was noted in each instance but was not compared to mercury concentrations found.

Autopsy and Sampling Procedures

The State was roughly divided into three general areas, northern Idaho, southwestern Idaho, and southeastern Idaho, relating to the locations of the six participating hospitals (Fig. 1). The hospitals, two of which were

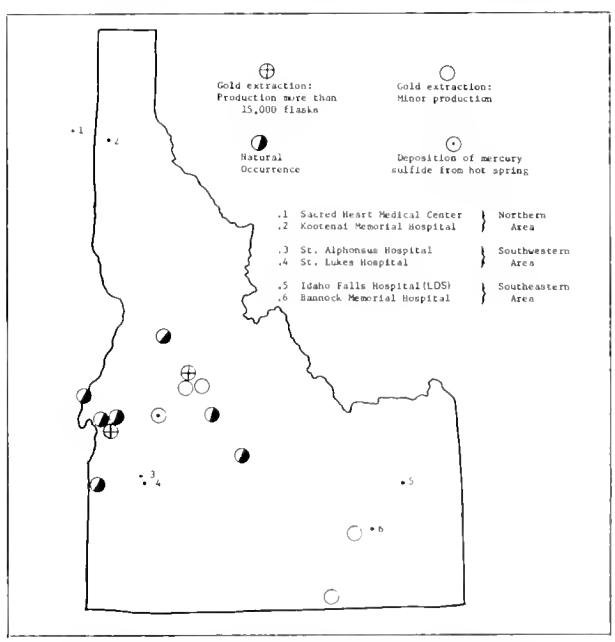

FIGURE 1. *Map of Idaho showing sites of sampling, natural mercury deposits, and gold mining*

[1] Research performed under U.S. Environmental Protection Agency Contract No. 68-02-0552 by the Epidemiologic Studies Program (formerly Pesticide Community Studies Program), Office of Pesticide Programs, EPA, through the Idaho Department of Health and Welfare.

[2] Epidemiologic Studies Program, Department of Health and Welfare, Statehouse, Boise, Idaho 83720.

located in each of these three areas, contributed 242 autopsy samples of kidney, liver, and brain tissues from patients who had died during the previous 12 months from a variety of causes unrelated to mercury poisoning. Because tissues analyzed were from autopsies, they could not be considered normal. However, mean levels drawn from individual cases should be close to normal.

Specimens were placed immediately in formaldehyde at the respective hospitals and sent to the laboratory at once or, in some cases, no more than 2 weeks before analysis. Formalin was analyzed before use and again after autopsy specimens had been stored in the solution. In no instance was mercury or any other background contaminant detected which might invalidate values obtained. Researchers selected homogeneous samples from each organ for analysis, taking care to prevent preanalytical contamination from handling. All glassware used was scrupulously cleaned with nitric acid and rinsed with distilled water.

Tissue specimens were placed on blotting paper and allowed to dry until most of the formalin had been absorbed or evaporated. Subsequently, a 1-5-g sample was ground in a Dual glass tissue grinder; a 1-g wet-weight sample was then removed for analysis. Results are based upon this 1-g sample. The sample was digested according to procedures outlined by the American Association of Analytical Chemists (*9*). Fifty ml distilled water was added to a 50-ml aliquot of the digest and placed in a 200-ml biological oxygen demand (BOD) bottle. Two ml of a 5 percent potassium persulfate solution, 4 ml of a 5 percent $KMnO_4$ solution, 2 ml of a 100-ml water solution containing 12 g NaCl and 12 g hydroxylamine, and 5 ml of a 10 percent $SnCl_2$ solution were added. The mixture was stirred between additions (*8*) and was immediately put under an air vaporizer. Results were recorded on a Coleman 50 analyzer by cold vapor. A standard curve of 0.01-2.00 μg mercury was used.

Results and Discussion

Mercury was found in 76 percent of all tissues tested; the mean value was 0.73 ppm. Mean levels by age, sex, and geographic area of the State for each of the tissues tested are listed in Table 1. Roughly 3.5 times more mercury occurred in kidney tissue than in liver and about 10 times more than in brain tissue. Kidney levels ranged to a high of 15.70 ppm, whereas highest concentrations for liver and brain were 5.80 and 0.94 ppm, respectively. Corresponding mean levels in the current study were 1.04, 0.34, and 0.08 ppm for the same tissues. In comparison, Matsumoto (*10*) reported levels of 6.60, 4.0, and 0.50 ppm in kidney, liver, and brain, respectively, in Japanese fetuses which succumbed to Minamata disease (*10, 11*).

Hospitals with the highest mercury levels in all three organs were located in southwestern Idaho where most of the natural mercury deposits are found (see Fig. 1 in reference *7*). The combined mean level for all tissues was 0.80 ppm in the southwest, whereas the mean level was only 0.22 ppm in the southeast and 0.43 ppm in the north. Nevertheless, it cannot be assumed that these deposits caused the higher levels. High concentrations were not found in this geographical area during a previous study by Benson and Gabica in which 1,000 hair samples from residents throughout the State were analyzed for total mercury (*12*).

Table 2 and the Benson/Gabica study (*12*) show that mercury levels vary according to sex of the subject once they approach or exceed 1 ppm. In general, levels in women were higher than those in men. Women over 65 years of age had more mercury in their tissues than had men in the same age group. The converse was true for people in the 46-55- and 20-45-year age groups although it was less marked in the latter. The higher mercury levels in females of advanced age have not been explained. No available data show evidence of differences in the environmental exposure of males and females. Differences between residue levels in the different sexes cannot be attributed to cosmetics used on skin and hair because the same distribution with respect to sex was found in all organs.

Mean residue concentrations in liver were higher in women than in men from all areas. Women also had higher average levels in the brain and kidney except for kidney tissue in the southeast and brain tissue in the north. Total residues for all three areas were higher among women in all tissues except kidney; in those tissues total values for men were slightly higher (Table 1).

Dal Cortivo et al. (*13*) found that brain, liver, and kidney tissue from autopsy specimens had respective mean mercury levels of 0.05, 0.10, and 0.20 ppm. On the other hand, Kevorkian et al. (*2*) found much higher mean levels: 0.25, 7.70, and 10.36 ppm, respectively.

Hyland et al. (*1*) and Howie et al. (*5*) reported results similar to those of the present study except that Hyland found only 0.65 ppm mercury in kidney samples. Howie's results were corrected from dry to wet weight for comparison by dividing values by five. Takeuchi (*14*) showed that mercury levels in cats averaged 2.00 ppm in the liver, 0.41 ppm in the kidney, and less than 0.10 ppm in the brain. This differs from the findings of the present study and from those of others in which highest concentrations were in kidneys. Takeuchi, however, is in accord with the present study in finding lower mercury levels in human brain tissue than in liver and kidney tissue. This is probably due to the selectivity of the blood/brain barrier, especially with respect to inorganic mercury (*15*). This barrier would not be active in the deposition of mercury into tissue of such organs as liver or kidney.

TABLE 1. *Distribution of mercury concentrations in tissue from human autopsy samples, Idaho—1973-74*

Area	Tissue	Sex	No. Samples	Positive Samples, %	Mean, ppm	Range, ppm
Southeast	K	M	14	93	1.07	0-3.04
		F	3	67	0.06	0-0.20
		M and F	17	88	0.56	0-3.04
	B	M	13	92	0.02	0-0.06
		F	1	100	0.02	0-0.02
		M and F	14	96	0.02	0-0.06
	L	M	18	78	0.06	0-0.41
		F	8	38	0.15	0-0.25
		M and F	26	58	0.11	0-0.41
	Total	M	45	88	0.39	0-3.04
		F	12	68	0.05	0-0.25
		M and F	57	78	0.22	0-3.04
Southwest	K	M	24	71	1.27	0.02-15.70
		F	22	96	1.90	0.18-12.50
		M and F	46	83	1.57	0.02-15.70
	B	M	9	89	0.11	0-0.16
		F	11	91	0.28	0-0.95
		M and F	20	90	0.19	0-0.95
	L	M	25	100	0.34	0.1-2.11
		F	24	100	0.95	0-5.07
		M and F	49	100	0.64	0-5.07
	Total	M	58	87	0.57	0-15.70
		F	57	96	1.04	0-12.50
		M and F	115	91	0.80	0-15.70
North	K	M	20	75	0.84	0-7.56
		F	11	91	1.14	0-5.78
		M and F	31	83	0.99	0-7.56
	B	M	6	83	0.04	0-0.25
		F	2	50	0.01	0-0.01
		M and F	8	66	0.03	0-0.25
	L	M	18	28	0.06	0-0.49
		F	13	23	0.48	0-5.80
		M and F	31	26	0.27	0-5.80
	Total	M	44	62	0.31	0-7.56
		F	26	55	0.54	0-5.80
		M and F	70	58	0.43	0-7.56
Statewide	K	M	58	80	1.06	0-15.70
		F	36	92	1.03	0-12.50
		M and F	94	86	1.04	0-15.70
	B	M	28	88	0.06	0-0.25
		F	14	80	0.10	0-0.94
		M and F	42	84	0.08	0-0.94
	L	M	61	69	0.15	0-2.11
		F	45	54	0.53	0-5.80
		M and F	106	61	0.34	0-5.80
	Total	M	147	79	0.64	0-15.70
		F	95	73	0.82	0-12.50
		M and F	242	76	0.73	0-15.70

NOTE: K = kidney
L = liver
B = brain
M = male
F = female

TABLE 2. *Mercury levels in tissue from human autopsy samples, Idaho—1973-74*

Age Range, years	Tissue	Sex	No. Samples	Range, ppm	Mean, ppm
0 - 19	B	M	7	0.00-0.73	0.07
		F	5	0.00-0.35	0.14
	L	M	8	0.00-1.11	0.12
		F	7	0.00-5.07	0.95
	K	M	4	0.01-0.64	0.11
		F	5	0.00-1.16	0.37
20 - 45	B	M	3	0.00-0.08	0.05
		F	4	0.06-0.16	0.05
	L	M	8	0.00-0.37	0.19
		F	5	0.00-0.41	0.14
	K	M	8	0.00-3.04	0.77
		F	4	0.05-0.85	0.33
46 - 55	B	M	2	0.00-0.05	0.02
		F	1	0.00-0.04	0.06
	L	M	8	0.00-2.40	0.33
		F	9	0.00-1.06	0.25
	K	M	11	0.01-7.56	2.95
		F	7	0.00-4.40	0.95
56 - 65	B	M	7	0.00-0.16	0.02
		F	2	0.00-0.14	0.08
	L	M	12	0.00-0.31	0.06
		F	8	0.00-2.26	0.63
	K	M	12	0.00-7.56	0.58
		F	7	0.00-0.91	0.50
66 - 75	B	M	6	0.00-0.01	0.00
		F	2	0.00-0.26	0.56
	L	M	16	0.02-0.09	0.11
		F	9	0.00-0.31	0.75
	K	M	15	0.00-0.66	0.26
		F	7	0.04-9.40	5.37
76 - 86	B	M	1	0.00-0.02	0.02
		F	1	0.00-0.33	0.33
	L	M	8	0.00-0.90	0.11
		F	8	0.00-5.80	1.00
	K	M	8	0.02-1.55	0.48
		F	6	0.00-12.50	0.74

NOTE: B = brain
L = liver
K = kidney
M = male
F = female

Acknowledgments

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Organochlorine Pesticide Residues in Human Milk, Western Australia—1970-71

Conway I. Stacey [1] and Brian W. Thomas [2]

ABSTRACT

Milk samples from 22 nursing mothers in the metropolitan area of Perth, Western Australia, have shown the presence of DDT, DDE, dieldrin, and HCB in amounts consistent with similar surveys in other countries. Although mean values tend to be slightly lower than expected, their wide range, 0.002-0.025 ppm for DDT, suggests that a much larger sample should be examined to obtain a more accurate mean. This view is supported by values obtained in another survey of the same area.

Introduction

During the past decade there has been considerable interest in the presenee of organochlorine pestieide residues in human milk and their effect on breast-fed infants. The United Nations World Health Organization (WHO) has determined that 0.01 mg/kg/day is the maximum safe intake of DDT. A number of surveys (*1-4*) indicate that the DDT intake of many breast-fed infants has exceeded that level. With the advent of worldwide publicity, however, accompanied by more vigorous controls in many countries, DDT residues in human milk appear to be decreasing and the trend is expected to continue.

The present investigation was initiated by the Nursing Mothers' Association (NMA) of Western Australia in 1970 when the local press was carrying articles on the use and effects of DDT and other chlorinated hydrocarbons. Members of NMA supplied samples which were examined for DDT, DDE, dieldrin, and HCB.

Sampling Procedues

In 1970-71, 22 donors supplied a total of 23 samples of approximately 50 ml each in specially prepared glass containers. Samples were frozen and stored until used. All donors lived within a 30-mile radius of the General Post Office, Perth, Western Australia, the area termed the Perth metropolitan area.

Each donor was asked to fill out a questionnaire indicating her weight and diet, and the frequency and form of pesticide use in her home. Apart from one woman who indicated a slight reduction of meat intake, no donor was on a special diet. All donors were considered to be in good health.

Analytical Procedures

Each 40-ml sample was homogenized and the milk fats were extracted using the single extraction method described in the *Pesticide Analytical Manual* (*5*) of the Food and Drug Administration, U.S. Department of Health, Education, and Welfare. A modified Moats column cleanup was employed using a florisil column eluted with 20 percent methylene chloride / hexane, and acetonitrile. The acetonitrile residue was further eluted from a MgO/celite column with hexane.

Analyses were performed using the following instrument parameters:

Chromatograph: Gas, Varian model 1400

Detector: Concentric tube; electron-capture, tritium

Columns: Glass, 2 m, packed with equal parts 3 percent QF-1 and 1 percent DC-200 on 100-120 mesh Varaport 30. For confirmation: glass, 1.5 m, packed with 5 percent SE-30 on 100-120 mesh Varaport 30.

In addition to gas chromatography, peak identities were confirmed by thin-layer chromatography using $AgNO_3$-incorporated alumina. Results were corrected to 100 percent recovery. This method detected organochlorines at a sensitivity level of 0.001 ppm (Table 1).

Excess milk from each sample was combined. Part of this composite was supplied to the Government

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TABLE 1. *Organochlorine pesticide residues in human milk, Western Australia—1970-71*

Sample No.	Residues in Whole Milk, ppm				
	DDT	DDE	Total DDT	Dieldrin	HCB
1	0.013	0.063	0.083	0.003	0.022
2	0.010	0.057	0.074	0.003	0.026
3	0.011	0.063	0.081	0.005	0.034
4	0.011	0.043	0.059	0.004	0.033
5	0.012	0.085	0.107	0.004	0.031
6	0.002	0.015	0.019	0.004	0.012
7	0.004	0.045	0.054	0.004	0.026
8	0.010	0.077	0.096	0.009	0.027
9	0.003	0.030	0.036	0.005	0.023
10	0.004	0.040	0.049	0.005	0.025
11	0.010	0.037	0.051	0.005	0.024
12	0.009	0.080	0.098	0.008	0.027
13	0.012	0.112	0.137	0.011	0.022
14	0.011	0.110	0.134	0.005	0.028
15	0.009	0.055	0.070	0.004	0.022
16	0.004	0.033	0.041	0.003	0.026
17	0.020	0.068	0.096	0.005	0.022
18	0.025	0.073	0.106	0.005	0.025
19	0.009	0.067	0.084	0.004	0.026
20	0.011	0.077	0.097	0.006	0.028
21	0.021	0.061	0.089	0.009	0.018
22	0.006	0.032	0.042	0.003	0.024
23	0.005	0.073	0.086	0.005	0.021

TABLE 2. *Organochlorine pesticide residues in a human milk composite, Western Australia—1970-71*

Sample	Residues in Whole Milk, ppm			
	DDE	DDT	Dieldrin	HCB
1 [1]	0.080	0.015	0.004	0.024
2 [2]	0.085	0.015	0.005	0.024
3	0.080	0.016	0.005	0.023

[1] Sample 1 analyzed by Government Chemical Laboratories, Perth, Western Australia.
[2] Samples 2 and 3 are duplicates analyzed by the Western Australian Institute of Technology.

Chemical Laboratories, Perth, Western Australia; the remainder was analyzed, in duplicate, at the Western Australian Institute of Technology (Table 2).

Results and Discussion

There is no apparent correlation between the pesticide residue level in the milk sample (Table 1) and the body weight of the donor, the lipid content of the 40-ml sample, or the frequency of pesticide use around the home (Table 3).

Results of the present survey show values ranging from 0.019 to 0.137 ppm total DDT, with an average value of 0.078 ppm. This represents an average infant intake of approximately 0.011 mg/kg/day, which is slightly in excess of the WHO maximum.

DDT residues in Perth residents seem much lower than those obtained in similar surveys from other parts of the world (Table 4), although caution should be exercised in making such direct comparisons.

Lofroth's deduction that breast-fed babies in Western Australia might have a dieldrin intake as high as 30 times the WHO level (*6*) is not substantiated by the present survey. However, this theory was based on an average dieldrin concentration of 0.67 ppm in adipose tissue from a survey performed in 1965 (*7*). More recent surveys have shown a decrease in this mean (*8*). This trend of decreasing levels is also evident in an independent survey carried out by the Public Health Department of Western Australia in 1969-70 (R. Lugg, Public Health Department, 1973: personal communication). The difference in DDT and dieldrin levels in the Public Health survey and the present study highlights the danger of comparing values obtained from a small number of samples.

A much larger sample is needed to obtain a reliable baseline level of DDT and dieldrin in Western Australia. However, the present survey, when viewed with earlier deductions, tends to support the thesis that organochlorine residue levels are decreasing in Western Australia and other parts of the world.

TABLE 3. *Physical and environmental factors affecting nursing mothers, pesticide survey, Perth, Western Australia—1970-71*

Donor No.	Body Wt, kg	Lipid wt (g) of 40-ml sample	Use of Pest Strip	Frequency of Pesticide Use in Home [1,2]
1	61.5	1.15	yes	f
2	60.5	0.84	no	r
3	46	2.615	no	f
4	48	3.095	no	r
5	57	0.81	no	r
6	74	1.005	yes	f
7	66	0.77	yes	f
8	51	2.43	yes	f
9	53.5	1.605	no	f
10	51.5	1.73	yes	r
11	54	1.15	no	f
12	52.5	1.045	no	f
13	56	1.265	no	r
14	60.5	0.955	no	r
15	54	0.94	yes	f
16	60.5	1.22	no	r
17	53.5	1.93	no	r
18	47.5	1.225	no	f
19	52.5	1.485	no	f
20	59	1.42	yes	f
21	46	2.07	no	f
22	60.5	0.40	no	f
23	57	0.83	no	f

[1] f = frequently: once a week or more
r = rarely: less than once a week
[2] A single donor, No. 22, reported using pesticides frequently in the garden.

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TABLE 4. *Mean pesticide residues in human milk from seven countries*

Country	Year	Residues in Whole Milk, ppm				
		DDT	DDE	Total DDT	Dieldrin	HCB
Western Australia [1]	1970-71	0.010	0.061	0.078	0.005	0.025
United Kingdom [2]	1963-64	0.045	0.073	0.127	0.006	ND
United States [3]	1960-61	0.08	0.04	0.12	ND	ND
United States [4]	1967-68	0.014	0.038	0.056	0.007	ND
Western Australia [5]	1969-70	0.04	0.12	0.17	0.015	0.075
Netherlands [6]	1971	0.016	0.030	0.049	0.003	ND
Belgium [7]	1969	0.048	0.072	0.128	0.004	ND
Sweden [8]	1970	0.039	0.067	0.114	0.001	ND
Germany [9]	1970	0.031	0.081	0.121	ND	ND

NOTE: ND = no data in the study cited.
[1] See present study.
[2] See Literature Cited, reference *3*.
[3] See Literature Cited, reference *2*.
[4] See Literature Cited, reference *9*.
[5] R. Lugg, Public Health Department, 1973: personal communication.
[6] See Literature Cited, reference *4*.
[7] See Literature Cited, reference *10*.
[8] See Literature Cited, reference *11*.
[9] See Literature Cited, reference *12*.

Mercury Residues in Breast Muscle of Wild Ducks, 1970-71 [1]

Thomas S. Baskett [2]

ABSTRACT

Samples of breast muscle from 327 ducks collected from October 1970 to March 1971 in the conterminous United States were analyzed for total mercury by flameless atomic absorption spectrometry. Mercury levels for the entire collection ranged from <0.01 to 3.91 ppm wet weight with a median of 0.10 ppm. Twenty-five ducks had levels equalling or exceeding the 0.5 ppm guideline for fish and shellfish established by the Food and Drug Administration, U.S. Department of Health, Education, and Welfare. Dabbling ducks, which are shallow-water feeders and mostly vegetarian in fall, winter, and spring, usually had lower levels than diving and sea ducks. Levels were generally higher in ducks collected in areas where environmental mercury levels were known to be greater than in ducks from nonsuspect areas. Despite the mobility of the ducks, levels seemed more closely linked to local environmental contamination than to various factors associated with large geographic areas.

Introduction

Discoveries of high mercury levels in birds and fish by scientists in Sweden (*1,2*), Finland (*3*), Canada (*4*), and the United States (*5*) have increased concern about mercury levels in wild waterfowl. These concentrations may affect the reproduction and survival of wildlife and the welfare of humans because waterfowl shot by hunters are usually eaten. The present study reports preliminary information on mercury levels in several species of wild ducks collected in the conterminous United States.

Sampling

From October 1970 through March 1971, 327 ducks were collected, principally by shooting. Dabbling ducks, shallow-water feeders which are usually vegetarian during the seasons of collection, comprised 176 of the total; divers and sea ducks, deep-water feeders which often feed on benthic animals, numbered 151. Dabbling ducks collected were: mallards (*Anas platyrhynchos*), 134; mottled ducks (*Anas fulvigula*), 16; gadwalls (*Anas strepera*), 16; black ducks (*Anas rubripes*), 5; and pintails (*Anas acuta*), 5. Divers and sea ducks collected were: lesser scaups (*Aythya affinis*), 108; canvasbacks (*Aythya valisineria*), 16; greater scaups (*Aythya marila*), 8; common goldeneyes (*Bucephala clangula*), 8; white-winged scoters (*Melanitta deglandi*), 4; ring-necked ducks (*Aythya collaris*), 3; common scoters (*Oidemia nigra*), 3; and surf scoters (*Melanitta perspicillata*), 1.

Collection locations are shown in Table 1 and Figure 1; they are coded alphabetically to correspond with Tables 2 and 3 and Figures 2-5. Collections were made in four areas with high environmental levels of mercury; in most areas industrial contamination was known or suspected. For comparison, other collections were made in 17 areas not known to have high environmental levels. In eight of the latter areas, ducks may have been contaminated by consumption of grain treated with mercuric fungicides. Comparisons were made between mercury burdens of ducks collected in five locations during early fall and those collected in late fall or winter. Collection sites for this series were: Mobile County, Ala.; Port Lavaca, Tex.; San Francisco Bay, Calif.; Tule Lake, Calif.; and Brigham City, Utah.

Mercury Analysis

Samples were analyzed for mercury content at the Denver Wildlife Research Center, Fish and Wildlife Service (FWS), U.S. Department of Interior, by a flameless atomic spectrophotometric procedure developed there (*6*). The procedure includes burning dried tissue with oxygen in a combustion flask and collecting

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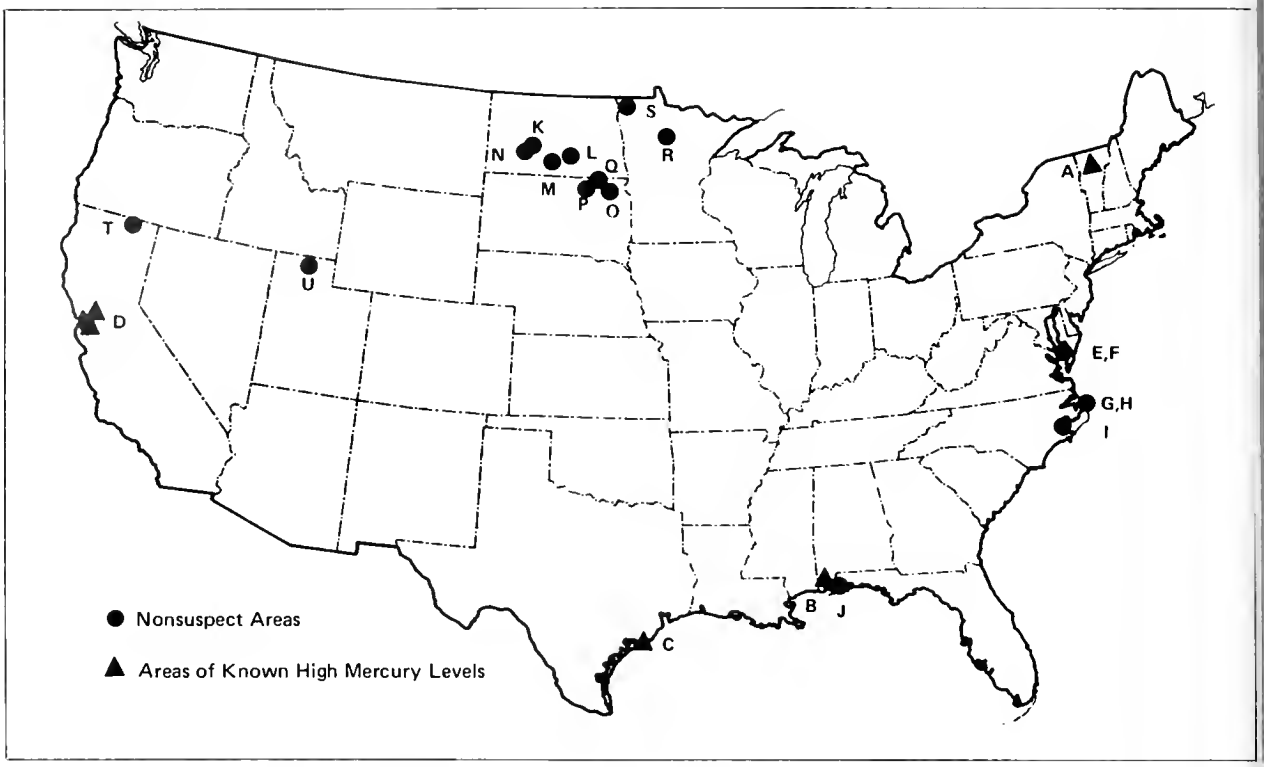

FIGURE 1. *Collection areas of wild ducks analyzed for mercury residues, 1970-71*

the combustion products in dilute HCl. Mercury is extracted from solution by amalgamation on a silver wire and is then volatilized into an atomic absorption cell by heating the wire electrically.

Total mercury residue levels were determined by analyzing a 1-g sample of breast muscle, the most frequently eaten tissue, from each bird. No special efforts were made to ensure a homogeneous subsampling of muscle tissue because previous replicate analysis had determined that mercury residues were distributed rather uniformly throughout the tissue (*7*).

Results and Discussion

Because this study was intended only to provide broad indications of mercury levels in ducks, collections were not made randomly, and detailed statistical analyses were not employed. The paper presents ranges, medians, and the number of ducks in each collection that exceeded the 0.5 ppm action level for mercury in edible portions of fish and shellfish. The action level, set by the Food and Drug Administration (FDA), U.S. Department of Health, Education, and Welfare, serves as a convenient reference point, but its relevance to hazards of eating wild ducks is quite limited. Fish and shellfish are consistently major dietary items for many people, but this is seldom, if ever, true of wild waterfowl shot in the conterminous States. Moreover, methylmercury is of principal concern in fish. Analyses in the present study were for total mercury, and the proportions of the more toxic forms, methyl and ethylmercury, were not determined.

Table 2 lists wet-weight mercury levels in breast muscle of ducks collected in areas having high environmental mercury levels which are known or suspected to result mostly from industrial wastes; Table 3 lists levels in ducks collected in nonsuspect areas. Figures 2-5 depict frequency distribution by 0.1 ppm mercury intervals, facilitating comparisons of levels in ducks collected in high-level regions (Fig. 2) and nonsuspect regions (Fig. 3-5), and levels of dabbling ducks with those of diving and sea ducks.

Mercury levels in ducks from the entire collection ranged from <0.01 to 3.91 ppm; the median was 0.10 ppm. Of the 327 ducks collected, 25 (7.6 percent) had levels equal to or greater than the 0.5 ppm action guideline.

DIVING AND SEA DUCKS VERSUS DABBLING DUCKS

In most collections, diving and sea ducks had higher mercury levels than had dabbling ducks. The range for all diving and sea ducks was 0.02-2.0 ppm with a median of 0.19 ppm. Of 151 collected, 16 (10.6 percent) had residues which met or exceeded the guideline level. For all dabblers, the range was <0.01-3.91 ppm with a median of 0.05 ppm. Nine of 176 dabblers (5.1 percent) had levels greater than or equal to 0.5 ppm. The generally higher levels in divers and sea ducks are illustrated in Figures 3-5.

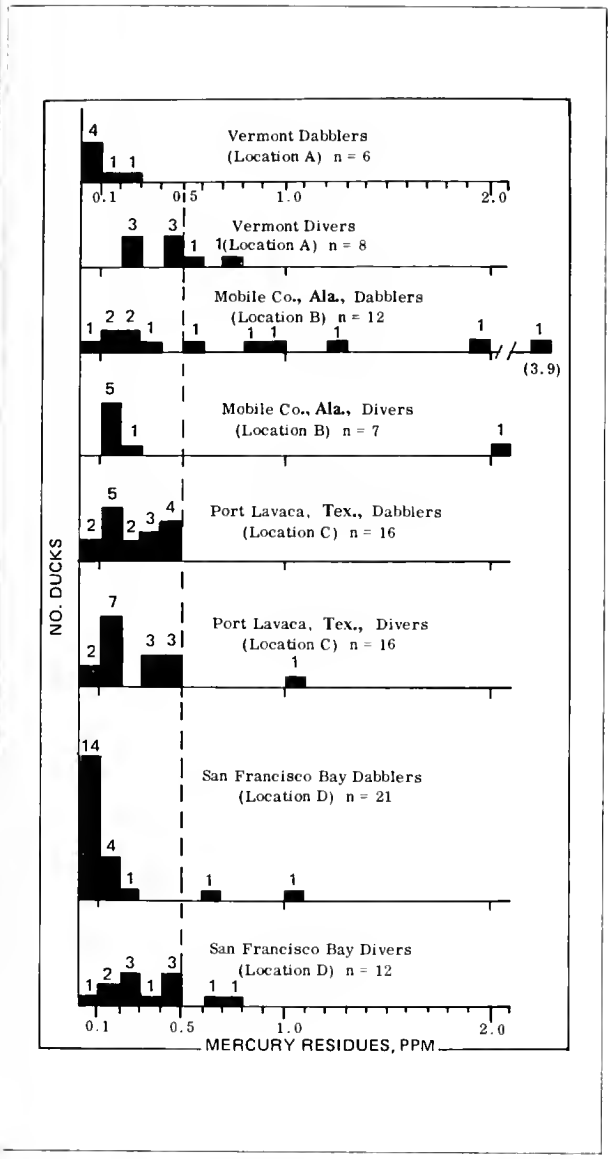

FIGURE 2. *Frequency distribution of mercury content in breast muscle of 98 ducks from areas of high environmental mercury levels*

These results were expected in light of the tendency of diving ducks to eat a higher proportion of animal food, often gleaned from bottom sediment, than do dabblers during fall and winter. For example, fall foods of a large series of lesser scaup (divers) reported by Martin et al. (*8*) were comprised of 22 percent animal food; the corresponding figure for mallards (dabblers) was 7 percent. Surface-feeding habits of dabblers may also contribute to their lower mercury burden, although they often feed in shallow waters by tipping their bodies underwater to obtain objects from bottom sediments.

MOBILE COUNTY, ALABAMA, COLLECTION

A notable exception to the tendency of diving ducks to have higher mercury content than that of dabblers occurred in collections near Chickasaw, Mobile County, Ala. (Table 2, Fig. 2). A group of 12 gadwall (dabblers) collected in or near the settling basin of a chlor-alkali plant had mercury levels in breast muscle ranging from 0.08 to 3.91 ppm with a median of 0.47 ppm; residues in 6 of the 12 exceeded 0.5 ppm. By contrast, concentrations in a group of 7 lesser scaup (divers) collected in the same region ranged from 0.14 to 2.0 ppm. The median was 0.16 ppm and only 1 of the 7 exceeded 0.5 ppm.

The gadwall data clearly show the potential for high mercury burdens in ducks exposed to a highly polluted environment. The high levels in gadwall compared with those in lesser scaup may be attributed to the earlier arrival of gadwall at the contaminated site; lesser scaup are late breeders and thus late fall migrants (*9*). In addition, gadwall wintering in the Mobile Bay region tend to stay in freshwater areas, whereas lesser scaup

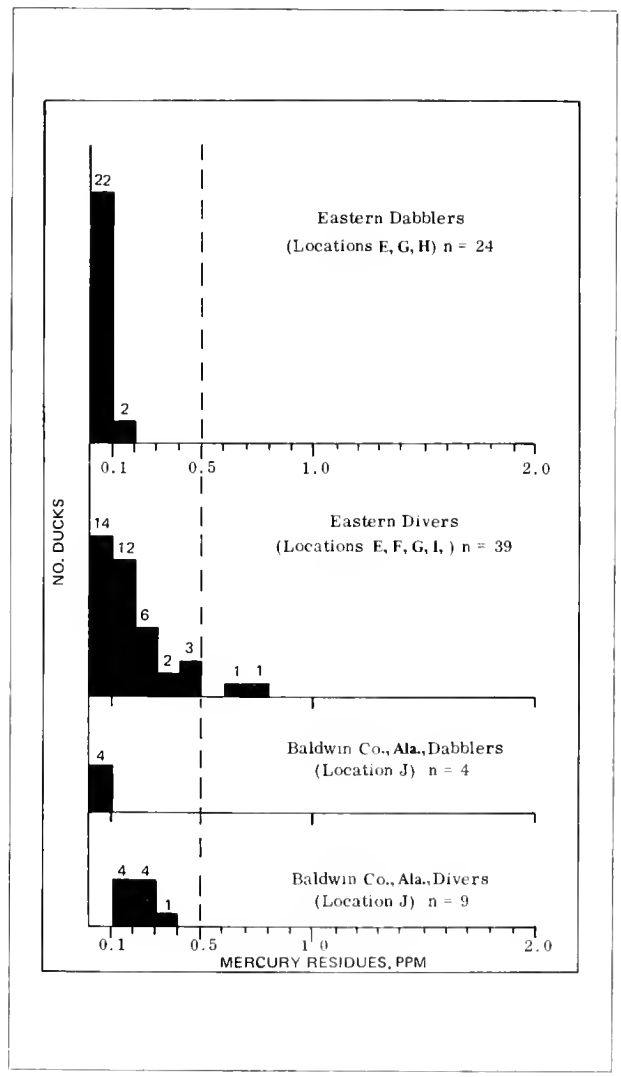

FIGURE 3. *Frequency distribution of mercury content in breast muscle of 76 ducks from eastern U.S. areas not known to have high environmental mercury levels*

use slightly more brackish water farther removed from sources of mercury contamination (W. W. Beshears, Jr., Alabama Department of Conservation and Natural Resources, Division of Game and Fish, 1975: personal communication). Although the gadwall diet contains only a very small proportion of animal food (*10*), it is one of the few dabblers that, on occasion, dives for food (*9*). Thus, gadwalls in this collection may have exposed themselves to bottom sludge with high mercury content.

HIGH-MERCURY AREAS VERSUS NONSUSPECT AREAS

Known high environmental mercury levels were reflected in concentrations in breast muscle of ducks. In dabblers from high-level areas, mercury residues ranged from 0.02 to 3.91 ppm with a median of 0.15 ppm; 8 of 55 (14 percent) met or exceeded the 0.5 ppm level. For dabblers from nonsuspect areas, comparable figures were: range, <0.01-1.47 ppm; median, 0.04 ppm; and number at or exceeding 0.5 ppm, 1 of 121 (0.8 percent).

Divers from areas of high mercury concentrations contained 0.03 to 2.0 ppm. The median was 0.27 ppm and 6 of 43 (14 percent) had residues equal to or greater than 0.5 ppm. Corresponding figures from nonsuspect areas were: range, 0.02-1.77 ppm; median, 0.18 ppm; number at or exceeding 0.5 ppm, 10 of 108 (9.2 percent).

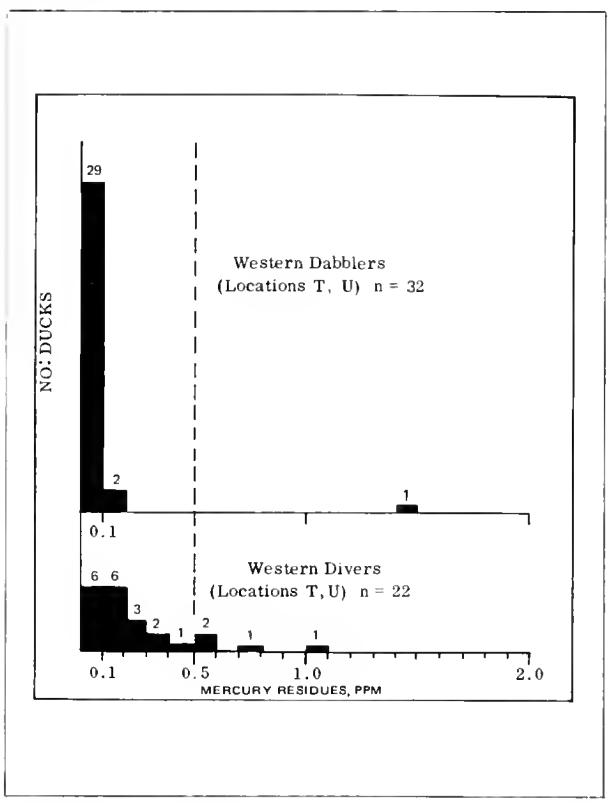

FIGURE 4. *Frequency distribution of mercury content in breast muscle of 54 ducks from western U.S. areas not known to have high environmental mercury levels*

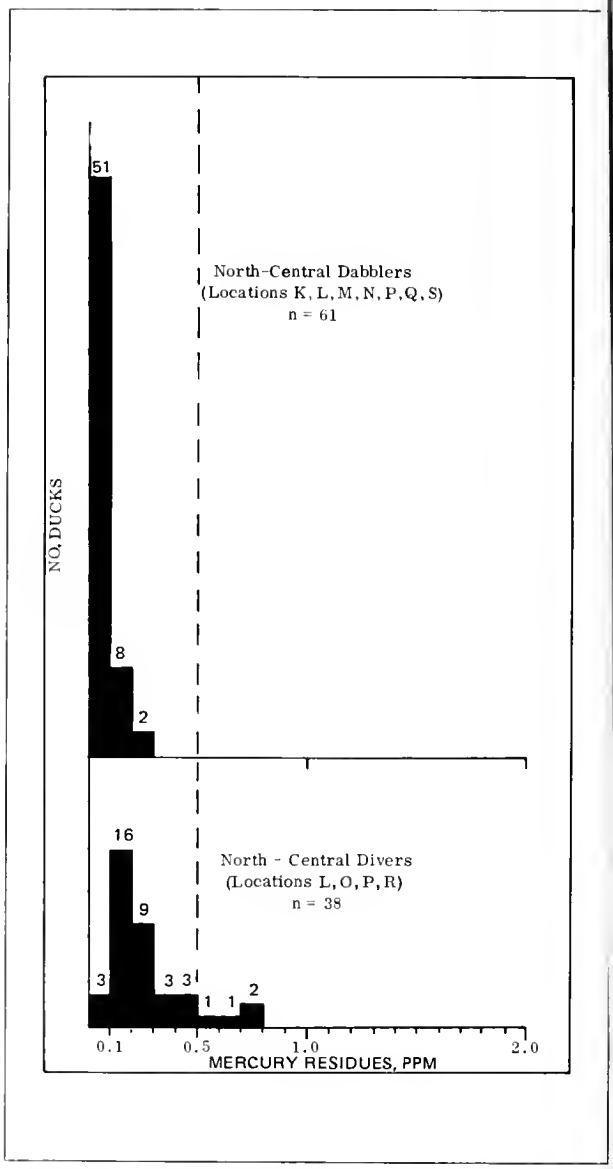

FIGURE 5. *Frequency distribution of mercury content in breast muscle of 99 ducks from north-central U.S. areas not known to have high environmental mercury levels*

The higher mercury content of ducks from some high-level areas is illustrated by comparing frequency distributions in Figure 2 with those in Figures 3-5. An example is the graph of the frequency distribution of dabblers from Port Lavaca, Tex. (Fig. 2, location C), which is flatter than that of dabblers from nonsuspect areas. The Port Lavaca dabblers were mottled ducks whose diet contains a higher proportion of animal food during fall and winter than that of other dabblers (*8*).

EARLY VERSUS LATE COLLECTIONS

The three gadwalls collected in Mobile County, Ala., December 9, 1970, had lower mercury levels than had 7 of the 9 collected February 2-4, 1971 (Table 2, location B). Gadwalls collected in December were adult,

whereas those collected in February were immature and presumably had had less time to accumulate mercury before arriving at Mobile Bay.

Although no correlation between the relationship of collection dates and mercury burdens of Mobile County lesser scaup could be established, it is probable that all lesser scaup were late migrants.

In the Tule Lake, Calif., collection (Table 3, location T) there were indications that lesser scaup collected in February had higher mercury burdens than had those collected in November (February range, 0.02-1.77 ppm; median, 0.39 ppm; number reaching or exceeding 0.5 ppm, 3 of 8; November range, 0.06-0.51 ppm; median, 0.20 ppm; number at or exceeding 0.5 ppm, 1 of 8). Tule Lake was not considered heavily contaminated with mercury, so no explanation of the heavier burdens in February ducks is offered. There was no indication of higher levels in Tule Lake mallards.

Factors mentioned above masked possible relationships of mercury burdens to the sex and age of the ducks. However, no evidence of consistently lighter burdens in immature ducks was detected.

GEOGRAPHIC RELATIONSHIPS

No large-scale geographic differences were discerned in mercury burdens of ducks collected in nonsuspect areas. As shown in Figures 3-5, most of the dabblers from each of the nonsuspect regions had residues falling in the lowest interval between 0.00 and 0.09 ppm. Only 15 of the 121 dabblers from all nonsuspect regions had levels above 0.09 ppm. Frequency distributions for divers were less regular but generally similar for all regions.

Local differences in environmental mercury levels seemed more significant than did broad geographic considerations as documented by the Alabama collection. Mercury levels of dabblers collected in a contaminated site in Mobile County (Table 2, location B; Fig. 2) were much higher than those of ducks collected in a nonsuspect area only 5-10 miles away in Baldwin County (Table 3, location J; Fig. 3).

Conclusions

Data indicate that despite the mobility of wild ducks, the principal human health hazard is in eating breast muscle of ducks shot in a few highly contaminated areas. Breast muscle of dabbling ducks from large regions of the United States was relatively free of dangerous contamination; only 1 of 121 dabblers collected in nonsuspect areas had values exceeding the FDA action guideline of 0.5 ppm for fish and shellfish. The potential hazard in eating divers is greater: about 9 percent of divers from nonsuspect areas had breast muscle levels exceeding 0.5 ppm. Livers of wild ducks, which are sometimes eaten, could be expected to have still higher mercury levels (*10-12*).

In evaluating the human health hazards, it should be borne in mind that wild ducks are unlikely to be a dietary staple for long periods and that contamination by many industrial sources has been corrected or has diminished since collections described in this paper were made in 1970-71. Prohibition of mercuric fungicides for crop seed treatment in 1970-71 might also result in somewhat lower levels, particularly among grain-eating dabblers from agricultural areas. There is considerable evidence that seed-grain treatment resulted in elevated mercury levels in ducks and other seed-eating birds in the plains provinces of Canada and the north-central United States (*10,13-15*). On the other hand, dabblers collected from the north-central States in the present study had such low mercury levels in breast muscle that substantial reduction from banning mercuric fungicides seems unlikely. Low levels in birds of this study which were shot in the fall may be caused in part by rapid excretion of mercury ingested with treated seed grain in spring (*1, 2*).

Little is known about the effects of mercury burdens of the magnitude reported here on the ducks themselves. In Swedish studies reviewed by Selikoff (*16*), muscle levels in pheasants (*Phasianus colchicus*) experimentally killed by treated seed ranged from 20 to 45 ppm, 5 to 11 times higher than levels in any duck analyzed in the present study. Other experimental studies with pheasants showed that chances that their eggs would hatch declined when mercury levels in the mothers' livers were in the range of 3 to 13 ppm (*13*). A diet containing 3 ppm mercury as methylmercury reduced reproductive success in mallards (*17*). Sublethal dosages of a mercuric fungicide adversely affected avoidance responses of coturnix quail chicks (*Coturnix coturnix*) (*18*). Mercury content of muscle tissues in the experimental birds was not reported (*17,18*) so results of these experimental studies cannot be related directly to those of the present study.

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TABLE 1. *Wild duck sampling sites, 1970-71*

Area	Sites
Regions with high environmental mercury levels	
(A) VERMONT: *Lake Champlain vicinity.* (Northern half of lake and impoundments within ¼ mile; possible sources of Hg include pulp mill, sewage, miscellaneous small industries, and outwash from natural deposits)	Addison, Panton, and Ferrisburg, Addison County; Missisquoi National Wildlife Refuge and Missisquoi Bay, Franklin County; North Hero, Grand Isle County.
(B) ALABAMA: *Mobile County.* (Ducks collected on or within 1 mile of settling basin of chlor-alkali plant)	Chickasaw, Mobile County.
(C) TEXAS: *Lavaca Bay.* (Collections within 15 miles of portion of Lavaca Bay then designated as polluted area; possible source of Hg: chlor-alkali plant)	Cox Bay, Mud Point, Smith Marsh, Calhoun County; Victoria Barge Canal near Bloomington, Victoria County.
(D) CALIFORNIA: *San Francisco Bay.* (Northeast portion: tidal water and marshes; possible sources of Hg include chlor-alkali plant, outwash from old gold extraction areas, and outwash of natural deposits. South portion: tidal waters; sewage, paint-processing plants, chipping paint from boats and yachts, and outwash of natural deposits)	Northern part: Joice and Grizzly Islands, Suisun Marshes, Solano County; Napa Marshes, Napa County. Southern part: opposite South San Francisco and Palo Alto, San Mateo and Santa Clara counties.

(Continued next page)

TABLE 1 (cont'd.). *Wild duck sampling sites, 1970-71*

	Area	Sites
	Regions not known to be contaminated	
(E)	MARYLAND: *Chesapeake Bay* (Bay waters and tidal inlets, middle one-third of Bay)	Poplar Island, Talbot County; Cove Point, Calvert County; Fishing Bay, Dorchester County.
(F)	MARYLAND: *West River.* (Tidewater)	Near junction of West and Rhodes Rivers, Anne Arundel County.
(G)	NORTH CAROLINA: *Corolla.* (Collections made in Currituck Sound, brackish water)	Corolla, Currituck County.
(H)	NORTH CAROLINA: *Grandy.* (Trap mortalities in Albemarle Sound; brackish water)	Grandy, Currituck County.
(I)	NORTH CAROLINA: *Pamlico Point.* (Pamlico Sound; brackish water)	Near Lowland, Pamlico County.
(J)	ALABAMA: *Baldwin County.* (Tidal delta)	Gustang Bay, Mobile Delta, near Daphne, Baldwin County.
(K)	NORTH DAKOTA: *Stanton.* (Missouri River)	Near Stanton, Mercer County.
(L)	NORTH DAKOTA: *Woodworth.* (Permanent and semipermanent glacial marshes)	Vicinity of Woodworth, Stutsman County.
(M)	NORTH DAKOTA: *Pettibone* (Permanent glacial marsh)	5 miles SW of Pettibone, Kidder County.
(N)	NORTH DAKOTA: *Audubon National Wildlife Refuge* (Feedlots)	Vicinity of Coleharbor, McLean County.
(O)	SOUTH DAKOTA: *Marshall County.* (Permanent glacial lake)	Piyas Lake, SE of Eden, Marshall County.
(P)	SOUTH DAKOTA: *McPherson County* (Dugouts or artificial stock water excavations, plus semipermanent and permanent glacial potholes)	Near Leola, McPherson County, and various points nearby in McPherson and adjacent Edmunds counties.
(Q)	SOUTH DAKOTA: *Sand Lake National Wildlife Refuge.* (Semipermanent glacial marsh)	Near Houghton, Brown County.
(R)	MINNESOTA: *Itasca County* (Large glacial lake)	Lake Winnibigoshish, Itasca County.
(S)	MINNESOTA: *Agassiz National Wildlife Refuge.* (Large artificial pool)	Near Middle River, Marshall County.
(T)	CALIFORNIA: *Tule Lake* and *Lower Klamath National Wildlife Refuges.* (Sumps on refuges, receiving drainage from agricultural lands)	Near Tulelake, Siskiyou County.
(U)	UTAH: *Brigham City.* (Marshes on and near Bear River National Wildlife Refuge)	Near Brigham City, Box Elder County.

TABLE 2. *Total mercury in breast muscle of ducks collected in areas with high environmental mercury levels, 1970-71*

(A) VERMONT: Lake Champlain vicinity	Mallard	M	Imm	0.09	11- 6-70	Common goldeneye	M	Ad	0.27	11-17-70
	Black duck	F	Ad	0.06	11-11-70		M	Imm	0.21	11-17-70
		F	Ad	0.17	11-21-70		M	Imm	0.54	11-20-70
		F	Ad	0.23	11-21-70		F	Ad	0.29	11-17-70
		F	Imm	0.09	11- 8-70		F	Ad	0.76	11-20-70
		F	Imm	0.04	11-21-70		F	Imm	0.46	11-12-70
							F	Imm	0.46	11-17-70
							F	Imm	0.42	11-29-70
	TOTAL DUCKS			6		TOTAL DUCKS			8	
	Range: Mercury levels, ppm			0.04-0.23		Range: Mercury levels, ppm			0.21-0.76	
	Median, ppm			0.09		Median, ppm			0.44	
	No. at 0.5 ppm or above			0 of 6		No. at 0.5 ppm or above			2 of 8	

(Continued next page)

TABLE 2 (cont'd.). *Total mercury in breast muscle of ducks collected in areas with high environmental mercury levels, 1970-71*

Location [1]	Dabbling Ducks					Diving and Sea Ducks				
	Species	Sex	Age	Mercury Level, ppm	Date	Species	Sex	Age	Mercury Level, ppm	Date
(B) ALABAMA: Mobile County	Gadwall	M	Ad	0.37	12- 9-70	Lesser scaup	M	Ad	0.15	2- 2-71
		M	Ad	0.24	12- 9-70		M	Ad	0.16	2- 2-71
		M	Ad	0.08	12- 9-70		M	Imm	0.16	12- 9-70
		M	Ad	0.18	2- 4-71		M	Imm	0.16	2- 2-71
		M	Imm	3.91	2- 2-71		M	Imm	0.27	2- 2-71
		M	Imm	0.22	2- 2-71		M	Imm	0.14	2- 2-71
		M	Imm	0.16	2- 2-71		F	Ad	2.00	12- 9-70
		M	Imm	1.9	2- 2-71					
		M	Imm	0.87	2- 2-71					
		M	Imm	0.97	2- 4-71					
		M	Imm	1.2	2- 4-71					
		M	Imm	0.57	2- 4-71					
	TOTAL DUCKS			12		TOTAL DUCKS			7	
	Range: Mercury levels, ppm			0.08-3.9		Range: Mercury levels, ppm			0.14-2.0	
	Median, ppm			0.47		Median, ppm			0.16	
	No. at 0.5 ppm or above			6 of 12		No. at 0.5 ppm or above			1 of 7	
(C) TEXAS: Port Lavaca	Mottled duck	M	Ad	0.18	11-11-70	Lesser scaup	M	Ad	0.19	11-11-70
		M	Ad	0.15	11-11-70		M	Ad	0.43	11-25-70
		M	Ad	0.09	11-11-70		M	Ad	0.16	11-25-70
		M	Ad	0.43	11-19-70		M	Ad	1.0	11-25-70
		M	ND	0.43	12-26-70		M	Ad	0.10	11-25-70
		M	ND	0.14	12-26-70		M	Ad	0.30	11-25-70
		M	ND	0.28	12-26-70		M	Ad	0.38	11-25-70
		M	ND	0.43	1- 4-71		M	ND	0.16	12-20-70
		M	ND	0.35	1- 6-71		M	ND	0.17	12-27-70
		F	Ad	0.07	11-11-70		M	ND	0.32	12-29-70
		F	Ad	0.15	11-15-70		M	ND	0.43	1-11-71
		F	Ad	0.25	11-15-70		M	ND	0.16	1-11-71
		F	Ad	0.10	11-19-70		F	Ad	0.40	11-20-70
		F	ND	0.37	12-26-70		F	ND	0.06	12-29-70
		F	ND	0.32	12-27-70		F	ND	0.09	2- 8-71
		F	ND	0.40	12-29-70		F	ND	0.12	2- 8-71
	TOTAL DUCKS			16		TOTAL DUCKS			16	
	Range: Mercury levels, ppm			0.07-0.43		Range: Mercury levels, ppm			0.06-1.0	
	Median, ppm			> 0.26		Median, ppm			0.18	
	No. at 0.5 ppm or above			0 of 16		No. at 0.5 ppm or above			1 of 16	
(D) CALIFORNIA: San Francisco Bay	Mallard	M	Ad	0.04	11- 9-70	Lesser scaup	M	Ad	0.68	12-12-70
		M	Ad	0.10	11- 9-70		F	Ad	0.22	12-12-70
		M	Ad	0.03	11- 9-70		F	Imm	0.13	12-12-70
		M	Ad	0.05	11- 9-70		F	Ad	0.03	12-12-70
		M	Ad	0.03	11- 9-70	Greater scaup	M	Ad	0.68	12-12-70
		M	Ad	0.24	1-26-71		M	Imm	0.20	12-12-70
		M	Imm	0.04	1-26-71		F	Ad	0.49	12- 7-70
		M	Imm	0.10	1-26-71		F	Ad	0.28	12- 7-70
		M	Ad	0.02	1-26-71		F	Ad	0.31	12- 7-70
		M	Ad	1.06	1-26-71		F	Imm	0.19	12- 9-70
		F	Ad	0.12	11- 9-70		F	Imm	0.41	12-12-70
		F	Ad	0.06	11- 9-70		F	Imm	0.44	12-12-70
		F	Ad	0.05	11- 9-70					
		F	Ad	0.03	1-26-71					
		F	Ad	0.02	1-26-71					
		F	Imm	0.62	1-26-71					
	Pintail	M	Ad	0.09	1-26-71					
		M	Imm	0.05	1-26-71					
		M	Imm	0.06	1-26-71					
		F	Ad	0.08	1-26-71					
		F	Imm	0.15	1-26-71					
	TOTAL DUCKS			21		TOTAL DUCKS			12	
	Range: Mercury levels, ppm			0.02-1.06		Range: Mercury levels, ppm			0.03-0.75	
	Median, ppm			0.06		Median, ppm			> 0.29	
	No. at 0.5 ppm or above			2 of 21		No. at 0.5 ppm or above			2 of 12	

NOTE: M = male, F= female, Imm = immature, Ad = adult.
ND = no data.

[1] See Table 1 for complete description of collection locations.

TABLE 3. *Total mercury in breast muscle of ducks collected in areas not known to be contaminated, 1970-71*

Location [1]	Dabbling Ducks: Species	Sex	Age	Mercury Level, ppm	Date	Diving and Sea Ducks: Species	Sex	Age	Mercury Level, ppm	Date
(E) MARYLAND: Chesapeake Bay	Mallard	M	Ad	0.01	1- 9-71	Common scoter	M	Ad	0.20	12- 1-70
		M	Imm	0.06	12-27-70		M	Ad	0.10	12- 1-70
		M	Imm	0.01	12-27-70		F	Ad	0.06	12- 1-70
		M	Imm	0.03	1- 2-71	Surf scoter	M	Ad	0.17	12- 1-70
		F	Ad	0.03	1- 2-71	White-winged scoter	M	Ad	0.08	12- 1-70
		F	Ad	0.06	1- 9-71		M	Ad	0.07	12- 1-70
		F	Imm	0.02	1- 2-71		M	Ad	0.43	12- 1-70
		F	Imm	0.01	1- 9-71		ND	Imm	0.61	12- 1-70
						Canvasback	ND	ND	0.09	12-31-70
							ND	ND	0.16	12-31-70
							ND	ND	0.05	12-31-70
							ND	ND	0.22	12-31-70
							ND	ND	0.11	12-31-70
							ND	ND	0.24	12-31-70
							ND	ND	0.15	12-31-70
							ND	ND	0.10	12-31-70
	TOTAL DUCKS 8 Range: Mercury levels, ppm 0.01-0.06 Median, ppm >0.02 No. at 0.5 ppm or above 0 of 8					TOTAL DUCKS 16 Range: Mercury levels, ppm 0.05-0.61 Median, ppm 0.13 No. at 0.5 ppm or above 1 of 16				
(F) MARYLAND: West River	No samples collected					Canvasback	ND	ND	0.16	3-71
							ND	ND	0.08	3-71
							ND	ND	0.08	3-71
							ND	ND	0.08	3-71
							ND	ND	0.12	3-71
							ND	ND	0.08	3-71
							ND	ND	0.10	3-71
							ND	ND	0.08	3-71
						TOTAL DUCKS 8 Range: Mercury levels, ppm 0.08-0.16 Median, ppm 0.08 No. at 0.5 ppm or above 0 of 8				
(G) NORTH CAROLINA: Corolla	Mallard	M	Ad	0.08		Lesser scaup	M	Ad	0.47	
		M	Ad	0.04			M	Imm	0.14	
		M	Ad	0.03	11- 8-70		M	Imm	0.23	11- 8-70
		M	Ad	0.08	to		M	Imm	0.20	to
		M	Imm	0.04	12- 5-70		M	Imm	0.42	12- 5-70
		F	Imm	0.05			F	Imm	0.10	
		F	Imm	0.06			F	Imm	0.37	
		F	Imm	0.12						
	TOTAL DUCKS 8 Range: Mercury levels, ppm 0.03-0.12 Median, ppm >0.05 No. at 0.5 ppm or above 0 of 8					TOTAL DUCKS 7 Range: Mercury levels, ppm 0.10-0.47 Median, ppm 0.23 No. at 0.5 ppm or above 0 of 7				
(H) NORTH CAROLINA: Grandy	Mallard	M	Ad	0.01	2-15-71	No samples collected				
		M	Ad	0.01	2-15-71					
		M	Imm	0.01	2-15-71					
		M	Imm	0.02	2-15-71					
		M	Imm	0.01	2-15-71					
		M	Imm	<0.01	2-15-71					
		F	Ad	0.16	2-15-71					
		F	Imm	0.01	1-15-71					
	TOTAL DUCKS 8 Range: Mercury levels, ppm <0.01-0.16 Median, ppm 0.01 No. at 0.5 ppm or above 0 of 8									
(I) NORTH CAROLINA: Pamlico Pt.	No samples collected					Lesser scaup	M	Ad	0.19	2-15-71
							M	Ad	0.35	2-15-71
							M	Ad	0.70	3-29-71
							M	Imm	0.08	2-15-71
							M	Imm	0.04	2-15-71
							M	Imm	0.03	3-29-71
							M	Imm	0.22	3-29-71
							F	Ad	0.03	3-29-71
						TOTAL DUCKS 8 Range: Mercury levels, ppm 0.03-0.70 Median, ppm >0.13 No. at 0.5 ppm or above 1 of 8				

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TABLE 3 (cont'd.). *Total mercury in breast muscle of ducks collected in areas not known to be contaminated, 1970-71*

Location [1]	Dabbling Ducks					Diving and Sea Ducks				
	Species	Sex	Age	Mercury Level, ppm	Date	Species	Sex	Age	Mercury Level, ppm	Date
(J) ALABAMA: Baldwin County	Gadwall	M	1mm	0.07	12- 9-70	Lesser scaup	M	Ad	0.24	11-26-70
		M	1mm	0.02	12- 9-70		M	Ad	0.21	11-26-70
		F	1mm	0.09	12- 9-70		M	Ad	0.20	2- 3-71
		F	1mm	0.04	12- 9-70		M	Imm	0.12	11-26-70
							M	Imm	0.16	11-27-70
							M	Imm	0.27	11-27-70
							M	Imm	0.18	11-27-70
							F	Imm	0.18	11-26-70
							F	Imm	0.34	2- 3-71
	TOTAL DUCKS 4 Range: Mercury levels, ppm 0.02-0.09 Median, ppm < 0.05 No. at 0.5 ppm or above 0 of 4					TOTAL DUCKS 9 Range: Mercury levels, ppm 0.12-0.34 Median, ppm 0.20 No. at 0.5 ppm or above 0 of 9				
(K) NORTH DAKOTA: Stanton	Mallard	M	ND	0.02	12-29-70	No samples collected				
		M	ND	0.03	12-29-70					
		M	ND	0.03	12-29-70					
		M	ND	0.02	12-29-70					
		M	ND	0.02	12-29-70					
		F	ND	0.02	12-29-70					
	TOTAL DUCKS 6 Range: Mercury levels, ppm 0.02-0.03 Median, ppm 0.02 No. at 0.5 ppm or above 0 of 6									
(L) NORTH DAKOTA: Woodworth	Mallard	M	Ad	0.05	10- 2-70	Lesser scaup	M	Ad	0.70	10- 6-70
		M	Ad	0.04	10- 2-70		M	Ad	0.11	10- 6-70
		M	Ad	0.02	10- 2-70		M	Ad	0.53	10- 6-70
		M	Ad	0.02	10- 3-70		M	Ad	0.21	10- 8-70
		F	Ad	0.02	10- 2-70		M	Ad	0.36	10-29-70
		F	Ad	0.01	10- 3-70		M	Ad	0.12	10-29-70
		F	Ad	0.03	10- 3-70		M	Ad	0.70	10-29-70
		F	Ad	0.05	10-29-70		F	Ad	0.43	10- 6-70
							F	Ad	0.18	10- 6-70
							F	Ad	0.12	10- 6-70
							F	Ad	0.22	10- 7-70
							F	Ad	0.04	10-29-70
							F	Ad	0.22	10-29-70
							F	Ad	0.37	10-29-70
							F	Ad	0.26	10-29-70
							F	Ad	0.43	10-29-70
	TOTAL DUCKS 8 Range: Mercury levels, ppm 0.01-0.05 Median, ppm > 0.02 No. at 0.5 ppm or above 0 of 8					TOTAL DUCKS 16 Range: Mercury levels, ppm 0.04-0.70 Median, ppm 0.24 No. at 0.5 ppm or above 3 of 16				
(M) NORTH DAKOTA: Pettibone	Mallard	M	Ad	0.18	11- 3-70	No samples collected				
		M	Ad	0.03	11- 3-70					
		M	Ad	0.04	11- 3-70					
		F	Ad	0.06	11- 3-70					
		F	Ad	0.18	11- 3-70					
		F	Ad	0.05	11- 3-70					
		F	Ad	0.07	11- 3-70					
	TOTAL DUCKS 7 Range: Mercury levels, ppm 0.03-0.18 Median, ppm 0.06 No. at 0.5 ppm or above 0 of 7									
(N) NORTH DAKOTA: Audubon NWR	Mallard	M	Ad	0.04	10-29-70	No samples collected				
		M	Ad	0.04	10-29-70					
		M	Ad	0.03	10-29-70					
		M	Ad	0.03	10-29-70					
		F	Ad	0.07	10-29-70					
		F	Ad	0.01	10-29-70					
		F	Ad	0.10	10-29-70					
		F	Ad	0.03	10-29-70					
	TOTAL DUCKS 8 Range: Mercury levels, ppm 0.01-0.10 Median, ppm > 0.03 No. at 0.5 ppm or above 0 of 8									

(Continued next page)

TABLE 3 (cont'd.). *Total mercury in breast muscle of ducks collected in areas not known to be contaminated, 1970-71*

Location [1]	Dabbling Ducks					Diving and Sea Ducks				
	Species	Sex	Age	Mercury Level, ppm	Date	Species	Sex	Age	Mercury Level, ppm	Date
(O) SOUTH DAKOTA: Marshall County	No samples collected					Lesser scaup	M	Ad	0.28	10-27-70
							M	Ad	0.20	10-27-70
							M	Ad	0.26	10-27-70
							M	Ad	0.40	10-27-70
							M	Ad	0.15	10-27-70
							F	Ad	0.65	10-27-70
							F	Ad	0.38	10-27-70
							F	Ad	0.15	10-27-70
						TOTAL DUCKS			8	
						Range: Mercury levels, ppm			0.15-0.65	
						Median, ppm			0.27	
						No. at 0.5 ppm or above			1 of 8	
(P) SOUTH DAKOTA: McPherson County	Mallard	M	Ad	0.02	10- 7-70	Lesser scaup	M	Ad	0.15	10-15-70
		M	Ad	0.03	10- 7-70		M	Ad	0.19	10-15-70
		M	Ad	0.02	10- 7-70		F	Ad	0.17	10-15-70
		M	Ad	0.06	10- 7-70		F	Ad	0.09	10-15-70
		M	Ad	0.04	10- 7-70		F	Ad	0.18	10-15-70
		F	Ad	0.02	10- 7-70		F	Ad	0.18	10-15-70
		F	Ad	0.03	10- 7-70					
		F	Ad	0.04	10- 7-70					
	TOTAL DUCKS			8		TOTAL DUCKS			6	
	Range: Mercury levels, ppm			0.02-0.06		Range: Mercury levels, ppm			0.09 0.19	
	Median, ppm			0.03		Median, ppm			>0.17	
	No. at 0.5 ppm or above			0 of 8		No. at 0.05 ppm or above			0 of 6	
(Q) SOUTH DAKOTA: Sand Lake NWR	Mallard	M	Ad	0.03	11-20-70	No samples collected				
		M	Ad	0.03	11-20-70					
		M	Ad	0.02	11-20-70					
		M	Ad	0.02	11-20-70					
		M	Ad	0.03	11-20-70					
		F	Ad	0.03	11-20-70					
		F	Ad	0.05	11-20-70					
		F	Ad	0.02	11-20-70					
	TOTAL DUCKS			8						
	Range: Mercury levels, ppm			0.02-0.05						
	Median, ppm			0.03						
	No. at 0.5 ppm or above			0 of 8						
(R) MINNESOTA: Itasca	No samples collected					Lesser scaup	M	Ad	0.07	10-15-70
							M	Ad	0.15	10-15-70
							M	Ad	0.20	10-15-70
							M	Ad	0.25	10-15-70
							M	Ad	0.15	10-15-70
							F	Ad	0.10	10-15-70
							F	Ad	0.19	10-15-70
							F	Ad	0.15	10-15-70
						TOTAL DUCKS			8	
						Range: Mercury levels, ppm			0.07-0.25	
						Median, ppm			0.15	
						No. at 0.05 ppm or above			0 of 8	
(S) MINNESOTA: Agassiz	Mallard	M	Ad	0.09	10- 8-70	No samples collected				
		M	Ad	0.07	10- 8-70					
		M	Ad	0.07	10- 8-70					
		M	Ad	0.04	10-28-70					
		M	Ad	0.03	10-28-70					
		M	Ad	0.10	10-28-70					
		F	Ad	0.04	10- 8-70					
		F	Ad	0.18	10- 8-70					
		F	Ad	0.08	10- 8-70					
		F	Ad	0.13	10- 8-70					
		F	Ad	0.17	10- 8-70					
		F	Ad	0.24	10-28-70					
		F	Ad	0.04	10-28-70					
		F	Ad	0.10	10-28-70					
		F	Ad	0.12	10-28-70					
		F	Ad	0.20	10-28-70					
	TOTAL DUCKS			16						
	Range: Mercury levels, ppm			0.03-0.24						
	Median, ppm			>0.09						
	No. at 0.5 ppm or above			0 of 16						

(Continued next page)

TABLE 3 (cont'd.). *Total mercury in breast muscle of ducks collected in areas not known to be contaminated, 1970-71*

	Dabbling Ducks					Diving and Sea Ducks				
Location [1]	Species	Sex	Age	Mercury Level, ppm	Date	Species	Sex	Age	Mercury Level, ppm	Date
(T) CALIFORNIA: Tule Lake and Lower Klamath NWR	Mallard	M	Ad	0.09	11-17-70	Lesser scaup	M	Ad	0.06	11-17-70
		M	Ad	0.03	11-17-70		M	Ad	0.11	11-17-70
		M	Ad	0.06	11-17-70		M	Ad	0.22	11-17-70
		M	Ad	0.02	11-17-70		M	Ad	0.10	11-17-70
		M	Ad	0.04	11-17-70		M	Ad	0.31	2-15-71
		M	Ad	0.17	11-17-70		M	Ad	0.72	2-22-71
		M	Ad	0.02	1- 5-71		M	Ad	0.32	2-22-71
		M	Ad	0.08	1- 5-71		M	Ad	0.02	2-22-71
		M	Ad	0.06	1- 8-71		M	Imm	1.77	2-22-71
		F	Ad	1.47	11-17-70		F	Ad	0.51	11-17-70
		F	Ad	0.02	11-17-70		F	Ad	0.16	11-17-70
		F	Ad	0.02	1- 1-71		F	Imm	0.29	11-17-70
		F	Ad	0.07	1- 1-71		F	Imm	0.23	11-17-70
		F	Ad	0.03	1- 5-71		F	Ad	0.58	2-15-71
		F	Ad	0.05	1- 8-71		F	Ad	0.02	2-22-71
		F	Ad	0.04	1- 8-71		F	Ad	0.49	2-22-71
	TOTAL DUCKS 16 Range: Mercury levels, ppm 0.02-1.47 Median, ppm > 0.04 No. at 0.5 ppm or above 1 of 16					TOTAL DUCKS 16 Range: Mercury levels, ppm 0.02-1.77 Median, ppm 0.26 No. at 0.5 ppm or above 4 of 16				
(U) UTAH: Brigham City	Mallard	M	Ad	0.05	10-25-70	Lesser scaup	M	Ad	0.14	10-31-70
		M	Ad	0.03	10-25-70		F	Imm	0.12	12-29-70
		M	Ad	0.02	10-25-70					
		M	Ad	0.02	10-25-70	Greater scaup	F	Ad	0.02	10-26-70
		M	Ad	0.01	12-14-70					
		M	Ad	0.02	12-14-70					
		M	Ad	0.06	12-14-70	Ring-necked duck	M	Ad	0.06	10-31-70
		M	Ad	0.02	12-15-70		M	Imm	0.09	10-28-70
		M	Imm	0.19	12-19-70		M	Imm	0.18	10-29-70
		F	Ad	0.01	10-25-70					
		F	Imm	0.03	10-25-70					
		F	Imm	0.08	10-25-70					
		F	Imm	0.02	10-25-70					
		F	Ad	0.05	12-14-70					
		F	Ad	0.06	12-14-70					
		F	Ad	0.02	12-14-70					
	TOTAL DUCKS 16 Range: Mercury levels, ppm 0.01-0.19 Median, ppm 0.02 No. at 0.5 ppm or above 0 of 16					TOTAL DUCKS 6 Range: Mercury levels, ppm 0.02-0.18 Median, ppm 0.10 No. at 0.05 ppm or above 0 of 6				

NOTE: M = male, F = female, Imm = immature, Ad = adult.
ND = no data.

[1] See Table 1 for complete description of collection locations.

Organochlorine Pesticide Residues in Small Migratory Birds, 1964-73

David W. Johnston [1]

ABSTRACT

Chlorinated hydrocarbon pesticide burdens, especially those of DDT and its metabolites, have been determined for 19 species of small terrestrial migratory birds killed chiefly at Florida television towers from 1964 to 1973. All 128 samples were sorted into pools by species. All pooled samples except one contained DDE and often DDT and DDD; dieldrin was present in 60 of the samples; but no PCB's were detected. In small subsamples, ΣDDT (p,p'-DDT, p,p'-DDD, and p,p'-DDE) residues sometimes differed between males and females, adults and immatures, and northbound and southbound migrants but results of these comparisons were inconclusive. ΣDDT burdens were highest in adipose tissue and much lower in liver and brain samples. Epecially among birds taken since 1970 have the pesticide levels in adipose tissue been at low levels, generally less than 3 ppm ΣDDT. These low quantities are comparable to those quoted in other reports on birds of similar trophic levels. The insectivorous and/or partly granivorous birds feeding on or near the ground tended to have higher ΣDDT levels than did the more arboreal species.

Introduction

Although the widespread occurrence and effects of biocides in natural ecosystems are matters of intense public interest, research reports on birds have concentrated on terminal members of food chains, the carnivorous and piscivorous species. These top carnivores are known to accumulate chlorinated hydrocarbon pesticides in fatty tissues. In species such as osprey (*Pandion haliaetus*), double-crested cormorant (*Phalacrocorax auritus*), and peregrine (*Falco peregrinus*), correlations have been made between pesticides, especially DDE, and population declines, mortality, and alteration of physiological processes resulting in impaired reproductive success (*1-3*). Particularly symptomatic of DDT burdens are decreases in eggshell thickness.

In terrestrial ecosystems, however, very little attention has been given to organisms of subterminal trophic levels wherein stored pesticides and pollutants could play important roles in population dynamics. For wild North American migratory birds the published literature contains scattered reports of pesticide burdens, but few of these reports contain data on large numbers of species or individuals (*3-17*). Additional studies have concentrated on pesticide effects on small bird populations (*18-24*) or laboratory experiments (*25-29*). The present investigation concerns pesticide burdens of subterminal members of food chains, the myriads of small insectivorous, granivorous, or frugivorous birds so vital in the metabolism of terrestrial ecosystems.

Sampling Methods

For at least 20 years thousands of small birds have collided with tall television towers and other person-made structures during their autumnal and vernal nocturnal migratory flights, or have died at airport ceilometers in the southeastern United States (*30-32*). The majority of the birds are insectivorous vireos and warblers that breed in eastern North America and winter in the West Indies or Central America. Alert local observers gather the dead birds in the early morning hours, usually within 6 hours after death, place them in plastic bags, and freeze them with feather coverings intact for later studies. The large sample sizes have proved valuable in migration and distributional analyses and weight and fat studies, and as scientific specimens and skeletons. For the present investigation a total of 19 species and 908 individuals were utilized. Autumnal individuals taken at the Florida sites at the beginning of protracted over-water flights were markedly obese: 30 percent or more of the body weight was stored subcutaneous and abdominal fat (*33,34*). On the other hand, the vernal migrants had completed a protracted flight from the south and were lean, having utilized much of the premigratory stored fat as a flight energy source (*33*).

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Collection sites for birds analyzed here included the following Florida locations: television towers WJKS and WJAX, Jacksonville; WDBO tower near Orlando; WCTV tower north of Tallahassee; the Vertical Assembly Building, Cape Canaveral; and the Vero Beach area.

Analytical Procedures

For an accurate analysis of so many birds, single-night kills were first sorted by species, then, when possible, by sex and age. A sample size of 10 was sought for given sex and age groups, but frequently fewer than 10 were available. Pooled samples of adipose tissue were dissected from the interfurcular subcutaneous depots. In initial analyses, liver and brain samples were also taken. An attempt was made to obtain approximately the same quantity of tissue from each bird in order not to bias the pooled sample. Pooled fat samples were weighed immediately to obtain a wet weight; these averaged 1.16 g with a range of 0.58-1.95 g. Each pooled sample was thoroughly ground and mixed with sodium sulfate in a VirTis homogenizer, then extracted for 10 hours in a Soxhlet apparatus using petroleum ether as a solvent. Following solvent evaporation, the lipid residues were weighed; average weight was 0.76 g with a range of 0.14-1.56 g. Lipid residues were partitioned with acetonitrile and hexane, and the acetonitrile fraction was cleaned on an 8 percent water deactivated florisil column using a 3:1 hexane:benzene eluant. The resulting eluate was concentrated or diluted in hexane, as necessary, for gas chromatography.

Most samples were processed on a Varian 600-D gas chromatograph containing a 6-ft-by-¼-in. glass column of 1:1 6.4 percent OV-210:1.6 percent OV-17 on chromosorb W with an electron-capture detector. A second glass column of 1.5 percent OV-17:1.95 percent QFI on Gas-Chrom Q of similar dimensions in a Varian model 2100 was used for confirmation. Other instrumental parameters were: injection port, 210° C; column, 212° C; detector, 215° C; and nitrogen flow rate, 45 ml/min. Recoveries for organochlorine compounds ranged from 75 to 95 percent. Sensitivity was greater than 0.01 mg/ml.

Results

SEX DIFFERENCES

Because the investigations reported here for small migratory birds are the first of this quantitative and comprehensive nature, a number of variables in the samples had to be evaluated and resolved at the outset. One question involved any possible differences in the pesticide burdens of the two sexes. Four species were selected at random and intraspecific samples of each sex were compared. Table 1 shows that the difference between ΣDDT (*p,p'*-DDT, *p,p'*-DDD, and *p,p'*-DDE) concentrations in each sex exceeded 50 percent in only two of the six comparisons. These variable differences suggest that, in general, attributing differences in ΣDDT burdens to sex is largely unwarranted.

AGE DIFFERENCES

Inasmuch as autumnal samples of migratory birds killed at television towers or ceilometers nearly always contain a high proportion of immature individuals, i.e., birds-of-the-year (*31,32*), it was deemed advisable to investigate possible differences in pesticide burdens in different intraspecific age groups. Eight species samples were used for comparisons (Table 2). In only 5 of the 12 pairings the percentage of difference in ΣDDT concentrations between age groups was 50 or more; hence it is doubtful that difference in age plays a significant role in pesticide burdens of these birds.

Because the immature birds were only 4-5 months old at the time of death, there is a limited number of sources which may have contributed to their ΣDDT

TABLE 1. *Differences between ΣDDT residues in adipose tissue of males and females of selected bird species, 1964-72*

Species	Date	Locality	Sample Size [1]	Body Weight, g	ΣDDT Residues, ppm wet weight	Percent Difference [2]
Dendroica striata (Blackpoll Warbler)	May 1971	WJKS	5♂	12.1	0.21	
	May 1971	WJKS	5♀	11.8	0.06	71
Dendroica caerulescens (Black-throated Blue Warbler)	Oct 1972	WDBO	10A♂	—	1.19	
	Oct 1972	WDBO	10A♀	—	0.66	44
	Oct 1972	WDBO	9I♂	—	1.10	
	Oct 1972	WDBO	10I♀	—	1.55	29
Seiurus aurocapillus (Ovenbird)	Oct 1964	WJAX	10A♂	23.4	5.35	
	Oct 1964	WJAX	9A♀	23.3	3.23	39
Setophaga ruticilla (American Redstart)	Oct 1964	WJXT	3A♂	—	10.25	
	Oct 1964	WJXT	12A♀	—	10.42	1
	May 1972	VAB	8♂	7.2	3.27	
	May 1972	VAB	10♀	6.7	0.97	70

NOTE: — = no data.
[1] A = adult; I = immature.
[2] Difference between values expressed as a percent of the larger value.

TABLE 2. *Differences between ΣDDT residues in adipose tissue of selected bird species of various age groups*

Species	Date	Locality	Sample Size [1]	Average Body Weight, g	Σ DDT Residues, ppm wet weight	Percent Difference [2]
Dumetella carolinensis (Gray Catbird)	Oct 1972	WCTV	10A	35.8	0.33	
	Oct 1972	WCTV	4I	36.6	0.27	18
Vireo olivaceus (Red-eyed Vireo)	Oct 1972	WCTV	10A	25.0	0.50	
	Oct 1972	WCTV	10I	24.1	0.18	64
Dendroica coronata (Yellow-rumped Warbler)	Nov 1966	WCTV	4A	10.4	7.09	
	Nov 1966	WCTV	4I	11.3	5.77	19
	fall 1969	WCTV	5A	11.7	5.31	
	fall 1969	WCTV	7I	12.7	7.56	30
Dendroica caerulescens (Black-throated Blue Warbler)	Oct 1972	WJKS	7A♂	12.4	1.35	
	Oct 1972	WJKS	7I♂	12.8	0.87	36
	Oct 1972	WDBO	10A♀	—	0.66	
	Oct 1972	WDBO	10I♀	—	1.55	57
	Oct 1972	WDBO	10A♂	—	1.19	
	Oct 1972	WDBO	9I♂	—	1.10	8
Seiurus aurocapillus (Ovenbird)	Oct 1964	WJXT	10A	25.3	3.33	
	Oct 1964	WJXT	9I	25.8	2.73	18
	Oct 1968	WJXT	10A	—	3.09	
	Oct 1968	WJXT	3I	—	1.24	60
Geothlypis trichas (Common Yellowthroat)	Oct 1972	WJKS	10A	11.4	4.47	
	Oct 1972	WJKS	10I♂	10.9	3.28	27
Setophaga ruticilla (American Redstart)	Oct 1971	WJKS	10A♀	8.9	5.62	
	Oct 1971	WJKS	10I♀	9.1	12.33	54
Zonotrichia albicollis (White-throated Sparrow)	fall 1966	WCTV	6A	—	2.47	
	fall 1966	WCTV	6I	—	15.09	84

NOTE: — = no data.
[1] A = adult; I = immature.
[2] Difference between values expressed as a percent of the larger value.

burdens: transfer of a DDT metabolite from parent to offspring in the egg; contaminated food obtained from parents; and food taken by the independent immature birds. In 8 of the 12 pairings, adults had the greater ΣDDT burdens, possibly because the 4-to-5-month-old immatures simply had had less time to ingest DDT-laden foods than had the adults aged 1 or more years. On the other hand, some immatures had greater DDT burdens than had the adults (Table 2). It is possible that second- or third-year adults had eliminated or translocated internally a portion of a DDT metabolite when they lost stored fat supplies during at least two previous long-distance flights (*35-39*). It is also possible that the immatures were raised in or migrated through areas with unusually high degrees of pesticide contamination.

ORGAN DIFFERENCES

In view of the facts that chlorinated hydrocarbon pesticides are especially fat-soluble and that fat content of vertebrate organs differs widely, the author analyzed three tissue or organ types: adipose tissue, liver, and brain. In every species sampled (Table 3), ΣDDT burdens progressively decreased from adipose tissue to liver to brain or from adipose tissue to brain on a wet-weight basis. Furthermore, the author found that extractable lipid also decreased from adipose tissue to liver to brain on a percentage basis. DDT burdens, expressed on a lipid-weight basis, also decreased from adipose tissue to brain. The difference in DDT burdens between adipose tissue and brain expressed on a wet-weight basis is approximately 10 times that expressed on a lipid basis, partly because extractable lipids from brains represent only about 10 percent of the wet weight. In most analyses here only adipose tissue was sampled for pesticide burdens.

INTRASAMPLE VARIATIONS

Because so many individual birds were available, pooled tissue samples from sex and age groups of the same species were deemed advisable. Although the author attempted to dissect approximately the same quantity of a given tissue from each bird for the pooled sample, there is always a chance of individual variation in pesticide burdens among such large composites.

In some instances it was possible to analyze separately a number of individuals of the same sex and age. For example, in a sample of five immature male yellow-billed cuckoos (Table 4), the mean ΣDDT burden was 0.57 ppm with a range of 0.12-1.06 ppm. Deviation of minimum and maximum figures from the mean value is at least 75 percent. In seven adult male common yellowthroats the mean ΣDDT burden was 3.27 ppm with a range of 1.93-5.39 ppm (Table 5). In this case the minimum deviation from the mean is approximately 40 percent. Although these sample sizes are small and the study deals with small quantities of ΣDDT burdens, the average intrasample variation of 50 percent has

TABLE 3. *Differences in pesticide residues in brain, fat, and liver of selected bird species*

Species	Tissue	Date	Locality	Sample [1]	Weight, g	Residues, ppm Wet Weight DDE	Σ DDT	Dieldrin	Residues, ppm Lipid Weight DDE	Σ DDT	Dieldrin
Mniotilta varia	fat	May 1971	VAB	6A	9.2	1.58	2.58	0	5.55	8.91	0
	brain					0.02	0.03	0	0.62	0.99	0
(Black-and-white Warbler)	fat	May 1972	VAB	10A	9.0	0.41	1.46	0	1.05	3.76	0
	brain					0.02	0.04	0	0.60	1.20	0
	fat	Nov 1972	GCM		9.1	1.74	2.34	0	5.60	7.53	0
	brain			9I		0.02	0.02	0	0.56	0.56	0
Dendroica caerulescens	fat	Sep 1970	WDBO	7A	11.0	1.06	1.59	0	1.45	2.17	0
	brain			5I		0.04	0.08	0	0.94	1.88	0
(Black-throated Blue Warbler)	liver					0.03	0.09	0	10.0	31.00	0
Dendroica palmarum	fat	Oct 1972	WJKS	8I	10.0	2.36	8.82	0.23	3.79	14.17	0.37
						0.26	0.52	0	13.05	26.10	0
	brain			8I	9.2	0.98	0.98	0	5.04	5.04	0
(Palm Warbler)	fat	Nov 1972	GCM	1A		0	0.02	0	0.29	0.29	0
	brain			1?							
Seiurus aurocapillus	fat	Oct 1972	WJKS	10A	23.2	1.76	2.78	0	2.12	3.54	0
	brain					0.02	0.02	0	0.62	0.62	0
(Ovenbird)	fat	Nov 1972	GCM	2A	20.1	0.48	0.69	0	1.23	1.78	0
	brain			4I		0	0	0	0	0	0
Seiurus noveboracensis	fat	May 1971	VAB	11	15.0	2.05	11.49	0	10.80	24.27	0
	brain					0.23	0.29	0	8.93	11.37	0
(Northern Waterthrush)	fat	Oct 1972	WJKS	6I	18.2	4.07	9.68	0.79	7.04	17.25	1.44
	brain					0.07	0.12	0	2.67	4.80	0
	fat	Nov 1972	GCM	9I	17.3	4.80	5.01	0	12.38	12.92	0
	brain					0.06	0.06	0	1.87	1.87	0
Geothlypis trichas	fat	Oct 1964	WJXT	6I♂	12.0	3.53	6.53	0.03			
	liver					1.01	1.39	0.01			
	brain					0.04	0.10	0.01			
(Common Yellowthroat)	fat	Oct 1964	WJXT	6A♀	9.5	3.11	3.63	0			
	liver					0.35	0.43	0			
	brain	Oct 1964	WJXT	6A♀	9.5	0.04	0.04	0			
	fat	May 1972	VAB	10A♂	8.9	4.11	4.43	0	9.50	10.23	0
	brain					0.02	0.02	0	0.75	0.75	0
	fat	Nov 1972	GCM	6I♂	9.5	1.01	1.01	0	3.51	3.51	0
	brain			4I♀		0.07	0.07	0	2.03	2.03	0
	fat	Oct 1972	WJKS	10I♂	10.9	2.15	3.28	0.11	3.81	5.83	0.19
Setophaga ruticilla	fat	Oct 1969	VAB	6A♀	8.2	2.01	4.65	0.51	2.57	5.94	0.65
	liver					0.52	0.91	1.93	6.01	10.50	1.93
	brain					0.08	0.24	0.02	0.68	2.04	0.20
(American Redstart)	fat	Oct 1972	WCTV	7I♀	—	2.29	6.02	0	3.20	8.42	0
	brain					0	0	0	0	0	0
	fat	May 1972	VAB	10♀	6.7	0.97	0.07	0			
	brain					0.02	0.02	0	0.80	0.80	0
	fat	May 1972	VAB	8♂	7.2	3.03	3.27	0	19.51	21.05	0
	brain					0.51	0.51	0	1.36	1.36	0
	fat	Nov 1972	GCM	10♀	6.8	2.92	2.92	0	14.3	14.3	0
	brain					0.10	0.10	0	2.89	2.89	0

[1] A = adult; I = immature.

TABLE 4. *Pesticide burdens in adipose tissue, yellowbilled cuckoo* (Coccyzus americanus)

	Date	Age [1] Sex	Body Weight, g	Residues, ppm Wet Weight DDT	DDD	DDE	Σ DDT	Dieldrin
Autumn	Oct 21, 1971	A♂	77.3	1.01	0.26	1.10	2.37	0.06
	Sept 29, 1970	A♀	66.2	0.15	0.04	0.18	0.37	0.21
	Sept 30, 1970	A?	72.5	0.27	0.07	0.25	0.59	0.01
	$\bar{x}$		72.0	0.48	0.12	0.51	1.11	0.09
	Oct 2, 1972	I♂	70.3	0.06	0	0.06	0.12	0.03
	Oct 11, 1971	I♂	78.3	0.20	0	0.28	0.48	0
	Oct 11, 1971	I♂	96.1	0.68	0	0.24	0.92	0
	Oct 11, 1971	I♂	79.7	0.50	0	0.55	1.06	0.01
	Oct 11, 1971	I♂	70.4	0.19	0	0.10	0.29	0
	$\bar{x}$		78.9	0.33	0	0.25	0.57	<0.01
Spring	May 10, 1972	♂	52.3	0	0	0.04	0.04	0
	Apr 9, 1973	♂	70.2	0	0	0.13	0.13	0.02
	May 10, 1972	♀	64.8	0	0	0	0	0
	Apr 10, 1973	♀	50.5	0	0	0.41	0.41	0
	$\bar{x}$		59.5	0	0	0.15	0.15	<0.01

[1] A = adult; I = immature.

TABLE 5. *Pesticide burdens in adipose tissue, adult male common yellowthroats* (Geothlypis trichas)—*October 6, 1964*

Specimen Number	Body Weight, g	Residues, ppm Wet Weight DDT	DDD	DDE	ΣDDT
1	9.7	0.71	0.25	2.25	3.21
2	11.3	0.71	0.25	2.24	3.20
3	10.5	0.56	0.07	1.71	2.33
9	11.2	0.81	0.18	3.35	4.34
10	10.5	0.57	0.12	4.70	5.39
11	12.0	0.14	0	1.79	1.93
12	9.8	0.25	0	2.21	2.46
$\bar{x}$	10.7	0.54	0.12	2.61	3.27

been helpful in assessing possible differences in sex or age samples as discussed above.

INTRASPECIFIC, INTERSPECIFIC, AND ANNUAL VARIATIONS

As demonstrated recently by Johnston (*17*), most of the migratory species studied here experienced a dramatic decrease in ΣDDT burdens between 1964 and 1973; this trend was believed to correlate with decreased DDT usage in the United States. Recognizing these intraspecific temporal declines and the additional variables pointed out above, one must exercise caution in assessing the voluminous data on the 18 species itemized in Table 6.

TABLE 6. *Pesticide burdens in adipose tissue of migratory birds, Florida—1964-73*

Species	Date	Locality	Sample [1]	Average Body Weight, g	Residues, ppm Wet Weight DDE	ΣDDT	dieldrin	Residues, ppm Lipid Weight DDE	ΣDDT	dieldrin
Chordeiles minor (Common Nighthawk)	Aug 1970	Vero Beach	6A	78.6	0.35	0.47	0.12	0.48	0.64	0.16
	Sept 1970	WDBO	2A	—	1.13	2.25	0	2.32	4.61	0
Dumetella carolinensis (Gray Catbird)	Oct 1972	WCTV	10A	35.8	0.21	0.33	0	0.62	0.97	0
	Oct 1972	WCTV	4I	36.6	0.09	0.27	0	0.28	0.84	0
	Fall 1973	WCTV	5I	36.9	0.88	1.16	0	1.28	1.68	0
Catharus ustulata (Swainson's Thrush)	Oct 1969	WCTV	8A	34.7	1.27	1.67	0	1.64	2.15	0
	May 1971	WCTV	7A	27.0	0.45	0.51	0	0.64	0.72	0
	Oct 1972	WCTV	7A	38.0	1.27	1.60	0.10	1.68	2.12	0.13
Catharus fuscescens (Veery)	Sept-Oct 1969	WCTV	4A	37.0	0.21	0.67	0.01	0.29	0.93	0.02
	May 1971	WCTV	10A	29.1	0.05	0.05	0	0.08	0.08	0
Vireo griseus (White-eyed Vireo)	Sept 1970	WDBO	8A	—	3.56	3.94	0.03	9.93	11.01	0.07
	Sept 1971	VAB	9A	—	1.92	3.01	0.01	3.17	4.96	0.02
	Oct 1972	WJKS	9A	14.5	2.11	4.26	0.05	2.57	5.18	0.06
Vireo olivaceus (Red-eyed Vireo)	Sept 1966	WCTV	10A	15.6	4.80	8.62	1.10	6.70	12.02	1.50
	March-Apr 1970	WCTV	7	16.2	0.50	0.81	0	0.42	0.68	0
	Oct 1972	WJKS	10I	18.6	3.00	3.22	0.17	4.00	6.82	0.22
	Oct 1972	WCTV	10A	25.00	0.08	0.50	0	0.16	0.96	0
	Oct 1972	WCTV	10I	24.1	0.02	0.18	0	0.04	0.31	0
	Fall 1973	WCTV	10A	—	0.36	0.61	0	0.47	0.79	0
Mniotilta varia (Black-and-white Warbler)	Fall 1969	WCTV	4♂	12.7	3.37	3.55	0	4.94	5.81	0
	Aug 1970	WCTV	4A	14.3	4.22	8.96	0.07	6.86	14.56	0.11
	Apr 1971	VAB	7A	9.1	6.16	8.93	0	21.54	31.24	0
	May 1971	VAB	6A	9.2	1.58	2.58	0	5.55	8.91	0
	May 1972	VAB	10A	9.0	0.41	1.46	0	1.05	3.76	0
	Oct 1972	WCTV	4I	13.4	2.70	5.41	0.12	5.66	11.33	0.25
	Nov 1972	GCM	mixed	9.1	1.74	2.34	0	5.60	7.53	0
	Fall 1973	WCTV	4I	11.5	0.29	0.50	0.05	0.36	0.63	0.06
Dendroica coronata (Yellow-rumped Warbler)	Nov 1966	WCTV	4A	10.4	3.33	7.09	0.13	9.73	20.72	0.38
	Nov 1966	WCTV	4I	11.3	2.97	5.77	0.11	6.88	13.37	0.26
	Fall 1969	WCTV	5A	11.7	3.17	5.31	0	16.18	27.08	0
	Fall 1969	WCTV	7I	12.7	5.23	7.56	0.05	18.98	27.41	0.19
	Fall 1970	WCTV	8A	10.9	1.42	2.55	0.12	1.49	2.69	0.13
	Fall 1971	WCTV	4A 4I	12.4	1.43	3.29	0	2.02	4.65	0
	Fall 1973	WCTV	5A	—	2.12	2.47	0.07	4.24	4.95	0.14
Dendroica striata (Blackpoll Warbler)	May 1971	WJKS	5♂	12.1	0.14	0.21	0	0.29	0.43	0
	May 1971	WJKS	5♀	11.8	0.06	0.06	0	0.12	0.12	0
	May 1972	VAB	10♂ 12♂	11.4	0.28	0.37	0	0.49	0.65	0
Dendroica caerulescens (Black-throated Blue Warbler)	Sept 1970	WDBO	7A 5I	11.0	1.06	1.59	0	1.45	2.17	0
	Oct 1972	WJKS	7A♂	12.4	0.55	1.35	0	0.70	1.72	0
	Oct 1972	WJKS	7I♂	12.8	0.14	0.87	0	0.19	1.17	0
	Oct 1972	WDBO	10A♂	—	0.28	1.19	0	0.39	1.64	0
	Oct 1972	WDBO	9I♂	—	0.66	1.10	0	0.87	1.45	0
	Oct 1972	WDBO	10A♀	—	0.22	0.66	0	0.36	1.04	0
	Oct 1972	WDBO	10I♀	—	0.78	1.55	0	1.08	2.14	0
	Oct 1972	Jax	10A♂	—	2.44	3.83	0.06	4.03	6.33	0.10
	Oct 1972	Jax	10I♂	—	1.57	2.60	0	2.73	4.53	0
	Fall 1973	WJKS	6A♂	13.1	0.28	0.41	0.04	0.35	0.51	0.05

(Continued next page)

TABLE 6 (cont'd.). *Pesticide burdens in adipose tissue of migratory birds, Florida—1964-73*

Species	Date	Locality	Sample [1]	Average Body Weight, g	Residues, ppm Wet Weight DDE	Σ DDT	Dieldrin	Residues, ppm Lipid Weight DDE	Σ DDT	Dieldrin
Dendroica palmarum (Palm Warbler)	Oct 1969	WCTV	5A	9.8	12.34	25.07	0.85	15.38	31.24	1.06
	Oct 1970	WCTV	8A	11.0	3.06	4.41	0.13	7.81	11.27	0.32
	Oct 1971	Jax	10A	10.9	2.64	5.05	0.29	3.81	7.29	0.41
	Oct 1972	WJKS	81	10.0	2.36	8.82	0.23	3.79	14.17	0.37
			81							
	Nov 1972	GCM	1A	9.2	0.98	0.98	0	5.04	5.04	0
	Oct 1971	Jax	1?	11.5	3.50	6.63	0.38	4.83	9.19	0.53
			10I							
	Fall 1973	WCTV	10A	—	0.61	0.70	0.21	1.28	1.47	0.44
Seiurus aurocapillus (Ovenbird)	Oct 1964	WJXT	10A	25.3	1.71	3.33	0	2.76	5.39	0
	Oct 1964	WJXT	9I	25.8	1.40	2.73	0	2.15	4.19	0
	Oct 1964	WJAX	10A♂	23.4	4.04	5.35	0.06	7.39	10.35	0.10
	Oct 1964	WJAX	9A♀	23.3	2.05	3.23	0.03	3.55	5.58	0.05
	Sept 1967	WJXT	5A	—	5.21	8.59	0.03	10.45	17.24	0.06
	Oct 1968	WJXT	10A	—	1.81	3.09	0.02	2.74	4.67	0.02
	Oct 1968	WJXT	3I	—	0.40	1.24	0	0.60	1.87	0
	Apr 1969	WJXT	8A	18.9	14.39	40.80	—	33.77	95.74	—
	Sept 1969	WCTV	5A	23.5	1.93	2.37	0.02	3.31	4.05	0.33
	Sept 1969	WCTV	5I	23.0	2.65	3.09	0.02	4.90	5.78	0.03
	Sept 1970	WDBO	3A	—	2.13	2.74	0.03	2.68	3.44	0.04
	Sept 1970	WDBO	4I	—	2.15	2.97	0	2.67	3.68	0
	May 1971	VAB	10A	17.7	1.69	2.27	0.03	3.40	4.57	0.21
	Oct 1971	WJKS	2A	—	1.29	1.89	0	1.57	2.30	0
	Oct 1971	WJKS	8I	—	1.09	2.37	0	1.37	2.97	0
	Oct 1972	WJKS	10A	23.2	1.76	2.78	0	2.12	3.54	0
	Nov 1972	GCM	mixed	20.1	0.48	0.69	0	1.23	1.78	0
	Sept 1973	WJXT	9A	23.7	0.32	0.38	0.02	0.41	0.49	0.02
Seiurus noveboracensis (Northern Waterthrush)	May 1971	VAB	1I	15.0	5.11	11.49	0	10.80	24.27	0
	Oct 1972	WJKS	6I	18.2	4.07	9.68	0.79	7.04	17.25	1.44
	Nov 1972	GCM	9I	17.3	4.80	5.01	0	12.38	12.92	0
Geothlypis trichas (Common Yellowthroat)	Oct 1964	WJXT	6A♀	9.5	3.11	3.63	0			
	Oct 1964	WJXT	6I♂	12.0	3.53	6.53	0.03			
			4♂							
	Apr 1969	WJXT	2♀	9.2	7.08	7.99	0	23.42	26.45	0
	Oct 1969	WCTV	5A♂	—	3.59	5.54	0	12.60	18.74	0
	Oct 1971	WJKS	9A♂	9.8	4.57	6.17	0	9.84	13.31	0
	May 1972	VAB	10A♂	8.9	4.11	4.43	0	9.50	10.23	0
Geothlypis trichas (Common Yellowthroat)	Oct 1972	WCTV	4A♂	11.0	3.56	4.22	0	10.86	12.91	0
	Oct 1972	WJKS	10I♂	10.9	2.15	3.28	0.11	3.81	5.83	0.19
	Oct 1972	WJKS	10A♂	11.4	3.40	4.47	0.11	5.80	7.65	0.18
	Nov 1972	GCM	10I 6♂ 4♀	9.5	1.01	1.01	0	3.51	3.51	0
	Fall 1973	WCTV	10I♂	—	1.53	1.87	0.11	2.26	2.76	0.16
Setophaga ruticilla (American Redstart)	Oct 1964	WJXT	3A♂	—	6.72	10.25	0.27	10.30	15.69	0.41
	Oct 1964	WJXT	12A♀	—	6.14	10.42	0.46	13.1	22.30	0.46
	Oct 1969	VAB	6A♀	8.2	2.01	4.65	0.51	2.57	5.94	0.65
	Oct 1971	WJKS	10A♀	8.9	3.05	5.62	0.37	4.13	7.61	0.50
	Oct 1971	WJKS	10I♀	9.1	5.29	12.33	—	7.01	16.34	—
	May 1972	VAB	8♂	7.2	3.03	3.27	0	19.51	21.05	0
	May 1972	VAB	10♀	6.7	0.97	0.97	0			
	Oct 1972	WJKS	10A♂	9.6	1.45	2.62	0.08	2.49	4.50	0.14
	Oct 1972	WCTV	7I♀	—	2.29	6.02	0	3.20	8.42	0
	Nov 1972	GCM	10♀	6.8	2.92	2.92	0	14.3	14.3	0
Dolichonyx oryzivorus (Bobolink)	Spr 1971	WCTV	10♂	33.9	0.50	0.90	0.08	0.83	1.47	1.0
Passerculus sandwichensis (Savannah Sparrow)	Oct 1966	WCTV	6I	14.4	15.48	18.68	0.18	31.93	38.53	0.38
Zonotrichia albicollis (White-throated Sparrow)	Fall 1966	WCTV	6A	—	2.33	2.47	0	4.52	4.79	0
	Fall 1966	WCTV	6I	—	7.67	15.09	0	20.02	39.39	0

NOTE: — = no data.
[1] A = adult, I = immature.

Some of the interspecific burdens are related to specific feeding habits. *Chordeiles minor* (common nighthawk), for example, captures flying insects which apparently contain minute quantities of DDT. Only a single year's sample of this bird was available; hence results are not conclusive. Species in Table 6 known to feed on insects at or near ground level include *Dendroica palmarum, Seiurus aurocapillus, S. noveboracensis, Geothlypis trichas, Dolichonyx oryzivorus, Passerculus sandwichensis,* and *Zonotrichia albicollis.* In the late 1960's and early 1970's when residue burdens in these species were relatively high (*17*), five of these species had the highest residues found in the present study, ranging from 11.5 to 40.8 ppm. Although annual samples are sometimes few, these data suggest that ground-feeding species may be more susceptible to DDT-contaminated foods

than are birds feeding at higher levels. The gray catbird (*Dumetella carolinensis*) and *Catharus* spp. thrushes consume significant quantities of fruits and some insects. Table 6 shows that these species had relatively low DDT burdens, 0.27-2.25 ppm.

Tables 4-6 illustrate the frequency of DDT or metabolites and dieldrin detection in the total samples. Of 128 samples involving 19 species and 908 individuals, only one sample, an individual *Coccyzus americanus*, lacked DDT or a metabolite. Dieldrin, however, occurred less frequently (absent in 68 samples) and in smaller quantities (n=45, mean=0.17 ppm) than the ΣDDT burden (n = 100, mean = 4.31 ppm). No PCB's were found in any species studied here despite the widespread occurrence of these pollutants in worldwide ecosystems.

SEASONAL VARIATIONS

The small birds studied here migrate annually from breeding grounds in the eastern United States to wintering quarters in the West Indies or Central or South America. Birds taken from the television tower kills in autumn represent southbound migrants en route to wintering quarters, whereas those collected in the spring are northbound to the breeding grounds. Several factors are important in determining the pesticide burdens of the two seasonal samples: the obese autumnal migrants had not yet expended much energy from their fat stores and therefore still retained large pesticide burdens, assuming that pesticides are subsequently lost or translocated from dwindling fat stores; the spring migrants collected in Florida had already lost much of the premigratory fat stores; an undetermined amount of pesticides had been excreted earlier by the birds; and environmental pesticide loads in the wintering grounds may differ from those of the birds' breeding habitat. There is no way to accurately assess all these factors, but data in Table 7 demonstrate that in 5 of 11 comparisons the spring (northbound) samples differed more than 50 percent from the autumnal (southbound) samples. Of the four species in Table 7, approximately one-half had higher autumnal DDT burdens. Coupled with these data are the seasonal burdens in yellow-billed cuckoos (Table 4) whose autumnal burdens were much higher than their spring burdens.

Persson (*40*) reported a much higher DDT content in spring than in autumn for the migratory whitethroats (*Sylvia communis*) breeding in Sweden. She stated, "This suggests that the birds were subjected to a considerably higher contamination by chlorinated hydrocarbons during the spring migration through North Africa and Europe than during the late summer in Sweden, where the use of DDT has been prohibited since 1970."

Discussion

Literature on DDT levels in passerine birds of similar trophic levels in the ecosystem suggests that the values reported here (Table 6) for migrants are reasonably comparable. Prey of peregrines in Alaska included migrant seed-eating passerines with ΣDDT burdens of 0.23-0.66 ppm and migrant insectivorous passerines with burdens of 0.45-1.51 ppm (*3*). Temple (*14*) reported that DDE levels in brains of five prey species of merlin (*Falco columbarius*) ranged from 0.18 to 3.17 ppm dry weight. Data on brain burdens in Table 3 are not strictly comparable to those of Temple because the present values are reported on a wet- or lipid-weight basis. For the latter, 15 samples averaged only 1.47 ppm, although 2 samples had high levels, 11.37 ppm

TABLE 7. *Pesticide burdens in adipose tissue of spring (northbound) vs. autumn (southbound) samples of selected bird species*

Species	Date	Location	Sample [1]	Average Body Weight, g	Residues, ppm Wet Weight Σ DDT	Percent Difference [2]
Mniotilta varia (Black-and-white Warbler)	May 1971	VAB	6A	9.2	2.58	
	Aug 1970	WCTV	4A	14.3	8.96	71
	May 1972	VAB	10A	9.0	1.46	
	Oct 1972	WCTV	4I	13.4	5.41	73
Seiurus aurocapillus (Ovenbird)	Apr 1969	WJXT	8A	18.9	40.80	
	Sept 1969	WCTV	5A	23.5	2.37	94
	May 1971	VAB	10A	17.7	2.27	
	Oct 1971	WJKS	2A	—	1.89	17
Geothlypis trichas (Common Yellowthroat)	Apr 1969	WJXT	4♂ 2♀	9.2	7.99	
	Oct 1969	WCTV	5A♂	—	5.54	31
	May 1972	VAB	10A	8.9	4.43	
	Oct 1972	WJKS	10A♂	11.4	4.47	1
Setophaga ruticilla (American Redstart)	May 1972	VAB	8♂	7.2	3.27	
	Oct 1972	WCTV	7I♀	—	6.02	46

NOTE: — = no data.
[1] A = adult; I = immature.
[2] Difference between values expressed as a percent of the larger value.

and 26.10 ppm. Healthy mockingbirds (*Mimus polyglottos*) and blue jays (*Cyanocitta cristata*) in southern Florida had a mean DDE level of 1.23 ppm in brain tissue (*7*). A variety of passerine birds (whole bodies) analyzed by Crabtree (*6*) and DeWitt et al. (*5*) revealed DDE levels usually less than 0.9 ppm and DDT concentrations ranging from 0 to 26 ppm. DDE levels in muscle of a few passerines in Texas were mostly less than 0.1 ppm (*10*). In his nationwide survey of starlings (*Sturnus vulgaris*), Martin (*8*) stated, "Most of the average residues found for DDT and metabolites occurred in the range of <0.1–3.0 ppm; and for dieldrin, in the range of <0.1–0.3 ppm" (whole body, wet weight). His report revealed several geographic variations, including the fact that the southern United States generally had the highest concentration of ΣDDT, up to 5 ppm. On the other hand, in Idaho, starling adipose tissue had a mean value of 19.23 ppm for DDE with an extreme of 66.97 ppm (*9*).

Despite the facts that thousands of small migrants are killed annually by colliding with towers and buildings and that the present study reveals a high incidence of pesticide burdens in many of these birds, the author finds no concrete evidence that such burdens caused them to fly into towers. Numerous instances in the preceding paragraph involved noncolliding feral songbirds with pesticide burdens of approximately the same magnitude as those of colliding birds.

Some ΣDDT burdens in Table 6 appear to be exceptionally high for certain species in recent years: 25.07 ppm for *Dendroica palmarum* in 1969; 40.80 ppm for *Seiurus aurocapillus* in 1969; 11.49 ppm for *Seiurus noveboracensis* in 1971; 12.33 ppm for *Setophaga ruticilla* in 1971; 18.68 ppm for *Passerculus sandwichensis* in 1966; and 15.09 ppm for *Zonotrichia albicollis* in 1966. Whether these relatively high burdens had any effects on the species at that time is unknown, but certainly if birds having such high burdens subsequently became prey, pesticide concentrations in the predators would be magnified and the consequences would likely be serious (*3*). By 1973 these relatively high concentrations in most of the small migratory birds cited above had significantly decreased to a mean ΣDDT burden of approximately 1.0 ppm (*17*).

Even such low burdens can be magnified by predators (*41*). Keith and Gruchy (*12*), writing about shorebirds as prey of peregrines, stated, ". . . it is not necessary to look for residue levels higher than 2 ppm in birds taken as food by raptors to account for the DDE levels in those raptors now associated with population damage."

As early as 1963 Bernard (*4*) suggested relationships among fat depots, DDT burdens, their lethal levels, and starvation. He stated, ". . . when the fat reserves are utilized (as in starvation), the DDT may be released to more sensitive areas (such as the brain) resulting in tremors followed by death. Some birds might retain sublethal amounts of DDT in fat all summer and perish in winter or during migration when fats are utilized." For migratory birds, especially those that experience excessive premigratory fat deposits such as the 19 species of the present study, Bernard's thesis might be correct, although there is as yet no first-hand evidence that obese, pesticide-laden birds ". . . perish . . . during migration when fats are utilized." Indeed there exists at least laboratory evidence that birds and some other vertebrates dispose of some pesticide quantities by a variety of mechanisms including kidney excretions (*42-45*) and oil secreted from uropygial glands (*45*). On the other hand, starved birds may experience redistribution of pesticides from diminished fat depots to skeletal muscles (*37*) or the central nervous system (*36,38*). By analyzing adipose tissue and brain of obese premigratory and lean postmigratory birds, the author concluded in an earlier report (*16*) that the lean postmigrants had not concentrated the DDT burdens in the remaining fat depots nor translocated them to the brain. DDT burdens of the postmigrants could have been partly excreted or translocated to tissues other than the brain.

The extent to which any DDT burdens reported here affected the bird populations is unknown. Certainly songbird breeding populations are known to decrease in areas heavily sprayed with DDT (*4,11,18-20,22,23*). Sublethal effects in feral birds are more difficult to detect; cases of eggshell thinning in songbirds have not been positively attributed to pesticides. Yet Jefferies (*27,29*) showed that Bengalese finches (*Lonchura striata*) fed DDT experienced a reduction in fertility, hatchability of eggs, and fledging success. When starved, some captive cowbirds (*Molothrus ater*) previously dosed on DDT mobilized the DDT to the point of death (*26,46*).

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Insecticide Residues in the Tuttle Creek Reservoir Ecosystem, Kansas—1970-71 [1]

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ABSTRACT

Various components of the aquatic ecosystem of Tuttle Creek Reservoir on the Big Blue River in northeastern Kansas were examined for organochlorine insecticide residues in 1970-71. Components examined were water, sediments, periphyton, zooplankton, insects, and whole-body samples of 10 common fish species.

Only dieldrin and ΣDDT residues were detected. Dieldrin was found in part of the nonfish samples at levels ranging up to 0.01 ppm and in 97 percent of the fish samples with a high level of 0.17 ppm. ΣDDT residues were also detected in part of the nonfish samples at levels ranging up to 0.42 ppm, and in 98 percent of the fish samples at levels as high as 0.57 ppm. Authors' findings are roughly similar to those of other surveys of Kansas fishes. All levels are relatively low compared with those reported in surveys from other parts of the Nation.

Introduction

The use of agricultural chemicals has become an accepted practice during the last few decades but the safety of many of these compounds has been challenged in the renewed awareness of environmental responsibility. Many people are concerned about the ecological effects of persistent residues and their potential hazard to humans who may be consuming them. Of special concern are effects of long-lived insecticides on fish and wildlife. Sport enthusiasts often are unsure whether the fish they catch are safe to eat.

This paper deals with residues of organochlorine insecticides in water, sediments, periphyton, zooplankton, insects, and fishes of Tuttle Creek Reservoir, a popular sport-fishing reservoir in Kansas. It is based on an extensive survey of residues in the reservoir ecosystem with emphasis on fish in a wide range of trophic levels.

Methods

STUDY AREA

Samples were collected from Tuttle Creek Reservoir, a flood control lake on the Big Blue River. The reservoir, which was completed in 1962, is about 8 km north of Manhattan in northeastern Kansas. At conservation level its surface area is about 6,400 ha. and it extends approximately 35 km northward into the river valley. The reservoir is long and narrow with a few short coves (Fig. 1). The deepest part over the flood plain (about 15 m) is near the dam; mean depth is about 8 m. Water conditions are typical of plains reservoirs in that thermal stratification rarely occurs and the water is fairly turbid.

The area which drains into the reservoir extends approximately 240 km northward into southeastern Nebraska (Fig. 1). The watershed above the dam is 2,591,000 ha. (6,400,000 acres), a large proportion of which is under agricultural cultivation. Major crops are grain sorghum, corn, and wheat.

COLLECTION OF SAMPLES

Fish samples were collected at two sites, one at the north end of the reservoir just north of Randolph Bridge and one near the southeast corner at McIntire cove (Fig. 1). At the north site, the central reservoir area was 2-3 m deep and could be sampled readily. Samples from the south side were collected from the cove because fish were scarce and difficult to sample in the deep open water. Samples from both sites were taken at various places from near shore to the middle of flood plain. Fishes were usually collected for 2 or 3 weeks during three seasons: summer 1970, fall 1970, and spring 1971.

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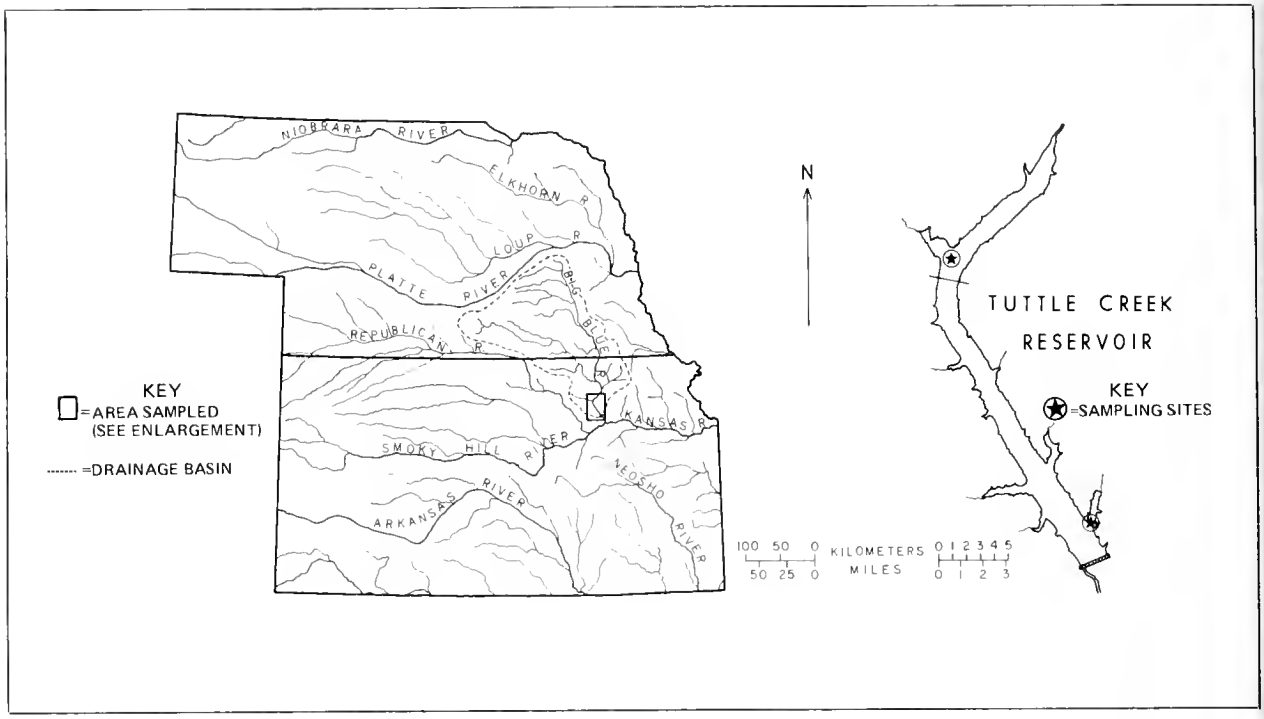

FIGURE 1. *Map of Kansas and Nebraska showing sampling sites of Tuttle Creek Reservoir drainage basin.*

Water samples were taken from the surface of the open water; sediment samples were taken with an Ekman dredge in open water and the surface inch was retained for analyses. Zooplankton was collected with a No. 20 mesh plankton net. Bottom insects were collected with an Ekman dredge and periphyton was scraped off rocks or trees on the edge of the reservoir. Fish were collected with bottom-fishing gill nets with eight mesh sizes ranging from ¾ to 4 in. square.

The ten species of fish collected for residue analysis included popular game fishes, the main forage fish, and the most common rough fish. These species, in increasing order of trophic position, included gizzard shad (*Dorosoma cepedianum*), river carpsucker (*Carpiodes carpio*), smallmouth buffalo (*Ictiobus bubalus*), carp (*Cyprinus carpio*), channel catfish (*Ictalurus punctatus*), freshwater drum (*Aplodinotus grunniens*), white crappie (*Pomoxis annularis*), white bass (*Morone chrysops*), walleye (*Stizostedion vitreum*), and longnose gar (*Lepisosteus osseus*). Fish were grouped into three size categories, small, medium, and large, because the degree of maturity may influence residue content. Immature young that were 1 year old or less were classified as small. Medium-size fishes were those starting to mature and to interest persons fishing in the reservoir. Large fishes were definitely mature and would be considered acceptable catch by sports enthusiasts.

Samples included up to 10 fish of one size of the same species. In most cases there were fewer but in several instances small fish that had hatched in the year of collection were taken in larger numbers to get enough biomass for analysis. Samples were frozen until analysis.

SAMPLE PROCESSING

The entire body of each fish was ground in a meat grinder. The ground material was mixed and a 100-g subsample was taken from each ground fish in order that larger fish did not bias the sample. Subsamples were pooled and homogenized in a blendor. A specific amount of distilled water was added to facilitate homogenizing. A sample of the homogenate was then taken and frozen in an aluminum foil package until residue was extracted. The only exception to this procedure was the treatment of small fish less than 1 year old when the individuals were very similar in size. After their entire bodies were ground, they were run through the blendor without subsampling.

Nonfish samples including unfiltered water were extracted directly for residue analysis.

RESIDUE EXTRACTION AND ANALYSIS

Subsamples measuring 10 g were placed in an omnimixer with 50 ml redistilled hexane and enough anhydrous sodium sulfate to absorb the water. The mixture was blended at high speed for 1-2 minutes, and was then decanted through No. 43 Whatman filter paper into a 100-ml suction flask. The residue was extracted with two additional portions of hexane as described above; extracts were filtered and combined in a suction flask. The container, filter paper, and contents were washed with a final 10-ml portion of hexane. The total hexane

extract was transferred to a round-bottom flask for concentration under vacuum at 35°-40° C to 2-3 ml hexane. The concentration was transferred quantitatively to a 15-ml centrifuge tube using small portions of hexane totaling 5 ml. An aliquot was used for cleanup and gas chromatographic (GC) analysis.

For the cleanup procedure a silica gel chromatographic microcolumn was prepared by loosely packing a plug of glass wool about 4 cm from the tip of a disposable pipette and then adding 1 g of high-purity silica gel (No. 950, 60-200 mesh). Prior to column chromatography, solvent extract was evaporated to 1 ml. For partial deactivation of silica gel, the 1 ml concentrated extract used for charging the column was saturated with 5 μl distilled water and transferred quantitatively to the column. It was permitted to percolate through the column at 1-2 ml/min. Column walls were rinsed with small hexane portions. When the solvent reached the top of the silica gel, elution with the desired solvent was begun.

Eluting solvents were 2, 7, and 70 percent benzene in hexane, 100 percent benzene, and 8 percent ethyl acetate in benzene. The eluate was collected in a 15-ml graduated centrifuge tube. Eluates were concentrated separately to 1 ml by a nitrogen stream just before GC (*1, 2*).

Analyses were performed with a Barber-Coleman GC equipped with an electron-capture detector. Operating conditions were as follows:

Column:	6 ft-glass packed with 3 percent DC-11 on 60-80 mesh silanized Gas-Chrom P
Temperature:	Column 200° C Detector 220° C Injector 240° C
Carrier Gas:	Nitrogen at a flow rate of 37 ml/min
Volume injected:	4 μl extract in hexane

Each sample was analyzed for endrin, aldrin, dieldrin, heptachlor, heptachlor epoxide, *o,p'*-DDT, *p,p'*-DDT, DDE, and *p,p'*-DDD. The sensitivity was 0.01 ppm. Residue levels were not corrected because recovery from fortified samples was essentially 100 percent.

Results and Discussion

FISH POPULATION

Table 1 lists the species of fishes collected in Tuttle Creek Reservoir during various studies (*3-5*), their relative abundance, trophic relation, and sport category. Species sampled are among the most common and, therefore, ecologically important. They include the major sport species and represent a wide range of trophic positions.

PESTICIDE RESIDUES

Results of pesticide residue analyses are given in Tables 2 and 3. Values other than trace residues were rounded to the nearest 0.01 ppm. No residues of endrin, aldrin, heptachlor, or heptachlor epoxide were detected in any sample. Dieldrin and ΣDDT residues were the only compounds detected.

Dieldrin was detected at 0.01 ppm in one of six water samples. It was not detected in any sediment samples but was detected in three of four periphyton samples at levels ranging up to 0.01 ppm. Five of six zooplankton samples had dieldrin levels as high as 0.01 ppm. Of the five insect samples, four contained dieldrin levels that ranged up to 0.01 ppm. Of the 102 fish samples, 97 percent contained dieldrin residues ranging from a trace to 0.17 ppm. Most residue values were less than 0.10 ppm. The few which were higher occurred in gizzard shad, river carpsucker, smallmouth buffalo, and freshwater drum, all nongame species.

ΣDDT residues were found in one of six water samples at a level of 0.02 ppm but not in any bottom sediment sample. It was detected in two of four periphyton samples; the highest level was 0.42 ppm. Four of the six zooplankton samples had traces of DDT compounds. ΣDDT residues were detected in four of five samples samples at levels up to 0.05 ppm. Of the fish samples tested, 98 percent contained detectable ΣDDT residues ranging from a trace to 0.57 ppm; most of these residues were less than 0.10 ppm. Higher amounts were found at least once in each species except carp and white

TABLE 1. *Fishes collected from Tuttle Creek Reservoir*

Species [1]	Relative abundance [2]	Trophic position [3]	Use category
Longnose Gar [4]	+ +	high	rough
Gizzard Shad [4]	+ + +	low	forage
Northern Pike	+	high	sport
Stoneroller	+	low	forage
Goldfish	+	low	rough
Carp [4]	+ + +	low and med	rough
Golden Shiner	+ +	med	forage
Suckermouth Minnow	+	low	forage
Minnows (*Notropis* sp.)	+ +	low	forage
Minnows (*Pimephales* sp.)	+	low	forage
River Carpsucker [4]	+ + +	low	rough
White Sucker	+ + +	low	rough
Smallmouth Buffalo [4]	+ + +	low	rough
Bigmouth Buffalo	+	low and med	rough
Black Buffalo	+	low	rough
Shorthead Redhorse	+	low	rough
Blue Catfish	+	med	sport
Black Bullhead	+	med	sport
Yellow Bullhead	+	med	sport
Channel Catfish [4]	+ + +	med	sport
Flathead Catfish	+ +	high	sport
White Bass [4]	+ + +	med and high	sport
Green Sunfish	+	med	forage
Orangespotted Sunfish	+	med	forage
Bluegill	+ +	med	forage and sport
Largemouth Bass	+ +	med and high	sport
White Crappie [4]	+ + +	med and high	sport
Black Crappie	+	med and high	sport
Walleye [4]	+ +	high	sport
Freshwater Drum [4]	+ + +	med	rough

[1] Accepted common names of fishes established by American Fisheries Society (See Literature Cited, reference 11).
[2] + = sparse, + + = moderately abundant, + + + = abundant.
[3] Low = omnivorous diet of algae, detritus, microcrustacea; medium = diet of microcrustacea, insects, and occasional small fish; high = diet mainly of other fishes.
[4] Analyzed in this study.

crappie. Highest levels in fishes were found in a freshwater drum sample (0.57 ppm) and a smallmouth buffalo sample (0.43 ppm).

No residue pattern was discernible in regard to time of year or end of reservoir sampled. Classical biological magnification was not noticeable in the fishes. Species at the lowest trophic level had residues as high or higher than those at the highest trophic positions.

Comparing these results with those of the National Pesticides Monitoring Program shows that levels in Tuttle Creek Reservoir are relatively low. Henderson et al. (*6, 7*) found that 75 percent of the whole-body fish samples taken nationally in 1967-68 contained dieldrin levels of nearly 2 ppm. In 1969 they found dieldrin in 93 percent of the samples with levels up to 1.59 ppm. In the present study dieldrin was detected in a higher percentage (97 percent) of samples but at considerably lower levels: the highest was 0.17 ppm. Henderson et al. (*6, 7*) showed ΣDDT levels as high as 45 ppm in 99 percent of the 1967 samples and as high as 57.8 ppm in 100 percent of the samples taken in 1969. The present study reports ΣDDT residues in almost all samples (98 percent), but the highest level detected was 0.57 ppm.

Results of other pesticide residue surveys in Kansas are similar to those of the current study. Klaassen and Kadoum (*8*) found dieldrin in 15 percent of the samples. The highest whole-body residue was 0.08 ppm in fish of the Smoky Hill River of western Kansas during 1967-69. ΣDDT residues were detected in 75 percent of these samples; the highest whole-body level was 0.10 ppm. The use of different species in other surveys makes the accuracy of direct comparisons questionable.

The Kansas Fõrestry, Fish and Game Commission (*9, 10*) found organochlorine insecticides in 98 percent of the fish samples in 1971. ΣDDT residues were detected in 89-96 percent of all samples collected; mean levels ranged from 0.19 to 0.21 ppm. Dieldrin was in 61-76 percent of the samples in amounts slightly higher than those detected in this survey. In 1972 the Commission found organochlorine insecticides in 91 percent of the fish samples. ΣDDT residues were detected in 89-90 percent of the samples with levels ranging from 0.03 to 0.27 ppm. Dieldrin levels ranging from 0.03 to 0.42 ppm were found in 40 percent of the samples.

TABLE 2. *Pesticide residues in aquatic ecosystem, north end of Tuttle Creek Reservoir—1970-71*

	SUMMER 1970 [1]						FALL 1970 [2]						SPRING 1971 [3]					
SAMPLE	SIZE [4]	DIELDRIN	DDE	DDD	*o,p'*-DDT	*p,p'*-DDT	SIZE [4]	DIELDRIN	DDE	DDD	*o,p'*-DDT	*p,p'*-DDT	SIZE [4]	DIELDRIN	DDE	DDD	*o,p'*-DDT	*p,p'*-DDT
Lake water		ND	ND	ND	ND	ND		ND	ND	ND	ND	ND		0.01	ND	0.01	0.01	ND
Bottom sediment								ND	ND	ND	ND	ND		ND	ND	ND	ND	ND
Periphyton								0.01	0.18	ND	0.06	0.18		T	ND	ND	ND	ND
Zooplankton		T	T	ND	ND	ND		ND	T	ND	ND	ND		0.01	ND	ND	ND	ND
Diptera larvae		ND	0.02	ND	ND	ND												
Mayfly (*Hexagenia*)													nymphs	0.01	0.01	ND	0.01	0.03
Gizzard shad	S(2)	0.05	0.01	ND	ND	ND	S(3)	0.08	0.04	0.06	0.04	0.17	M(2)	0.04	0.02	0.02	0.01	0.05
	L(4)	0.07	0.02	ND	ND	ND	M(6)	0.07	0.04	0.02	0.04	0.16	L(6)	0.02	0.01	0.02	ND	0.02
							L(4)	0.09	0.07	0.04	0.05	0.20						
River carpsucker	L(10)	0.16	0.06	ND	ND	ND	S(1)	0.01	0.01	T	0.01	0.03	L(10)	0.05	0.05	0.03	0.03	0.10
							L(10)	0.16	0.07	0.03	0.01	0.25						
Smallmouth buffalo	L(10)	0.14	0.07	ND	ND	ND	L(3)	0.12	0.08	0.06	0.02	0.27	L(10)	0.08	0.06	0.08	0.04	0.09
Carp	L(10)	0.01	0.03	ND	ND	ND	L(1)	0.02	0.04	0.01	0.01	0.03	L(10)	0.01	0.01	0.01	ND	ND
Channel catfish	S(4)	0.01	0.01	ND	ND	ND	S(3)	0.02	0.01	ND	ND	0.05	M(10)	0.03	0.01	0.02	ND	ND
	L(9)	0.04	0.04	ND	ND	ND	L(10)	0.04	0.05	0.02	ND	0.06	L(8)	0.03	0.03	0.02	ND	ND
Freshwater drum	S(10)	0.01	0.01	ND	ND	ND	S(4)	0.02	0.01	0.01	ND	0.03	S(2)	0.02	0.01	T	0.01	0.03
	L(10)	0.13	0.06	ND	ND	ND	L(3)	0.08	0.12	0.02	0.02	0.23	L(5)	0.03	0.02	0.01	0.01	0.53
White crappie	S(10)	0.01	0.01	ND	ND	ND	S(7)	0.01	0.01	ND	ND	ND	S(10)	ND	T	ND	ND	ND
	L(10)	T	ND	ND	ND	ND	M(10)	T	T	ND	ND	0.03	M(10)	ND	ND	ND	ND	ND
							L(10)	0.01	0.02	0.01	0.01	0.04	L(4)	0.02	0.01	0.01	ND	ND
White bass	S(1)	0.01	0.01	ND	ND	ND	L(10)	0.03	0.02	0.02	0.01	0.05	S(2)	0.02	0.01	0.02	ND	0.01
													L(10)	0.03	0.01	0.02	ND	0.01
Walleye							S(1)	0.05	0.02	0.02	0.01	0.08	S(1)	0.04	0.02	0.01	0.01	0.02
													L(2)	0.08	0.03	0.03	ND	0.02
Longnose gar	M(4)	0.03	0.05	0.04	0.01	0.03							M(1)	0.07	0.02	0.01	ND	ND

NOTE: ND = not detected.
T = trace.
[1] Samples collected August 3-5.
[2] Samples collected October 30-November 5.
[3] Samples collected April 7-May 20.
[4] S, M, L = small, medium, large. Number of individuals in each sample reported in parentheses.

TABLE 3. *Pesticide residues in aquatic ecosystem, south end of Tuttle Creek Reservoir—1970-71*

	Summer 1970 [1]						Fall 1970 [2]						Spring 1971 [3]					
Sample	Size [4]	Dieldrin	DDE	DDD	*o,p'*-DDT	*p,p'*-DDT	Size [4]	Dieldrin	DDE	DDD	*o,p'*-DDT	*p,p'*-DDT	Size [4]	Dieldrin	DDE	DDD	*o,p'*-DDT	*p,p'*-DDT
Lake water		ND	ND	ND	ND	ND		ND	ND	ND	ND	ND		ND	ND	ND	ND	ND
Bottom sediment								ND	ND	ND	ND	ND		ND	ND	ND	ND	ND
Periphyton								ND	0.03	ND	ND	ND		T	ND	ND	ND	ND
Zooplankton		T	T	ND	ND	ND		0.01	T	ND	ND	ND		0.01	ND	ND	ND	ND
Mayfly (*Hexagenia*)	nymphs	T	T	ND	ND	ND							nymphs	0.01	0.01	ND	0.01	0.02
	adults	0.01	ND	ND	ND	ND												
Gizzard shad	S(80)	0.02	0.01	0.01	0.01	0.02	S(37)	0.01	ND	0.01	ND	ND	S(10)	0.03	0.01	0.02	ND	ND
	M(10)	0.07	0.01	0.03	T	0.02	M(10)	0.02	ND	0.01	ND	ND	M(10)	0.02	0.01	0.02	ND	ND
	L(10)	0.17	0.03	0.06	T	0.01	L(10)	0.03	0.02	0.03	ND	ND	L(10)	0.04	0.02	0.03	ND	ND
River carpsucker	S(12)	0.01	T	0.01	T	0.01	S(9)	T	0.01	ND	ND	ND	S(4)	0.01	0.01	T	ND	ND
	L(10)	0.05	0.02	0.02	0.01	0.02	L(10)	0.03	0.03	0.02	ND	ND	L(4)	0.03	0.02	0.02	ND	ND
Smallmouth buffalo	L(10)	0.10	0.05	0.05	0.03	0.04	L(10)	0.03	0.04	0.02	0.02	0.07	L(3)	0.03	0.03	0.02	ND	ND
Carp	M(10)	0.02	0.03	0.02	0.01	T	L(5)	0.01	0.01	ND	ND	ND	L(10)	0.01	0.04	0.02	ND	ND
Channel catfish	S(10)	0.01	0.01	T	0.01	0.01	S(10)	0.01	0.01	T	0.01	0.04	S(4)	0.01	T	ND	ND	ND
	L(10)	0.07	0.07	0.06	0.01	0.05	L(10)	0.02	0.02	0.02	0.01	0.03	M(7)	0.02	0.03	0.01	ND	0.01
													L(10)	0.03	0.06	0.01	ND	0.06
Freshwater drum	S(12)	0.02	0.01	0.01	T	0.01	S(10)	0.02	0.01	0.01	0.01	0.04	S(3)	0.01	T	T	ND	ND
	L(8)	0.01	0.01	ND	ND	T	L(3)	0.04	0.02	0.01	0.01	0.04	L(4)	0.04	0.02	0.02	ND	ND
White crappie	S(10)	T	T	ND	ND	ND	S(3)	0.02	0.01	0.01	ND	ND	S(8)	0.01	0.01	T	ND	ND
	L(10)	0.01	0.01	0.01	T	0.01	M(10)	ND	T	ND	ND	ND	M(10)	T	T	ND	ND	ND
							L(2)	T	0.01	ND	ND	ND						
White bass	S(4)	0.01	0.01	T	T	0.01	S(4)	0.01	0.01	0.01	ND	ND	S(10)	0.03	0.01	0.01	ND	ND
	L(2)	0.02	0.02	0.01	T	0.01	L(10)	0.01	0.01	0.01	ND	ND	M(10)	0.05	0.02	0.02	ND	0.02
Walleye	S(5)	0.01	0.19	0.01	0.01	0.01	S(10)	0.01	0.01	0.01	ND	ND	S(9)	0.04	0.02	0.02	ND	ND
	L(6)	0.07	0.04	0.04	0.01	0.03	L(10)	0.02	0.03	0.01	0.01	0.02	L(6)	0.09	0.03	0.04	ND	ND
Longnose gar	M(10)	0.02	0.04	0.05	T	0.02	L(1)	0.05	0.08	0.08	0.02	0.06						

NOTE: ND = not detected.
T = trace.
[1] Samples collected August 7-18.
[2] Samples collected October 20-November 1.
[3] Samples collected March 30-May 20.
[4] S, M, L = small, medium, large. Number of individuals in each sample reported in parentheses.

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RESIDUES IN FOOD AND FEED

Pesticide Residues in Total Diet Samples (VIII)

D. D. Manske and R. D. Johnson [1]

ABSTRACT

During the eighth year of the Total Diet Study, residues remained at the relatively low levels reported previously. A total of 35 market baskets were collected in 32 cities which ranged in population from less than 50,000 to 1,000,000 or more. Averages and ranges of residues found are reported for the period June 1971 through July 1972 by region and food class. Results of recovery studies within various classes of residues are also presented.

Introduction

This report presents results obtained in the Total Diet Program (*1*) of the Food and Drug Administration (FDA), U.S. Department of Health, Education, and Welfare, for the period June 1971 through July 1972. The amounts and types of residues found from June 1964 through April 1971 have been described in earlier reports (*2-8*). Seven samples were collected in each of the five regions at 35 different grocery markets. These markets were located in 32 different cities. Unless otherwise stated, the conditions, procedures, methodology, and limits of quantitation were the same as those described in the last report (*7, 9-13*. Also: H. K. Hundley and J. C. Underwood, Food and Drug Administration, 1970: personal communication; and J. Okrasinski, Food and Drug Administration, 1970: personal communication).

Results

A total of 1,003 residues of 35 different materials were found in samples in the current reporting period, which covered 35 market baskets. In the previous reporting period, 1,081 residues of 33 different chemicals were found in 30 market baskets. Because of the procedural changes made during the previous reporting period, it is difficult to assess the significance of the overall values for frequency of occurrence. An example of one of these changes was the discontinuance of the bromide analysis in the middle of the previous reporting period. The 35 different residues found are listed in decreasing order of frequency in Table 1.

[1] Kansas City Field Office Laboratory, Food and Drug Administration, U.S. Department of Health, Education, and Welfare, Kansas City, Mo. 64106.

TABLE 1. *Pesticide residues in food composites, June 1971 - July 1972*

Pesticide	No. Composites With Residues	No. Positive Composites With Residues Reported As Trace [1]	Range, ppm
CADMIUM	256	0	0.01-0.14
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	110	41	0.001-0.016
DDE 1,1-dichloro-2,2-bis (*p*-chlorophenyl) ethylene (isomers other than p,p' also included in reportings)	104	64	0.002-0.048
MALATHION diethyl mercaptosuccinate, *s*-ester with *o,o*-dimethyl phosphorodithioate	70	10	0.004-0.492
DDT 1,1,1-trichloro-2,2-bis (*p*-chlorophenyl) ethane (isomers other than p,p' also included in reportings)	64	47	0.004-0.045

(Continued next page)

TABLE 1 (cont'd.). *Pesticide residues in food composites, June 1971 - July 1972*

Pesticide	No. Composites With Residues	No. Positive Composites With Residues Reported As Trace [1]	Range, ppm
TDE 1,1-dichloro-2,2-bis (*p*-chlorophenyl) ethane (isomers other than p,p′ also included in reportings)	57	41	0.005-0.043
PCB's (polychlorinated biphenyls). Calculated as Aroclor ® with varied chlorine content—54% and 60% reported this period	51	46	0.035-0.15
DIAZINON *o,o*-diethyl *o*-(2-isopropyl-6-methyl-4-pyrimidinyl) phosphorothioate	51	32	0.002-0.016
BHC 1,2,3,4,5,6-hexachlorocyclohexane, mixed isomers except gamma	47	32	0.01-0.013
HEPTACHLOR EPOXIDE 1,4,5,6,7,8,8-heptachloro-2,3-epoxy-3a,4,7,7a-tetrahydro-4,7-methanoindan	33	27	0.003-0.020
MERCURY	23	0	0.02-0.08
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)	20	16	0.003-0.010
LINDANE 1,2,3,4,5,6-hexachlorocyclohexane, 99% or more gamma isomer	17	11	0.001-0.005
PARATHION *o,o*-diethyl *o-p*-nitrophenyl phosphorothioate	13	9	0.005-0.006
CIPC isopropyl *n*-(3-chlorophenyl) carbamate	10	0	0.008-1.40
ETHION *o,o,o′,o′*-tetraethyl *s,s′*-methylene bisphosphorodithioate	9	3	0.007-0.027
ARSENIC (As_2O_3)	8	0	0.1-0.7
DICOFOL (KELTHANE®) 4,4′-dichloro-α-(trichloromethyl) benzhydrol	8	2	0.005-0.77
METHYL PARATHION *o,o*-dimethyl *o-p*-nitrophenyl phosphorothioate	7	5	0.007-0.010
ORTHOPHENYLPHENOL 2-hydroxydiphenyl	7	3	0.1-0.4
CARBARYL 1-napthyl methyl carbamate	6	5	0.02
BOTRAN ® 2,6-dichloro-4-nitroaniline	5	1	0.006-0.069
HCB hexachlorobenzene	4	0	0.002-0.011
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	4	3	0.006
PERTHANE 1,1-dichloro-2,2-bis (*p*-ethyl phenyl) ethane	4	0	0.013-0.215
PCA pentachloroaniline	3	0	0.005-0.023
CAPTAN *n*-trichloromethylthio-4-cyclohexane-1,2-dicarboximide	2	1	0.007
PHOSALONE *o,o*-diethyl *s*-(6-chloro-2-oxobenzoxazdin-3-yl) methyl phosphorodithioate	2	0	0.034-0.089
METHOXYCHLOR 1,1,1-trichloro-2,2-bis (*p*-methoxyphenyl) ethane	2	1	0.015
TOXAPHENE chlorinated camphene containing 67% to 69% chlorine	1	0	0.10
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 approximate 50% related compounds	1	0	0.59
RONNEL *o,o*-dimethyl *o*-2,4,5-trichlorophenyl phosphorothioate	1	1	T
PCNB pentachloronitrobenzene	1	1	T
2,4-D 2,4-dichlorophenoxyacetic acid	1	0	0.01
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-dimethano naphthalene	1	1	T

[1] Trace implies residues detected and qualitatively confirmed at too low a level to be quantified. See reference *(7)* for further explanation.

TABLE 2a. *Levels of pesticide residues commonly found—by food class and region, June 1971 - July 1972*

Chemical	Baltimore	Boston	Kansas City	Los Angeles	Minneapolis
			Residues, ppm		
			I. Dairy Products		
DIELDRIN					
Average	0.001	T	0.001	T	T
Positive Composites					
Number	6	3	7	7	4
Range	T-0.002	T-0.001	T-0.005	T-0.001	T-0.001
DDE					
Average	T	T	T	0.007	T
Positive Composites					
Number	4	2	2	6	2
Range	T	T	T	T-0.015	T
BHC					
Average	0	T	T	T	T
Positive Composites					
Number	0	4	2	2	5
Range	0	T	T	T	T
HEPTACHLOR EPOXIDE					
Average	T	T	0.001	T	T
Positive Composites					
Number	2	1	5	1	3
Range	T	T	T-0.004	T	T
CADMIUM					
Average	T	T	0.01	T	T
Positive Composites					
Number	2	1	5	1	1
Range	0.01	0.01	0.01-0.03	0.01	0.01
			II. Meat, Fish, and Poultry		
DIELDRIN					
Average	0.003	0.002	0.002	0.003	0.002
Positive Composites					
Number	7	7	5	7	6
Range	T-0.007	T-0.003	T-0.006	T-0.009	T-0.005
DDE					
Average	0.01	0.004	0.004	0.032	0.002
Positive Composites					
Number	7	7	5	7	7
Range	T-0.03	T-0.009	T-0.012	0.015-0.048	T-0.006
DDT					
Average	0.011	0.002	0.005	0.003	T
Positive Composites					
Number	6	5	6	6	4
Range	T-0.045	T-0.008	T-0.015	T-0.023	T
PCB's					
Average	0.012	T	T	T	T
Positive Composites					
Number	3	2	3	6	2
Range	T-0.081	T	T	T	T
TDE					
Average	0.003	T	0.001	0.001	T
Positive Composites					
Number	5	2	3	3	3
Range	T-0.013	T	T-0.006	T-0.008	T
CADMIUM					
Average	0.01	0.01	0.01	0.02	0.01
Positive Composites					
Number	2	4	5	3	5
Range	0.02-0.03	0.01-0.04	0.01-0.03	0.01-0.07	0.01-0.02
MERCURY					
Average	0.01	0.02	0.01	0.01	0.01
Positive Composites					
Number	4	6	2	3	4
Range	0.02-0.03	0.02-0.03	0.03	0.02	0.02
ARSENIC					
Average	T	T	T	0.1	T
Positive Composites					
Number	2	2	1	1	2
Range	0.1	0.1-0.2	0.1	0.7	0.1-0.2
			III. Grain and Cereal		
PCB's					
Average	0.014	T	T	0.005	T
Positive Composites					
Number	4	4	5	4	3
Range	T-0.101	T	T	T-0.035	T

(Continued next page)

TABLE 2a (cont'd.). *Levels of pesticide residues commonly found—by food class and region, June 1971 - July 1972*

Chemical	Baltimore	Boston	Kansas City	Los Angeles	Minneapolis
MALATHION					
Average	0.017	0.017	0.019	0.019	0.018
Positive Composites					
Number	7	7	7	7	7
Range	T-0.033	T-0.038	T-0.029	0.008-0.025	0.011-0.031
DIAZINON					
Average	0.001	T	0.001	T	0.001
Positive Composites					
Number	4	3	5	2	6
Range	T-0.006	T	T-0.006	T-0.003	T-0.005
CADMIUM					
Average	0.03	0.04	0.03	0.02	0.03
Positive Composites					
Number	7	7	7	7	7
Range	0.01-0.05	0.02-0.05	0.02-0.05	0.01-0.04	0.02-0.03
IV. Potatoes					
CIPC					
Average	0.105	—	0.291	0.001	0.039
Positive Composites					
Number	3	0	4	1	2
Range	0.080-0.504	—	0.012-1.40	0.008	0.102-0.170
DIELDRIN					
Average	T	T	0.003	T	0.001
Positive Composites					
Number	2	2	4	2	2
Range	T-0.002	T-0.001	T-0.016	0.001-0.002	T-0.004
CADMIUM					
Average	0.02	0.06	0.05	0.06	0.05
Positive Composites					
Number	7	6	7	7	7
Range	0.02-0.04	0.03-0.14	0.02-0.10	0.02-0.09	0.03-0.10
V. Leafy Vegetables					
DIAZINON					
Average	0.003	0.003	0.001	0.002	T
Positive Composites					
Number	2	3	1	1	2
Range	0.011	T-0.015	0.008	0.016	T-0.002
PARATHION					
Average	0.002	T	T	—	T
Positive Composites					
Number	5	1	1	0	1
Range	T-0.006	T	T	—	T
CADMIUM					
Average	0.08	0.03	0.05	0.06	0.05
Positive Composites					
Number	6	6	7	7	7
Range	0.01-0.4	0.02-0.05	0.02-0.09	0.03-0.11	0.02-0.08
VI. Legume Vegetables					
CADMIUM					
Average	0.01	0.01	0.01	<0.01	<0.01
Positive Composites					
Number	2	2	3	2	1
Range	0.02-0.03	0.02-0.05	0.02	0.01-0.02	0.02
VII. Root Vegetables					
CADMIUM					
Average	0.03	0.02	0.02	0.02	0.02
Positive Composites					
Number	6	5	7	6	7
Range	0.02-0.07	0.02-0.04	0.01-0.04	0.01-0.05	0.01-0.03
VIII. Garden Fruits					
DIELDRIN					
Average	0.002	0.002	0.001	T	0.001
Positive Composites					
Number	6	4	4	3	2
Range	T-0.004	T-0.006	T-0.003	T-0.002	T-0.004
TDE					
Average	0.012	0.001	0.006	T	—
Positive Composites					
Number	5	4	5	1	0
Range	T-0 043	T-0.006	T-0 034	T	—

Continued next page)

TABLE 2a (cont'd.). *Levels of pesticide residues commonly found—by food class and region, June 1971-July 1972*

Chemical	Baltimore	Boston	Kansas City	Los Angeles	Minneapolis
CADMIUM					
Average	0.02	0.02	0.02	0.01	0.03
Positive Composites					
Number	6	5	7	5	7
Range	0.01-0.06	0.01-0.08	0.01-0.05	0.01-0.02	0.02-0.06
IX. Fruits					
KELTHANE					
Average	T	0.003	—	0.007	0.014
Positive Composites					
Number	1	1	0	2	3
Range	T	0.019	—	T-0.046	0.009-0.077
ETHION					
Average	—	0.003	0.006	0.001	0.002
Positive Composites					
Number	0	3	2	3	1
Range	—	T-0.011	0.013-0.027	T-0.007	0.014
ENDOSULFAN (I, II, and the Sulfate)					
Average	0.001	T	0.003	0	0
Positive Composites					
Number	2	2	2	0	0
Range	T-0.006	T	T-0.020	0	0
X. Oils, Fats, and Shortening					
MALATHION					
Average	0.071	0.098	0.039	0.005	0.015
Positive Composites					
Number	6	6	5	2	6
Range	T-0.19	0.02-0.492	0.01-0.131	T-0.028	T-0.029
DDE					
Average	0.001	T	T	0.001	0.001
Positive Composites					
Number	4	4	6	3	3
Range	T-0.005	T-0.003	T-0.002	T-0.006	T-0.007
DDT					
Average	0.001	0.002	T	T	0.001
Positive Composites					
Number	3	4	3	1	2
Range	T-0.009	T-0.007	T	T	T-0.01
CADMIUM					
Average	0.02	0.01	0.02	0.03	0.02
Positive Composites					
Number	6	5	6	6	7
Range	0.01-0.04	0.01-0.06	0.01-0.04	0.02-0.04	0.01-0.05
TDE					
Average	0.002	0.002	T	T	0.001
Positive Composites					
Number	4	3	3	1	2
Range	T-0.015	T-0.006	T	T	T-0.009
DIELDRIN					
Average	T	T	0.002	T	T
Positive Composites					
Number	2	3	2	1	1
Range	T-0.001	T	0.003-0.015	T	0.002
XI. Sugars and Adjuncts					
BHC					
Average	T	0.001	0.001	T	T
Positive Composites					
Number	1	3	2	2	4
Range	0.002	0.001-0.003	0.002-0.003	T	T-0.001
CADMIUM					
Average	<0.01	<0.01	0.01	0.01	0.01
Positive Composites					
Number	1	1	3	3	3
Range	0.02	0.02	0.01-0.03	0.01-0.05	0.01-0.02

NOTE: Seven composites examined from each of five regions: Baltimore, Boston, Kansas City, Los Angeles, and Minneapolis. Residues listed ar averages of the seven composites from each site.
— denotes not applicable.
T = trace; see definition, Table 1.

TABLE 2b. *Pesticides found infrequently—by food class and region, June 1971 - July 1972*

Pesticide	Region	No. Composites	Residues, ppm
	1. Dairy Products		
Mercury	Boston	1	0.02
TDE	Kansas City	1	T
	Baltimore	1	T
DDT	Baltimore	1	T
	Los Angeles	2	T, T
Methoxychlor	Baltimore	1	T
PCB's	Boston	1	T
	Los Angeles	1	T
	II. Meat, Fish, and Poultry		
Heptachlor Epoxide	Kansas City	3	T, T, 0.003
	Baltimore	5	T, T, T, T, 0.003
	Boston	2	T, T
	Los Angeles	1	T
	Minneapolis	3	T, T, T
Lindane	Kansas City	1	T
	Baltimore	1	0.001
	Boston	2	T, T
	Los Angeles	1	T
BHC	Kansas City	4	T, T, T, 0.001
	Baltimore	2	T, T
	Boston	3	T, T, T
	Los Angeles	1	T
	Minneapolis	1	T
Diazinon	Baltimore	1	T
	Minneapolis	1	T
	III. Grain and Cereal		
Mercury	Boston	1	0.02
Parathion	Baltimore	1	0.006
Dieldrin	Kansas City	1	0.002
	Minneapolis	1	0.002
Lindane	Los Angeles	3	T, 0.002, 0.002
DDT	Baltimore	1	T
	Boston	2	T, T
	Los Angeles	1	T
DDE	Kansas City	1	T
	Boston	1	T
	Los Angeles	1	T
TDE	Boston	1	T
	Los Angeles	1	T
	Minneapolis	1	T
Ronnel	Kansas City	1	T
Heptachlor Epoxide	Los Angeles	1	T
BHC	Los Angeles	2	0.002, 0.004
Chlordane	Boston	1	0.059
	IV. Potatoes		
BHC	Baltimore	1	0.005
Endrin	Baltimore	2	T, T
	Boston	1	T
Heptachlor Epoxide	Boston	1	T
	Minneapolis	2	T, 0.020
Mercury	Los Angeles	1	0.03
DDT	Baltimore	2	T, 0.006
	Boston	1	T
	Los Angeles	1	T
	Minneapolis	1	T
DDE	Kansas City	2	T, T
	Baltimore	2	T, T
	Boston	2	T, T
	Los Angeles	2	T, 0.007
	Minneapolis	2	T, T
TDE	Boston	1	T
PCB's	Baltimore	1	T
Diazinon	Baltimore	1	T
	Minneapolis	1	0.004
Endosulfan (I, II, and the Sulfate)	Baltimore	1	T

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TABLE 2b (cont'd.). *Pesticides found infrequently—by food class and region, June 1971 - July 1972*

Pesticide	Region	No. Composites	Residues, ppm
V. Leafy Vegetables			
Methyl Parathion	Kansas City	2	T, T
	Baltimore	1	T
	Boston	1	T
	Minneapolis	2	T, 0.010
Carbaryl	Kansas City	1	0.02
	Baltimore	1	T
HCB	Baltimore	1	0.002
Botran	Baltimore	1	0.013
BHC	Baltimore	1	0.005
Perthane	Baltimore	1	0.215
	Boston	1	0.03
Endosulfan (I, II, and the Sulfate)	Boston	3	T, T, T
	Los Angeles	3	T, 0.028, 0.017
	Minneapolis	1	T
DDE	Kansas City	1	T
	Baltimore	2	T, T
	Boston	1	T
	Los Angeles	2	T, 0.011
DDT	Boston	1	T
	Los Angeles	1	0.007
TDE	Boston	1	T
Malathion	Boston	1	0.020
2,4-D	Los Angeles	1	0.01
Kelthane	Boston	1	0.041
Dieldrin	Los Angeles	1	T
	Minneapolis	1	T
Toxaphene	Los Angeles	1	0.1
VI. Legume Vegetables			
DDE	Kansas City	1	T
	Los Angeles	1	T
DDT	Kansas City	1	T
	Baltimore	1	T
Dieldrin	Boston	1	0.014
PCB's	Los Angeles	1	T
	Minneapolis	1	T
TDE	Kansas City	1	T
	Baltimore	1	T
	Los Angeles	1	T
Parathion	Minneapolis	1	T
VII. Root Vegetables			
DDE	Baltimore	3	T, T, 0.010
	Los Angeles	1	T
Parathion	Baltimore	1	0.005
DDT	Baltimore	1	0.004
Dieldrin	Boston	1	T
	Los Angeles	1	T
PCB's	Los Angeles	1	T
Lindane	Boston	1	T
Mercury	Kansas City	1	0.08
VIII. Garden Fruits			
Carbaryl	Kansas City	1	T
	Minneapolis	1	T
BHC	Kansas City	2	0.009, 0.009
	Los Angeles	2	T, 0.013
	Minneapolis	1	T
Diazinon	Kansas City	1	T
	Baltimore	1	T
	Boston	1	T
	Minneapolis	1	T
PCB's	Boston	1	T

(Continued next page)

TABLE 2b (cont'd.). *Pesticides found infrequently—by food class and region, June 1971 - July 1972*

Pesticide	Region	No. Composites	Residues, ppm
DDE	Boston	1	T
	Los Angeles	3	T, T, T
Endrin	Los Angeles	1	0.006
Parathion	Los Angeles	1	T
Lindane	Los Angeles	1	T
Endosulfan (I, II, and the Sulfate)	Kansas City	1	T
	Baltimore	3	T, T, T
	Boston	2	T, T
DDT	Baltimore	1	T
	Boston	1	T
	Los Angeles	2	T, T
Heptachlor Epoxide	Los Angeles	1	T
	Minneapolis	1	T
IX. Fruits			
Perthane	Baltimore	1	0.013
	Boston	1	0.027
Dieldrin	Boston	1	T
	Los Angeles	1	0.001
Phosalone	Baltimore	1	0.089
	Los Angeles	1	0.034
Captan	Kansas City	1	0.007
	Minneapolis	1	T
Botran	Kansas City	1	T
	Baltimore	1	0.069
	Boston	1	0.006
	Minneapolis	1	0.043
Orthophenylphenol	Kansas City	3	0.3, 0.1, 0.4
	Baltimore	1	T
	Los Angeles	1	T
	Minneapolis	2	T, 0.1
BHC	Kansas City	1	T
Aldrin	Kansas City	1	T
Methoxychlor	Baltimore	1	0.015
Malathion	Boston	3	T, 0.004, 0.053
	Minneapolis	3	T, 0.012, 0.006
DDT	Boston	1	T
Lindane	Baltimore	1	T
Cadmium	Kansas City	3	0.01, 0.01, 0.02
	Baltimore	1	0.01
	Boston	1	0.02
	Los Angeles	1	0.02
	Minneapolis	2	0.01, 0.02
Diazinon	Kansas City	1	T
	Baltimore	2	T, 0.002
	Los Angeles	2	T, T
	Minneapolis	1	0.002
Methyl Parathion	Boston	1	0.007
Carbaryl	Los Angeles	1	T
	Minneapolis	1	T
DDE	Boston	1	T
	Los Angeles	2	T, T
TDE	Los Angeles	1	T
X. Oils, Fats, and Shortening			
PCB's	Kansas City	3	T, T, 0.05
	Baltimore	1	0.15
	Los Angeles	1	T
	Minneapolis	1	T
Pentachloroaniline	Baltimore	1	0.005
	Boston	1	0.023
	Minneapolis	1	0.022
HCB	Baltimore	1	0 004
	Boston	1	0.004
	Minneapolis	1	0.011
Parathion	Kansas City	1	T
BHC	Boston	1	T

(Continued next page)

TABLE 2b (cont'd.). *Pesticides found infrequently—by food class and region, June 1971 - July 1972*

Pesticide	Region	No. Composites	Residues, ppm
PCNB	Boston	1	T
Heptachlor Epoxide	Boston	1	T
Diazinon	Los Angeles	1	T
XI. Sugars and Adjuncts			
Dieldrin	Kansas City	2	T, T
Lindane	Kansas City	1	0.003
	Baltimore	2	T, T
	Boston	1	0.005
	Los Angeles	1	0.007
	Minneapolis	1	T
Malathion	Kansas City	1	T
	Baltimore	2	0.01, 0.005
PCB's	Kansas City	1	T
	Minneapolis	1	T
Diazinon	Kansas City	3	T, T, T
	Boston	2	T, T
	Los Angeles	1	T
	Minneapolis	1	T
DDE	Kansas City	1	T
	Los Angeles	1	T
	Minneapolis	1	T
DDT	Kansas City	1	T
	Minneapolis	1	T
TDE	Kansas City	1	T
	Minneapolis	1	T
XII. Beverages			
Cadmium	Kansas City	2	0.01, 0.02
	Boston	2	0.05, 0.01
	Minneapolis	1	0.01

NOTE: Seven composites examined from each of five regions: Baltimore, Boston, Kansas City, Los Angeles, and Minneapolis. Residues listed are averages of the seven composites from each site.
T = trace; see definition, Table 1.

The most common residues, maximum levels of those residues, and residues reported less frequently are discussed below for each of the 12 food composites. Findings are reported in more detail in Tables 2a and 2b. Averages were calculated by dividing the sums of the residues found by the total number of composites examined from each region (seven in all cases). None of the reported findings have been corrected for recovery. Table 3 summarizes recovery studies.

DAIRY PRODUCTS

Of 35 composites examined, 32 contained residues. Organochlorine residues were the most prevalent, appearing in 32 composites. The most common and their maximum concentrations were dieldrin, 0.005 ppm; DDE, 0.015 ppm; BHC, trace; and heptachlor epoxide, 0.004 ppm. Also found were DDT, polychlorinated biphenyls (PCB's), methoxychlor, and TDE. Cadmium appeared in 10 of 35 composites at levels of 0.01-0.03 ppm. Mercury was found in 1 of 35 composites at 0.02 ppm.

MEAT, FISH, AND POULTRY

Eight organochlorine compounds were found in varying combinations in all 35 composites. Most common organochlorine residues and their maximum concentrations were DDE, 0.048 ppm; dieldrin, 0.009 ppm; DDT, 0.045 ppm; TDE, 0.013 ppm; and PCB's, 0.081 ppm. Heptachlor epoxide, BHC, and lindane were also found. Trace levels of diazinon were found in 2 of 35 composites. Arsenic was found in 8 composites: 0.1-0.7 ppm; mercury in 19 composites: 0.02-0.03 ppm; and cadmium in 19 composites: 0.01-0.07 ppm.

GRAIN AND CEREAL PRODUCTS

Organophosphorus residues were the most common in this commodity class. Malathion was found in all 35 composites at a maximum level of 0.038 ppm; diazinon was found in 20 composites at a maximum level of 0.006 ppm. Ten organochlorine compounds occurred in various combinations in 27 composites. The most common of these were PCB's at a maximum level of 0.101 ppm. Other residues detected were DDT, DDE, TDE, dieldrin, BHC, lindane, ronnel, chlordane, heptachlor epoxide, and parathion. Cadmium appeared in all 35 composites ranging from 0.01 to 0.05 ppm and mercury appeared in 1 composite at 0.02 ppm.

POTATOES

Ten organochlorine compounds were detected in 27 of the 35 composites. The most common of these com-

TABLE 3. *Recovery experiments on pesticides found in total diet samples, June 1971 - July 1972*

Pesticide	Type of Food Composite	Spike Level, ppm	Range of Blank Levels, ppm	Range of Total Recovered, ppm	No. Recovery Experiments
CARBARYL	Nonfatty	0.2	0-T	0.05-0.20 (0.19)	69
ARSENIC	Fatty	0.2	0-0.10 (0.00)	0.04-0.31 (0.15)	33
	Nonfatty	0.2	0-0.040 (0.00)	0.01-0.33 (0.15)	66
CADMIUM	Fatty	0.10	0-0.020 (0.006)	0.078-0.122 (0.100)	12
	Nonfatty	0.10	0-0.020 (0.004)	0.070-0.131 (0.103)	17
	Fatty	0.05	0-0.010 (0.003)	0.038-0.220 (0.061)	15
	Nonfatty	0.05	0-0.010 (0.002)	0.040-0.072 (0.051)	20
MERCURY	Fatty	0.06	0-0.025 (0.006)	0.041-0.095 (0.061)	35
	Nonfatty	0.06	0-0.008 (0.001)	0.038-0.077 (0.060)	70
CHLORDANE	Fatty	0.2	0	0.098-0.167 (0.145)	5
	Nonfatty	0.2	0	0.136-0.231 (0.179)	10
PARATHION	Fatty	0.02	0	0.013-0.018 (0.015)	10
	Nonfatty	0.02	0-0.006 (0.001)	0.013-0.027 (0.019)	10
	Nonfatty	0.01	0-0.005 (0.001)	0.0058-0.013 (0.0087)	10
2,4-DB	Fatty	0.03	0	0-0.039 (0.019)	19
	Nonfatty	0.03	0	0-0.042 (0.022)	38
MCP	Fatty	0.02	0	0.003-0.015 (0.009)	7
	Nonfatty	0.02	0	0.007-0.24 (0.014)	18
MALATHION	Fatty	0.05	0-0.018 (0.006)	0.029-0.060 (0.047)	3
	Nonfatty	0.02	0	0.016-0.026 (0.020)	5
	Nonfatty	0.05	0-0.019 (0.003)	0.035-0.063 (0.048)	6
DIELDRIN	Fatty	0.01	0-0.007 (0.003)	0.010-0.015 (0.013)	3
	Nonfatty	0.01	0-0.006 (0.001)	0.009-0.018 (0.012)	6
DIAZINON	Fatty	0.02	0	0.012-0.018 (0.015)	11
	Nonfatty	0.02	0-0.002	0.014-0.024 (0.018)	21
RONNEL	Fatty	0.01	0	0.004-0.011 (0.007)	4
	Nonfatty	0.01	0	0.008-0.011 (0.010)	6
	Nonfatty	0.02	0	0.011-0.022 (0.016)	4
ETHION	Fatty	0.02	0	0.014-0.017 (0.016)	4
	Nonfatty	0.02	0	0.015-0.019 (0.016)	5
	Nonfatty	0.01	0	0.007-0.011 (0.009)	5
ALDRIN	Fatty	0.005	0	0.0025-0.0028 (0.0027)	3
	Nonfatty	0.005	0	0.0030-0.0056 (0.0042)	6
BHC	Fatty	0.003	0-0.0010 (0.0002)	0-0.0034 (0.0020)	6
	Nonfatty	0.003	0	0-0.0048 (0.0027)	11
PCB's	Fatty	0.05	0	0.021-0.078 (0.042)	5
	Nonfatty	0.05	0	0.023-0.056 (0.045)	10

NOTE: Numbers in parentheses represent average residue levels.

pounds and their maximum levels were dieldrin, 0.016 ppm; CIPC (chlorpropham), 1.40 ppm; DDE, 0.007 ppm; and DDT, 0.006 ppm. Also detected were heptachlor epoxide, endrin, PCB's, BHC, TDE, endosulfan, and diazinon. Cadmium was found in 34 composites ranging from 0.02 to 0.14 ppm and mercury was found in 1 composite at 0.03 ppm.

LEAFY VEGETABLES

Residues of 12 organochlorines were discovered in varying combinations in 16 composites. Organophosphorus residues appeared in 17 composites. The most common of these compounds and their maximum levels were diazinon, 0.016 ppm; parathion, 0.006 ppm; endosulfan, 0.028 ppm; methyl parathion, 0.010 ppm; and DDE, 0.011 ppm. Cadmium was found in 33 of 35 composites ranging from 0.01 to 0.40 ppm. Other residues were DDT, perthane, toxaphene, kelthane (Dicofol), botran, hexachlorobenzene (HCB), BHC, dieldrin, TDE, 2,4-D, malathion, and carbaryl.

LEGUME VEGETABLES

Five organochlorine residues were observed in 6 of 35 composites. These included trace levels of PCB's, DDT, TDE, and DDE; 0.014 ppm dieldrin was detected. A trace level of parathion was discovered in one composite. Cadmium was observed in 10 composites ranging from 0.01 to 0.05 ppm.

ROOT VEGETABLES

Five organochlorine residues were found in 7 of 35 composites. The most common and their maximum levels were DDE, 0.010 ppm; and dieldrin, which appeared in trace amounts. Mercury was observed in 1 composite at 0.08 ppm and cadmium was found in 31 composites ranging from 0.01 to 0.07 ppm. Other residues were PCB's, lindane, DDT, and parathion.

GARDEN FRUITS

Various combinations of 10 organochlorine residues were detected in 29 of 35 composites. The most common of these and their maximum levels were dieldrin, 0.006 ppm; TDE, 0.043 ppm; BHC, 0.013 ppm; and endosulfan, which appeared in trace amounts. Cadmium was found in 30 composites ranging from 0.01 to 0.08 ppm. Other residues were DDE, DDT, heptachlor epoxide, PCB's, lindane, endrin, diazinon, parathion, and carbaryl.

FRUITS

Residues of 13 organochlorines were discovered in 19 of 35 composites. The most common of these and their maximum levels were kelthane, 0.077 ppm; endosulfan, 0.020 ppm; botran, 0.069 ppm; and DDE, which appeared in trace quantities. Five organophosphorus residues were observed in varying combinations in 20 of 35 composites. The most common and their highest levels were ethion, 0.027 ppm; malathion, 0.053 ppm; and diazinon, 0.002 ppm. Cadmium appeared in eight composites ranging from 0.01 to 0.02 ppm. Other residues were captan, perthane, dieldrin, TDE, DDT, BHC, methoxychlor, lindane, aldrin, methyl parathion, phosalone, carbaryl, and *o*-phenylphenol.

OILS, FATS, AND SHORTENING

Of 35 composites, 26 showed residues of 10 organochlorines. The most common and their maximum levels were DDE, 0.007 ppm; DDT, 0.010 ppm; TDE, 0.015 ppm; dieldrin, 0.015 ppm; and PCB's, 0.15 ppm. Malathion was detected in 25 composites; maximum level was 0.492 ppm. Cadmium was found in 30 composites ranging from 0.01 to 0.06 ppm. HCB, PCA, heptachlor epoxide, BHC, PCNB, parathion, and diazinon were also discovered.

SUGARS AND ADJUNCTS

Varying combinations of seven organochlorines occurred in 18 of 35 composites. The most common and their maximum levels were BHC, 0.003 ppm; and lindane, 0.007 ppm. Trace levels of diazinon appeared in seven composites. Cadmium was found in 11 composites. DDE, TDE, DDT, dieldrin, PCB's, and malathion were also observed.

BEVERAGES

Cadmium appeared in 5 of the 35 composites ranging from 0.01 to 0.05 ppm. No other residues occurred in these composites.

Discussion

Of the 420 composites examined, organochlorine residues were found in 226, or 54 percent. Organophosphorus residues were found in 117 composites, or 27.8 percent. Corresponding quantities of organochlorines in previous years were 61.4 percent, 1970-71; 74.2 percent, 1969-70; and 64.7 percent, 1968-69. For organophosphorus residues during the same years, corresponding amounts were 21.4, 20.6, and 16.4 percent.

Carbaryl occurred in six composites during the present reporting period; five of these were at trace levels. This appears nearer normal than in the previous reporting period, during which a high of 20 composites contained carbaryl residues.

All eight findings of arsenic occurred in Group II: Meat, Fish, and Poultry. Levels ranged from 0.1 to 0.7 ppm.

Cadmium residues appeared in all 12 composites; maximum level was 0.40 ppm. Of the 420 composites examined, 256 contained cadmium.

Only one composite with a chlorophenoxy acid herbicide was found during this reporting period; no pentachlorophenol (PCP), which is detected by the chlorophenoxy acid method, was found.

Mercury residues were discovered in 23 of 420 composites; 19 appeared in Group II: Meat, Fish, and Poultry. Current analyses of individual commodities within

this composite corroborate the previous Total Diet report (*7*) showing seafood to be the main source of mercury in the diet.

Recovery studies were conducted for all classes of chemicals sought throughout the entire year (Table 3). Each recovery experiment consisted of a single determination for the unfortified food composite and a single determination for the fortified sample. These were performed simultaneously; hence the fortification level was occasionally below the level present in the sample. In other cases, not enough recoveries were run to permit statistical evaluation; such recovery data are not reported.

At very low fortification levels recoveries may range from 0 to 200 percent. As the fortification level is raised however, the recovery improves. Recovery data demonstrate 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.

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GENERAL

Occurrence of Chlorinated Hydrocarbon Insecticides, Southern Florida—1968-72 [1]

Harold C. Mattraw, Jr.

ABSTRACT

The frequency with which chlorinated hydrocarbon insecticides appear in samples of southern Florida surface waters decreased sharply between 1968 and 1972. Sediment analyses attest to the earlier widespread use of chlordane, DDT, and dieldrin. Insecticide residues are more frequently detected in southern Florida than in other U.S. cropland soils. Transport of DDT, DDD, and DDE from the Everglades agricultural area into water conservation areas and undeveloped parts of the Everglades of southeastern Florida is facilitated by a system of water-management canals. Canal sediments within the urban area of southern Florida have high DDD, DDE, and dieldrin residue concentrations which may reflect local use of insecticides rather than their transport from adjacent agricultural areas.

Introduction

The flat terrain, abundant water, and subtropical climate of southern Florida have encouraged an extensive agricultural economy. Chlorinated hydrocarbon insecticides were heavily applied to ensure high agricultural productivity between 1940 and 1965 but recent restrictions have reduced use to a few specific crops. The persistence of several of the restricted insecticides and the potential of the hydrologic system to disperse them throughout the area have resulted in the initiation of several programs by the Geological Survey, U.S. Department of Interior, to analyze water and sediment from much of southern Florida (*1*).

LAND USE

The division of southern Florida into general land-use categories is shown in Figure 1. Urban development, previously restricted to the elevated coastal ridge, is now moving into adjacent areas. Agriculture has occupied two areas: the Everglades agricultural area, muck lands south of Lake Okeechobee, and the eastern agricultural area, parts of the rocky glades and sandy flatlands adjacent to the urban area. The Everglades is primarily saw grass marsh. The northern part has been converted to a water conservation area with an extensive system of canals and levees; the southern part includes most of the Everglades National Park, which receives regulated water discharge from the water conservation areas. The western part of the Big Cypress watershed has been partly drained to facilitate development, but the eastern part is still largely swamp.

WATER-MANAGEMENT SYSTEM

The Kissimmee River basin forms the northern end of the regional water-management system. Most of the surface flow (*2*) that enters Lake Okeechobee from the Kissimmee and from several streams is diverted westward through the Caloosahatchee River to the Gulf of Mexico or eastward through the St. Lucie Canal to the Atlantic Ocean (Fig. 1). A system of levees, canals, control structures, pumping stations, and water-storage areas permits the management of the freshwater resources of Palm Beach, Broward, and Dade Counties. Levees impound water in Lake Okeechobee and the water conservation areas and protect the eastern and Everglades agricultural areas and urban area from flooding during the rainy season, June through October. Large pumping stations protect the Everglades agricultural area and flood-prone areas immediately east of the conservation areas by pumping surplus surface runoff into Lake Okeechobee or the conservation areas. Water can be transferred from conservation areas into Everglades National Park, agricultural areas, or to the cities as demand dictates.

INSECTICIDE SOURCES AND DISPERSION MECHANISMS

Chlorinated hydrocarbon insecticides applied to croplands persist in the soil (*3*). Inadvertent spraying of waterways adjacent to croplands facilitates insecticide dispersion by the hydrologic system. Volatilization into

[1] Geological Survey, U.S. Department of Interior, 901 S. Miami Avenue, Miami, Fla. 33130.

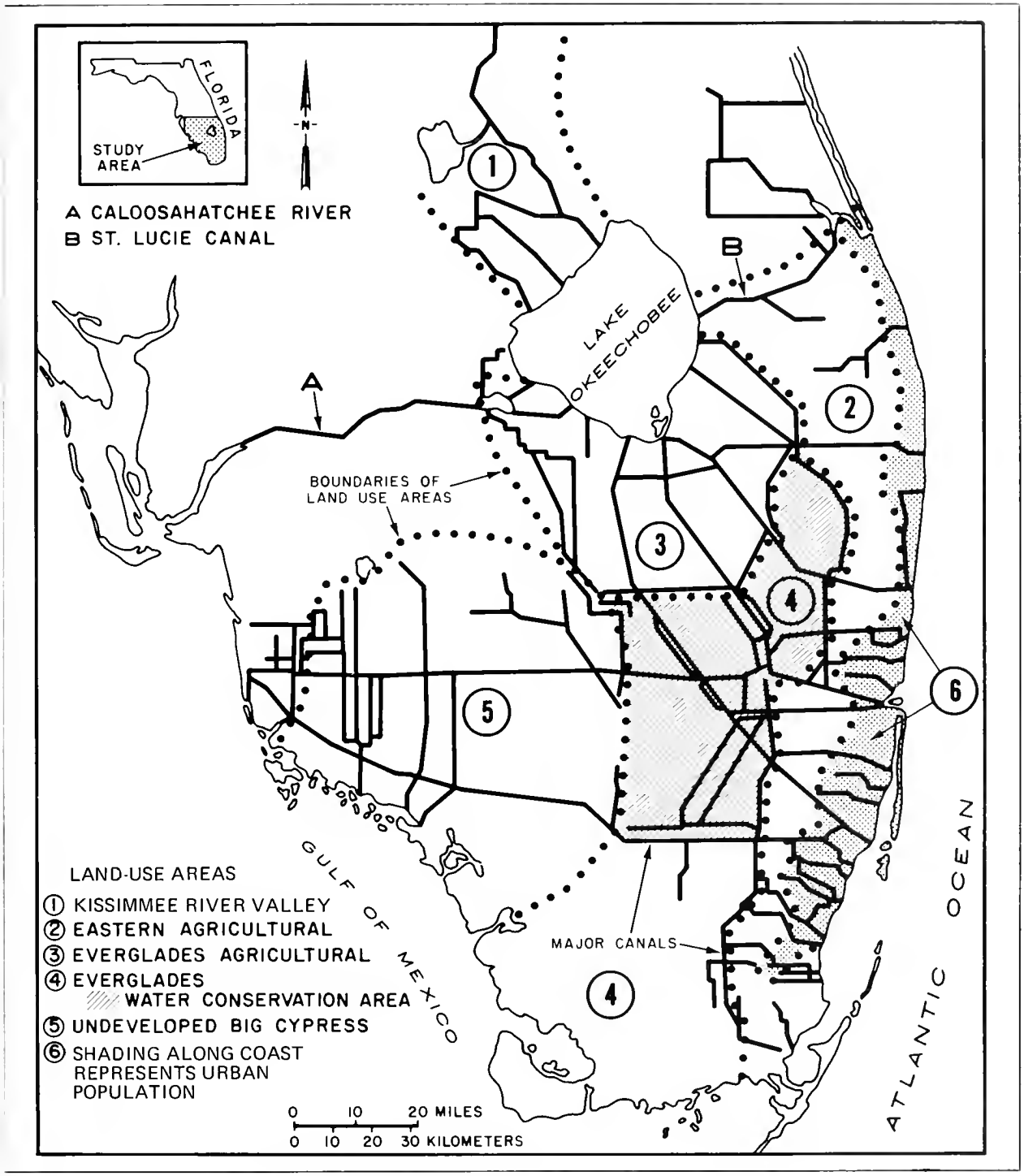

FIGURE 1. *Major canals and land-use areas, southern Florida*

the atmosphere also disperses insecticides when the volatile fraction remains in the vapor phase or is adsorbed to particulate matter in the atmosphere. The sorbed fraction returns to the ground surface as dry fallout or in rainfall. Erosion of treated soils provides a third mechanism for introduction of insecticides into the hydrologic system. The urban area provides additional pathways for insecticides through the discharge of industrial effluents, treated sewage, and storm water runoff.

Analytical Techniques

Data were not collected within any strict statistical design. Water samples were taken several inches below

the surface in hexane-rinsed 1-liter glass or teflon bottles. This sampling method has been used because most southern Florida water bodies are very shallow. Samples collected in the canal system were obtained in the same manner so results would not be influenced greatly by the highly variable suspended loads characteristic of these regulated canals (*4*). In Geological Survey studies, analyses for 11 chlorinated hydrocarbon insecticides were run using dual-column electron-capture gas chromatography according to procedures outlined by Goerlitz and Brown (*5*). Identifications were confirmed by mass spectrometry when sufficient sample remained. Interferences from PCB concentrations were corrected in 1970 (*6*). All earlier chromatograms were reviewed and corrected if necessary. The detection limit is about 0.005 μg/liter for water. Values between 0.005 and 0.01 μg/liter are reported as 0.01 μg/liter and values greater than 0.10 μg/liter are rounded to two significant figures.

The top 2 inches of bottom sediment was collected in wide-mouth hexane-rinsed glass jars using the jar as a sampling device. Sediments from canals too deep to sample directly were collected using an Ekman dredge. If sufficient material was collected, the subsample analyzed was taken from the middle of the collected sample. Insecticides were extracted from sediment samples with an acetone/hexane solvent. The extract was washed with distilled water, dried over Na_2SO_4, and concentrated and cleaned on alumina (*7*). Sediment samples were also analyzed for moisture content and insecticide concentrations are reported on a dry-weight basis. Sample recovery of chlorinated hydrocarbon insecticides in bottom materials averaged 97.9 percent (*8*). The detection limit was 0.05 μg/kg; values between 0.05 and 0.1 are reported as 0.1 μg/kg. Values greater than 1.0 μg/kg are rounded to two significant figures.

Results

WATER

The number of surface water samples analyzed from southern Florida and the percentage containing detectable insecticide concentrations are shown in Figure 2. The limit of detection was 0.005 μg/liter. Of the 11 compounds for which technicians tested, only 5, DDT, DDD, DDE, dieldrin, and lindane, were detected in water samples. The majority of the identifications were at the lower detection limit of 0.005 μg/liter. These detections may be caused by insecticides adsorbed on suspended organic matter.

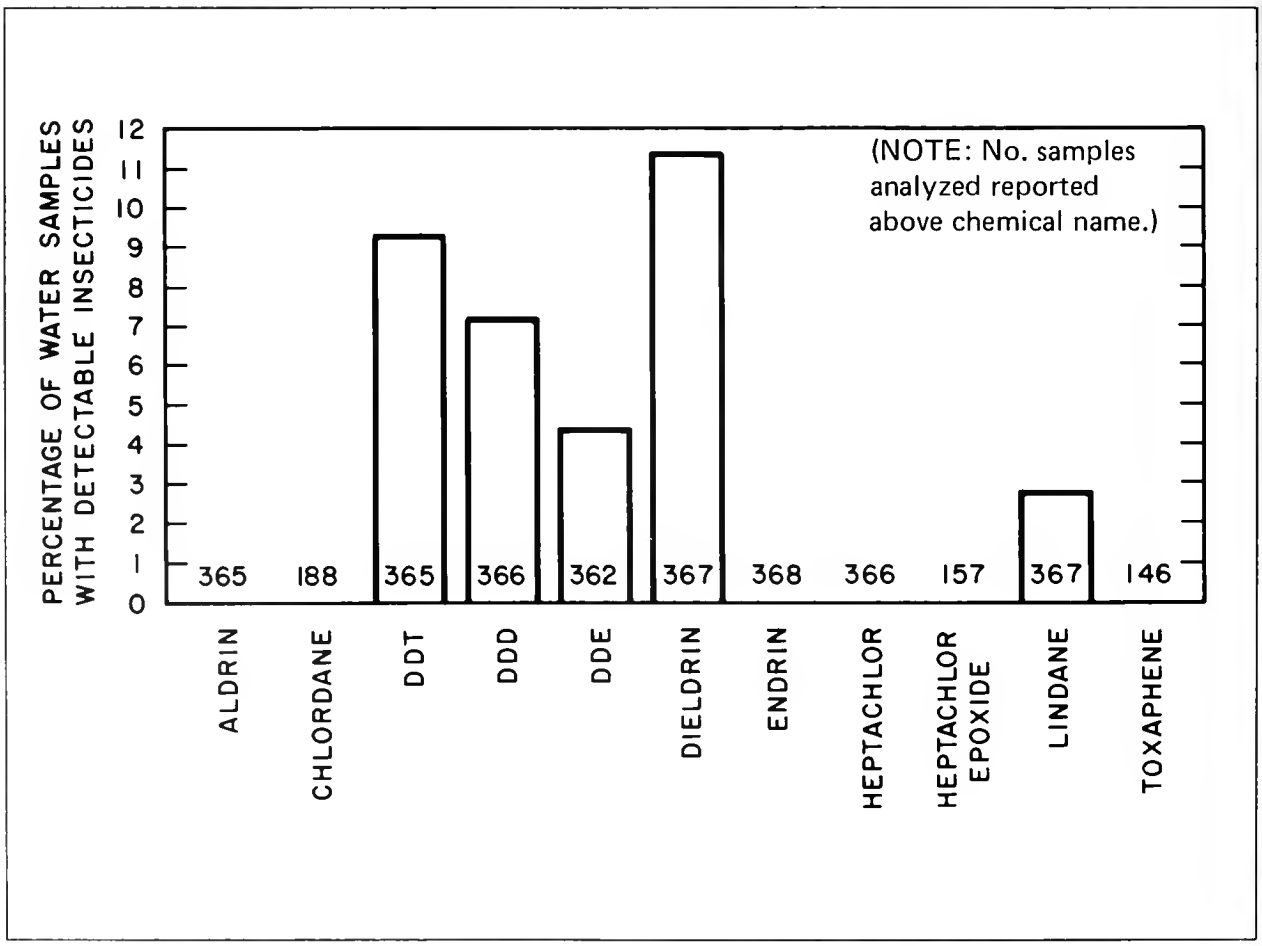

FIGURE 2. *Chlorinated hydrocarbon detections in surface waters, southern Florida—1968-72*

TABLE 1. *Detection of insecticides in surface waters, southern Florida—1968-72*

Insecticide	1968		1969		1970		1971		1972	
	No. positive samples / No. samples analyzed	Positive samples, %	No. positive samples / No. samples analyzed	Positive samples, %	No. positive samples / No. samples analyzed	Positive samples, %	No. positive samples / No. samples analyzed	Positive samples, %	No. positive samples / No. samples analyzed	Positive samples, %
DDT	17/21	81	7/26	27	11/47	23	4/109	3.7	2/166	1.2
DDD	9/22	41	4/26	15	6/49	12	7/122	5.7	6/163	3.8
DDE	5/22	23	3/26	12	1/45	2.2	6/122	4.9	5/163	3.1
Dieldrin	5/23	22	0/26	0	0/48	0	11/110	10	24/161	15

The frequency of chlorinated hydrocarbon detection in southern Florida water samples declined between 1968 and 1972 (Table 1). Rainfall samples collected in southern Florida during the same period have shown a concomitant decrease (A. L. Higer, Geological Survey, USDI, Miami, Fla., 1973: written communication). The decrease in the frequency of detectable insecticide residues in southern Florida probably reflects restrictions on agricultural applications of these chemical compounds. Annual synoptic surveys of U.S. surface waters indicate a peak occurrence of chlorinated hydrocarbon insecticides in 1966 (*9*).

SEDIMENT

The number of southern Florida sediment samples and the percentage containing detectable insecticide concentrations (0.05 μg/kg) are shown in Figure 3. Most frequently detected were chlordane, DDT, DDD, DDE, and dieldrin. Less than 5 percent of the samples analyzed contained aldrin, lindane, or toxaphene. Chlordane, dieldrin, DDT, DDD, and DDE were detected in a higher percentage of sediment samples from this study than in soil samples collected for the National Soils Monitoring Program (*10*). Aldrin was detected less frequently (Table 2), probably indicating a different insecticide-use pattern in southern Florida than in the rest of the Nation.

Concentrations of DDD in southern Florida sediments are illustrated by land-use areas in Figure 4. Sediment samples from the Everglades agricultural area, where DDT and DDD were directly applied to soils, showed the highest percentage of samples containing DDD and the highest concentrations. DDD concentrations occurred in decreasing order in the urban area, Everglades area, eastern agricultural area, and the undeveloped Big Cypress watershed. The Big Cypress is remote from areas of DDT and DDD application and probably receives most of its insecticides from atmospheric transport mechanisms. The highest DDD concentration reported in the undeveloped Big Cypress was 6 μg/kg.

Specific pesticide concentrations were compared to the percent of samples containing that amount or less to obtain cumulative frequencies of detection. The relation between DDE concentrations and the cumulative frequencies of detection is illustrated in Figure 5. Distribution of DDE residues in sediment by land-use area is similar to that of DDD (Fig. 4). The slopes of the semilogarithmic plots for DDE and DDD are nearly equal. This similarity indicates that the occurrence of various concentrations of these two pesticides within any one land-use area is essentially the same. The similarity of concentrations and cumulative frequencies of DDD and DDE detection (Fig. 4,5) indicate that their dispersion with distance from source areas and persistence with time are comparable.

A comparison of DDD and DDE concentrations in canal and marsh sediments of the Everglades area is shown in Figure 6. The slopes of the lines representing concentrations of these two pesticides versus cumulative frequencies of detection are similar. The general slope of the lines showing concentrations versus cumulative

TABLE 2. *Frequency of insecticide residue detection in cropland soil and sediment, southern Florida—1969-72*

Insecticide	Cropland soil: positive samples, %, 1969	Sediment: positive samples, %, 1969-72
Dieldrin	27.8	53.3
DDE	24.8	80.5
DDT	22.2	37.3
DDD	15.3	80.3
Aldrin	10.9	2.2
Chlordane	8.7	32.7
Heptachlor Epoxide	8.0	ND
Toxaphene	4.2	3.2
Heptachlor	3.9	ND
Endrin	2.3	ND
Lindane	0.9	0.7

NOTE: ND = not detected

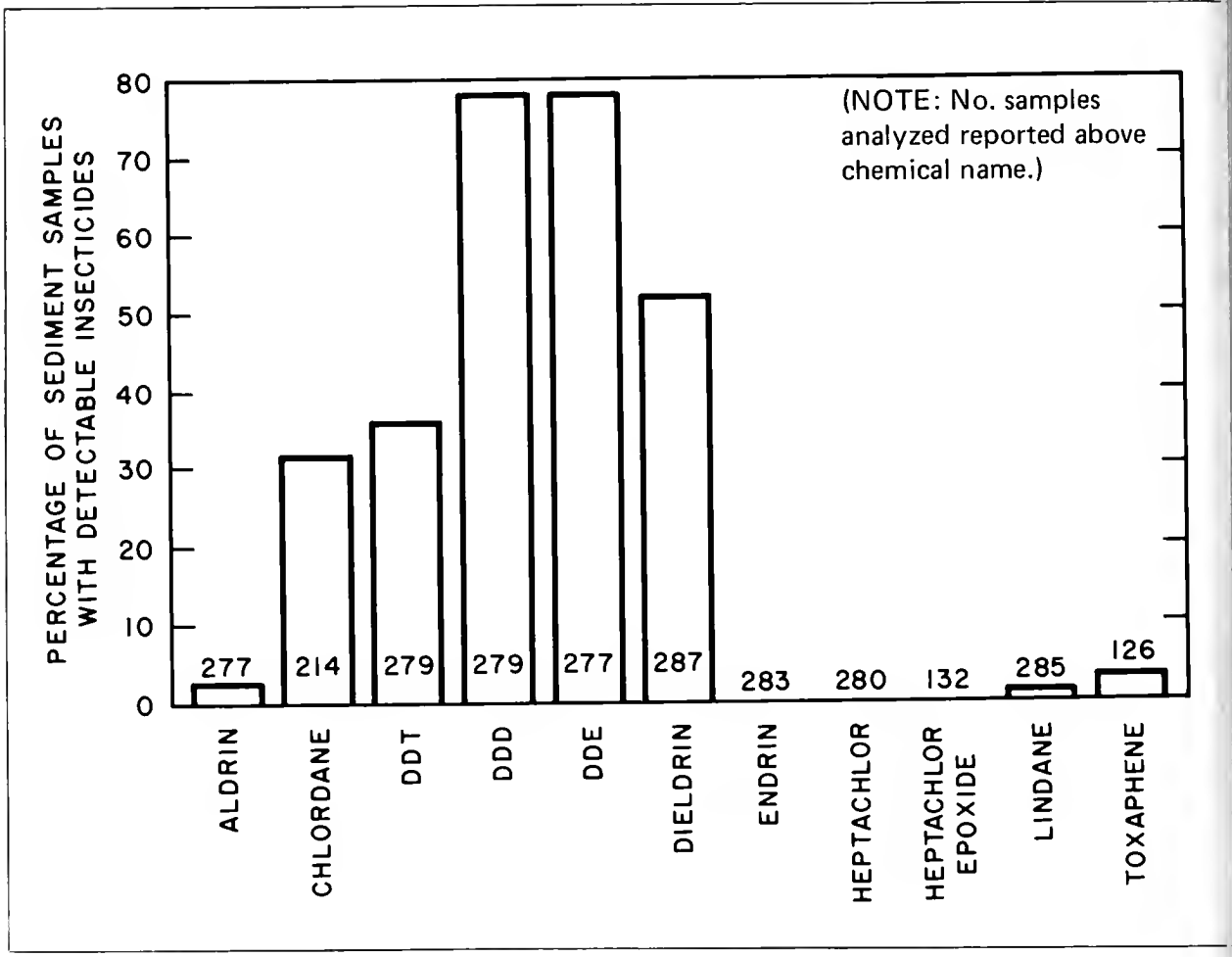

FIGURE 3. *Chlorinated hydrocarbon detections in sediment, southern Florida—1968-72*

frequencies of detection for these compounds in the canal environment is steeper than the slope for marsh sediments. The higher DDD and DDE concentrations in some canal sediment samples indicate higher introduction rates from the Everglades agricultural area.

The less frequent occurrence of DDD and DDE in sediments from the Everglades canal system appears to indicate active transport of sediment within the canals. The fine-grained, organically rich sediments have high residue levels and are apparently accumulating in a few areas where channel geometry and low velocity of flow encourage settling. Thus relatively few areas with high concentrations of insecticide-rich sediments would be expected in the canal system.

The low slope of the graph of DDD and DDE concentrations versus cumulative frequencies of detection for marsh areas (Fig. 6) is probably indicative of the uniform aerial introduction of insecticides. Because the sluggish surface water flow within marsh areas is less efficient in redistributing these insecticide loads, sediment concentrations display less variability. The high frequency with which DDD and DDE are detected in sediment samples from marsh areas is caused by th proximity of the two primary areas of insecticide use the Everglades agricultural area and the eastern agri cultural area. Time does not appear to be a significan variable in controlling the slope of the concentratio versus the cumulative frequency of detection plot.

The concentration of dieldrin in sediments amon the various land-use areas is illustrated in Figure 7 Dieldrin in sediments is more frequently detected an has higher concentrations in the urban area than in an other land-use region. The use of dieldrin for eradica tion of domestic termites would account for its mor frequent occurrence in urban area sediments. Low ove all dieldrin concentrations in all land-use areas indicat a lower use rate than that of DDT (*11*).

The undeveloped Big Cypress watershed has the low est dieldrin concentrations and the lowest frequency o dieldrin detection. Because dieldrin moves from solutio to the atmosphere more slowly than do other chlorinate hydrocarbons (*12*), it is usually retained more readil in the aqueous phase than are the more volatile DDT DDD, and DDE. This behavior would explain its ver

ow occurrence in sediments from the Big Cypress watershed, which receives most of its input from the atmosphere. The generally low frequency of detectable dieldrin suggests a lower application rate.

Summary

Restrictions on insecticide use have resulted in less frequent detection of several chlorinated hydrocarbons in southern Florida surface waters between 1968 and 1972. Occurrence of these insecticides is expected to continue to decrease.

The tendency for insecticides to be adsorbed by particulate matter is well illustrated by the higher frequency of detectable residues in sediment samples than in water samples. The prior widespread application of chlorinated hydrocarbons in southern Florida and the ability of sediment to retain insecticides and residues are indicated by a frequency of occurrence which is higher than that determined in the National Soils Monitoring Program. An extensive canal system transports sediment and adsorbed chlorinated hydrocarbon insecticides from a high application area, the Everglades agri-

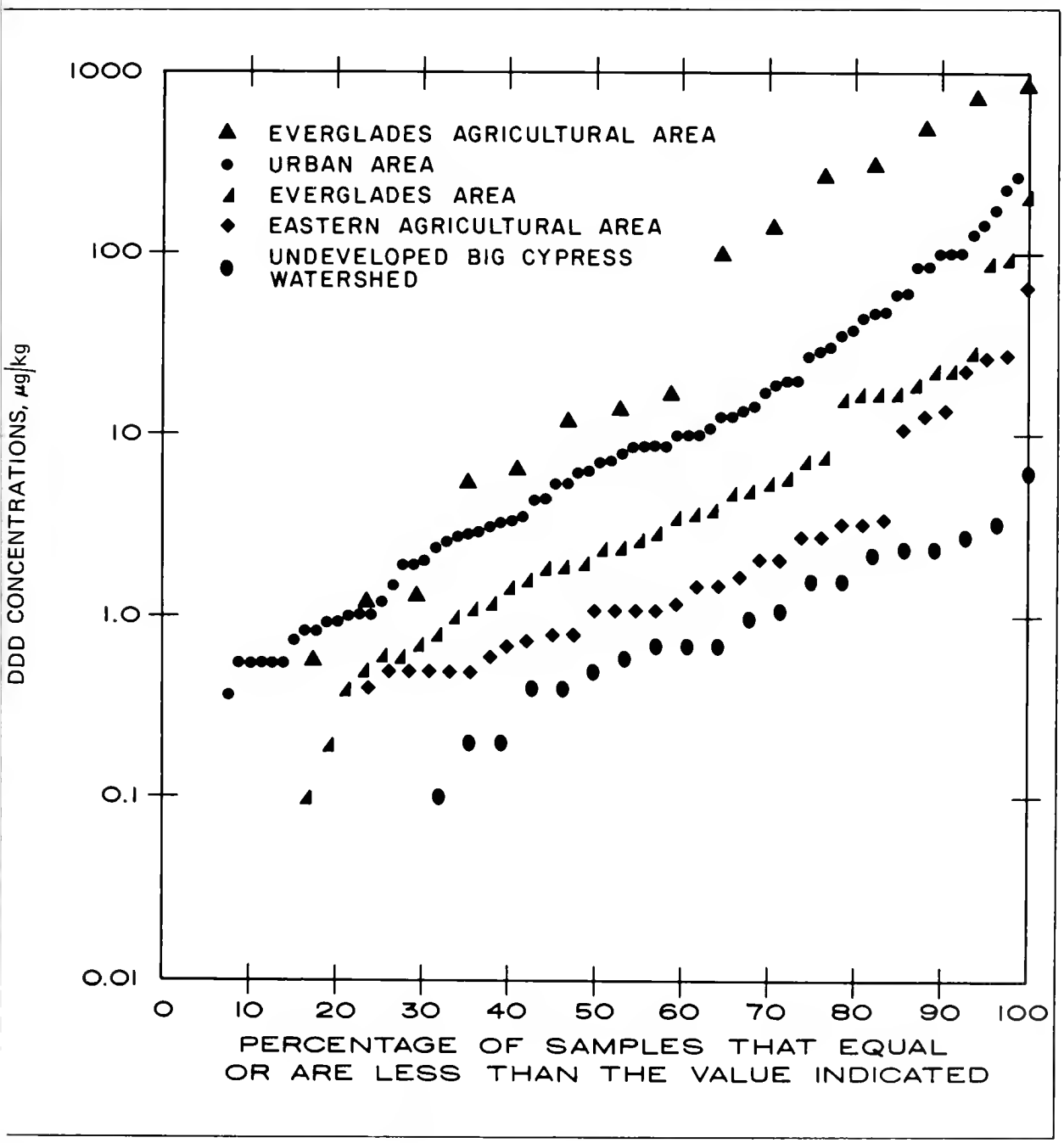

FIGURE 4. *DDD concentrations in sediment, southern Florida—1968-72*

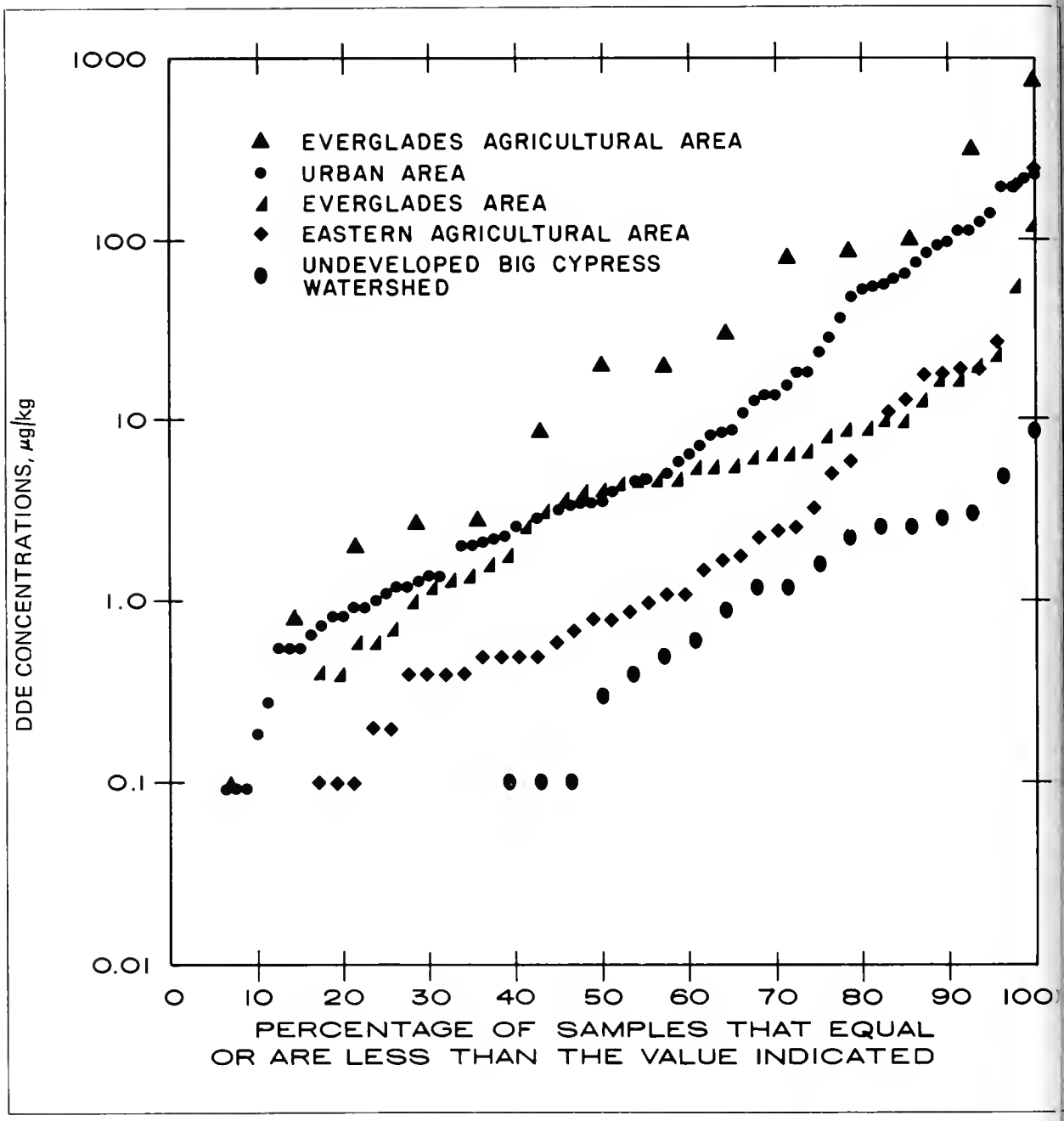

FIGURE 5. *DDE concentrations in sediment, southern Florida—1968-72*

cultural area, into the Everglades. The adjacent undeveloped Big Cypress watershed receives little channelized runoff from agricultural areas and has lower concentrations of DDD, DDE, and dieldrin than do the Everglades.

Concentrations of DDD, DDE, and dieldrin in sediments reflect land use. The complex interplay between proximity to high application areas, canals transporting surface water flow, and the various transport mechanisms indicates that numerous sediment analyses are required to establish the general pattern of insecticide distribution. The variability of concentrations within ar one area indicates a need to sample numerous locatio before establishing rigid reference standards. Maximu concentrations of sediments in natural areas of southe Florida appear to be 6 µg/kg for DDD, 9 µg/kg f DDE, and less than 1 µg/kg for dieldrin.

Acknowledgments

Water and sediment samples were gathered by Ge logical Survey personnel in Miami through cooperati programs with numerous city, county, State, and Fe

ral agencies. Noteworthy are the programs with Bro-ard County, the National Park Service, the U.S. Army Corps of Engineers, and the Central and Southern Florida Flood Control District. Analytical work was done by the Geological Survey Organics Laboratory, Washington, D.C.

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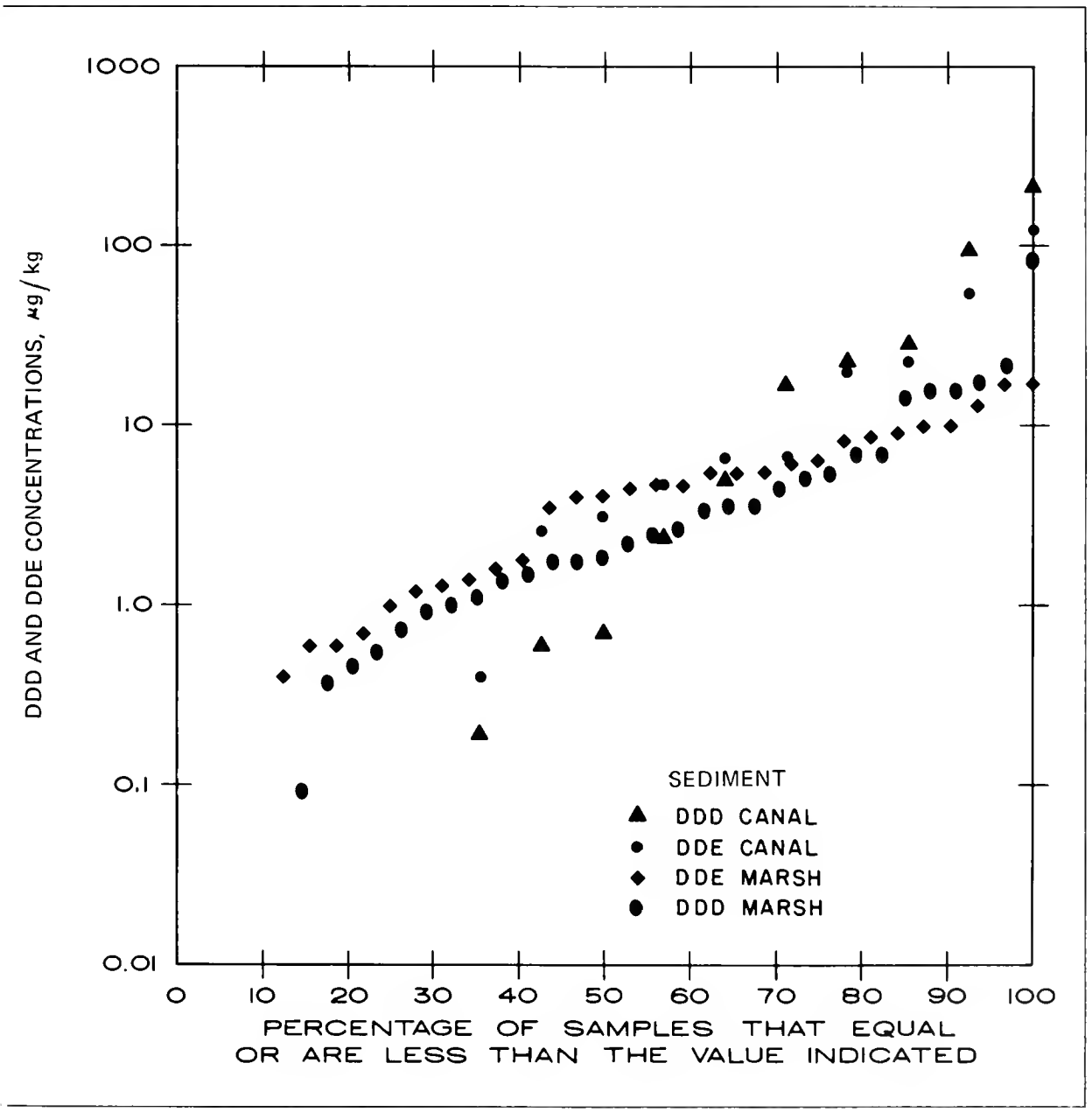

FIGURE 6. *DDD and DDE concentrations in sediment, Everglades marsh and canal—1968-72*

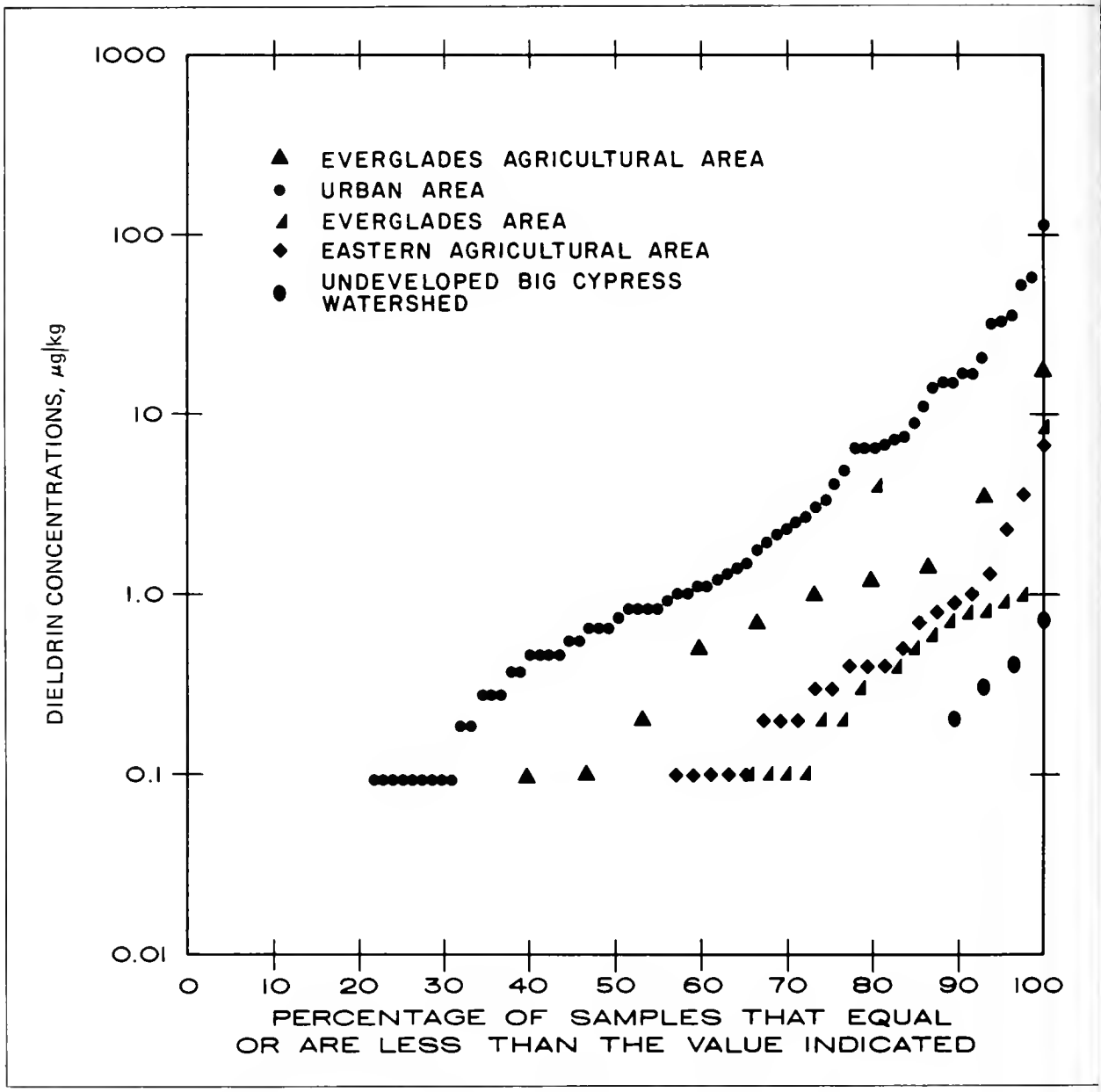

FIGURE 7. *Dieldrin concentrations in sediment, southern Florida—1968-72*

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APPENDIX

Chemical Names of Compounds Discussed in This Issue

LDRIN	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
HLORDANE	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.
DD	See TDE.
DE	Dichlorodiphenyl dichloro-ethylene (degradation product of DDT) Main component (*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
DT	α-Bis (*p*-chlorophenyl) β,β,β-trichloroethane. Numerous isomers in addition to *p,p'*-DDT are possible, and some are present in the commercial product. *o,p'*-DDT [1,1,1-Trichloro-2-(*o*-chlorophenyl)-2-(*p*-chlorophenyl)ethane]
IELDRIN	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
NDRIN	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
CB	Hexachlorobenzene
EPTACHLOR	1,4,5,6,7,8,8-Heptachloro-3a,4,7,7a-tetrahydro-4,7-*endo*-methanoindene
EPTACHLOR EPOXIDE	1,4,5,6,7,8,8-Heptachloro 2,3-epoxy-3a,4,7,7a-tetrahydro-4,7-methanoindane
NDANE	*Gamma* isomer of benzene hexachloride 1,2,3,4,5,6-hexachlorocyclohexane of 99+% purity
CB'S (POLYCHLORINATED BIPHENYLS)	Mixtures of chlorinated biphenyl compounds having various percentages of chloride
DE	2,2-Bis(*p*-chlorophenyl)-1,1-dichloroethane
DXAPHENE	Chlorinated camphene (67-69% chlorine). Product is a mixture of polychlorinated bicyclic terpenes with chlorinated camphenes predominating.

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Martha Finan
Joanne Sanders
Editors

CONTENTS

Volume 9 December 1975 Number 3

RESIDUES IN WATER

Analysis of Various Iowa Waters for Selected Pesticides: Atrazine, DDE, and Dieldrin—1974 [1,2]

John J. Richard, Gregor A. Junk, Michael J. Avery, Nancy L. Nehring, James S. Fritz, and Harry J. Svec

ABSTRACT

Atrazine, DDE, and dieldrin were extracted and concentrated from various surface, subsurface, and finished waters using the macroreticular resin method. Organic components in the concentrates from these waters were separated by gas chromatography; the amounts of the three pesticides in the waters ranged from 0.5 to 42,000 parts per trillion by weight. Every major watershed in the State of Iowa revealed some degree of pesticide contamination and seasonal variations were consistent with agricultural runoff models. Atrazine concentrations were highest of the three pesticides, a symptom of its widespread use in the corn belt. DDE also appeared in substantial quantities, providing further evidence of the persistence of DDT and its metabolites. Water from several shallow wells and finished water from many water treatment plants were also contaminated. Current treatment processes do not effectively remove these pesticides.

Introduction

The present study was undertaken during the 1974 growing season to ascertain the degree and extent of contamination by dissolved pesticides of surface, subsurface, and finished drinking waters in the State of Iowa.

All major watersheds and several smaller ones were included in the survey of surface waters. During periods of heavy runoff, appreciable sediment was present but no attempt was made to measure pesticides sorbed in the suspended particles; thus pesticide content of surface waters quoted here represents only part of the total burden. For the subsurface and finished waters, quoted values accurately reflect the total pesticide burden because sediment was not a factor.

The survey of subsurface waters included both shallow- and deep-well systems within and outside the alluvial plains of contaminated rivers. The survey of finished water covered most of the major cities in the State including those which obtain their raw water from subsurface supplies.

Three pesticides were selected for monitoring: atrazine, DDE, and dieldrin. They are readily separated from interferences using gas chromatography (GC) and were present in amounts sufficient for quantification using electron-capture gas chromatography (EC/GC). These three pesticides were found in most of the water samples.

Atrazine is used in large amounts for weed control in cornfields and has appeared in runoff from small test plots of soil treated with atrazine (*1-7*). Aldrin and DDT have been used extensively in previous years and several investigators have found their metabolites, dieldrin and DDE, in Iowa rivers (*8-11*).

The most convenient method for isolating dissolved organic materials from the water prior to separation, identification, and quantification was by sorption on XAD-2 resin (*12-14*). The resin absorption method has two major advantages over solvent extraction: large sample volumes are possible without elaborate equipment, and the ratio of solvent used to amount of water sampled is very small.

Materials and Methods

Petroleum ether (30°-60°C) and acetonitrile were pesticide quality. Diethyl ether was redistilled. Organic-free water was obtained by passing distilled water through a column containing XAD-2 resin and fresh activated charcoal. Organic-free sodium sulfate was obtained by heating anhydrous sodium sulfate at 400°C in a muffle furnace for 2 hours. The XAD-2 macroreticular resin received from Rohm and Haas in Philadelphia was prepared for column packing by slurrying in methanol and decanting to remove the fines and purifying by sequen-

[1] Supported in part by National Science Foundation Contract GP 33526X.

[2] Ames Laboratory, U.S. Atomic Energy Commission, and the Energy and Mineral Resources Research Institute, Iowa State University, Ames, Iowa 50010.

tial Soxhlet extraction with methanol and acetonitrile (*12*). The purified resin was stored in a glass-stoppered bottle under methanol.

A Beckman GC-5 gas chromatograph equipped with a helium-dicharge EC detector was used for the gas chromatography. A 1.5 percent OV-17/1.95 percent QF-1 column was used for separating and quantifying the biocides. When large amounts of DDE were present, the dieldrin was quantified using a 5 percent OV-210 column.

The pesticide identifications were verified by comparing retention times using a 5 percent OV-210 column and a 10 percent DC-200 column. Additional confirmations were made using a Du Pont 21-490-1 gas chromatograph / mass spectrometer. When interference peaks on the EC gas chromatograms precluded accurate quantification of atrazine, samples were chromatographed on a 5 percent OV-1 column and mass fragmentography was employed to quantify the amount of atrazine present.

GRAB SAMPLES

Grab samples of surface waters were collected in 4-liter amber reagent bottles. No velocity or depth integration was attempted to determine exact pesticide suspension. However, the sampling procedure was duplicated for each surface water supply. The sampling site for the three small streams, Skunk River, Indian Creek, and Fernald Drainage Ditch, was a single transverse position located at the centroid of flow halfway between the surface and the bottom. Water from sites 6, 7, 8, and 9 were analyzed in triplicate from various sampling sites and results varied by less than 1 percent. All other grab samples of surface waters were taken 6 inches below the surface. The collected water samples were allowed to settle overnight before extraction with the XAD-2 resin.

The apparatus used for extracting the pesticides is shown in Figure 1. The settled water sample was decanted into the 5-liter reservoir and passed through the resin by gravity flow at a rate of 25-50 ml/min. When the water level reached the upper glass wool plug sediment from the bottle was transferred to the reservoir using several rinses with organic-free water. After all the water had passed through the resin, the stopcock was closed, the reservoir was removed, and 15 ml diethyl ether was added to the resin. About 5 ml was allowed to flow through the resin and collect in a 60-ml separatory funnel. The stopcock was then closed for 15-30 minutes after which the remaining 10 ml ether was collected in the separatory funnel. This elution procedure was repeated with a second 15-ml portion of ether which was combined with the first. The water layer was drained from the separatory funnel and final traces of water were removed from the eluate by adding 10-15 ml petroleum ether and 2-3 g anhydrous sodium sulfate. The mixture was shaken approximately 30 seconds and the liquid extract was transferred quantitatively to a concentration flask. The extract was concentrated to 1 ml using the micro-distillation procedures described previously (*12*). A 1-5-μl aliquot of the concentrated sample was gas-chromatographed without further treatment.

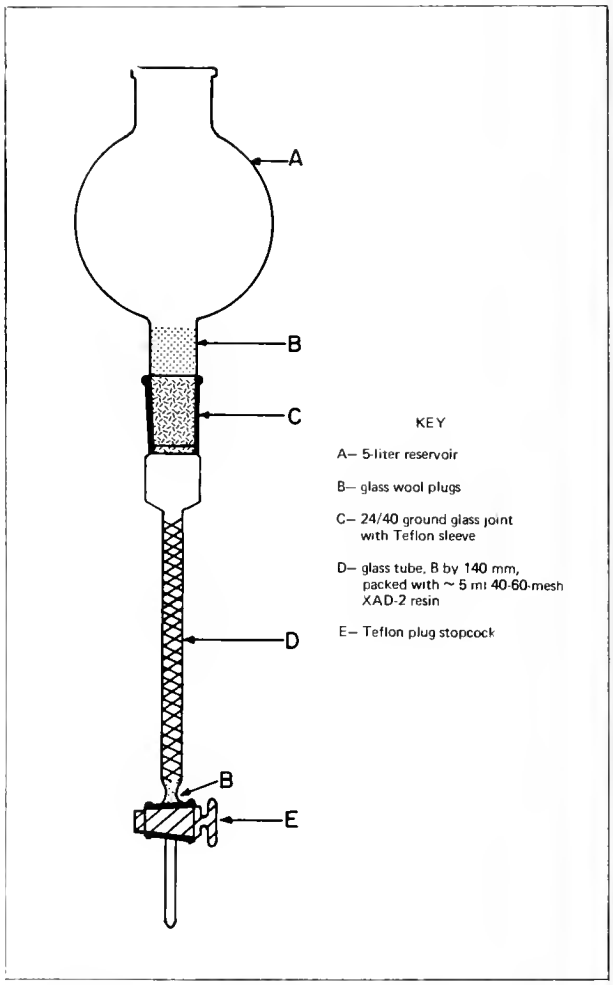

FIGURE 1. *Apparatus for extracting organic solutes from water*

This grab sampling procedure was also used for finished water samples unless low contamination was suspected or found in preliminary assays; in those cases an 8- to 16-liter water sample was used. An earlier study reported recoveries of atrazine, DDE, and dieldrin from water spiked at 20 parts per trillion (ppt) as 83, 81, and 93 percent, respectively, for the XAD-2 resin sorption procedure (*12*). In this study additional tests of the recovery of atrazine at the amounts reported here revealed values between 77 and 84 percent.

COMPOSITE SAMPLES

The composite sampling procedure described below represents the average amount of pesticides present in the water over a 24-hour sampling period. The apparatus used is shown in Figure 2. Sampling was accom-

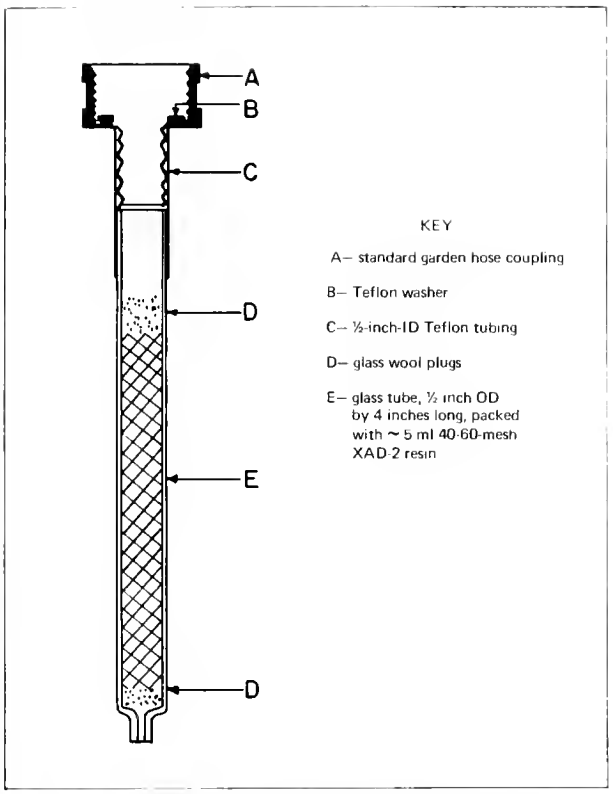

FIGURE 2. *Apparatus for extracting organic solutes from finished drinking water*

plished by attaching the standard garden hose coupling to a water faucet adjusted to deliver a flow of approximately 50 ml/min. After about 70 liters of water had been sampled during the 24-hour period, the XAD-2 column was removed from the coupling. Teflon sleeves were used to attach a reservoir and Teflon plug stopcocks to appropriate ends of the column. The column was then eluted with diethyl ether and the eluate was treated as described above for grab water samples. To insure that the capacity of the resin was not exceeded, tests were made using flows up to 150 ml/min and both longer and shorter sampling periods. All tests produced identical results which agreed with grab sample volumes of 8 liters. Either sampling procedure may be used for surface, subsurface, or finished waters, although grab sampling was used exclusively for all surface waters.

Results and Discussion

Surface water samples were collected from rivers, reservoirs, and tributaries in major watersheds in the State of Iowa (Fig. 3). A small river, a creek, and a drainage ditch near Ames, Iowa, were sampled weekly and after each major rainfall. Des Moines and Raccoon Rivers and Rathbun and Redrock Reservoirs were sampled periodically throughout summer 1974. The Des Moines city finished water was sampled several times throughout spring and summer 1974. Finished waters from each of the other major cities in the State were sampled at least once during 1974. Atrazine had been found previously in many of these finished waters during a 1972 survey.

In general, pesticide contamination existed in all waters which originated from shallow wells in the alluvial plains of contaminated rivers and in all finished waters that originated from either surface waters or shallow wells. Amounts of the three pesticides present in the various waters are presented and discussed in separate sections.

SURFACE WATER

Concentrations of atrazine, DDE, and dieldrin in water collected from the South Skunk River near Ames appear in Table 1. The first general rainfall in the river basin after corn planting in 1974 occurred June 8. That 3-inch rainfall was so intense that significant runoff and erosion occurred in the watershed upstream from the sampling point. Pesticide levels in the South Skunk River during the week immediately following the heavy rainfall correlate with discharge data for the river from the Geological Survey, U.S. Department of Interior.

TABLE 1. *Pesticide concentrations in South Skunk River near Ames, Iowa—1974*

Sampling Date	Residues, ng/l iter		
	Atrazine	DDE	Dieldrin
6/9	12,000	1,820	33
6/11	3,900	475	6
6/16	420	45	3
6/19	2,300	688	36
6/22	2,000	688	76
6/27	1,575	87	10
7/2	540	16	13
7/9	230	10	10
7/16	260	14	6
7/22	250	6	5
7/30	500	62	15
8/8	170	4	4
8/11	300	9	5
8/19	160	5	4
8/25	190	2	4
9/12	250	3	3
9/22	< 100	3	3
10/13	< 100	3	2

NOTE: Samples taken at site No. 1; see map, Figure 3.

Residues decreased with time following the June 8 rainfall. A similar pattern was established previously in studies of much smaller watersheds (*2-4*) and very small test plots (*1, 6*) where factors influencing pesticide loss were more closely controlled. The same pattern of pesticide loss after a single rainfall is evident for Indian Creek data in Table 2 and drainage ditch data in Table 3. However, no discharge data were available for those streams so no exact correlations between runoff and amount of pesticide in the water is possible.

Table 4 gives the concentration of atrazine, DDE, and dieldrin in Des Moines and Raccoon Rivers and Redrock and Rathbun Reservoirs. Values for the various

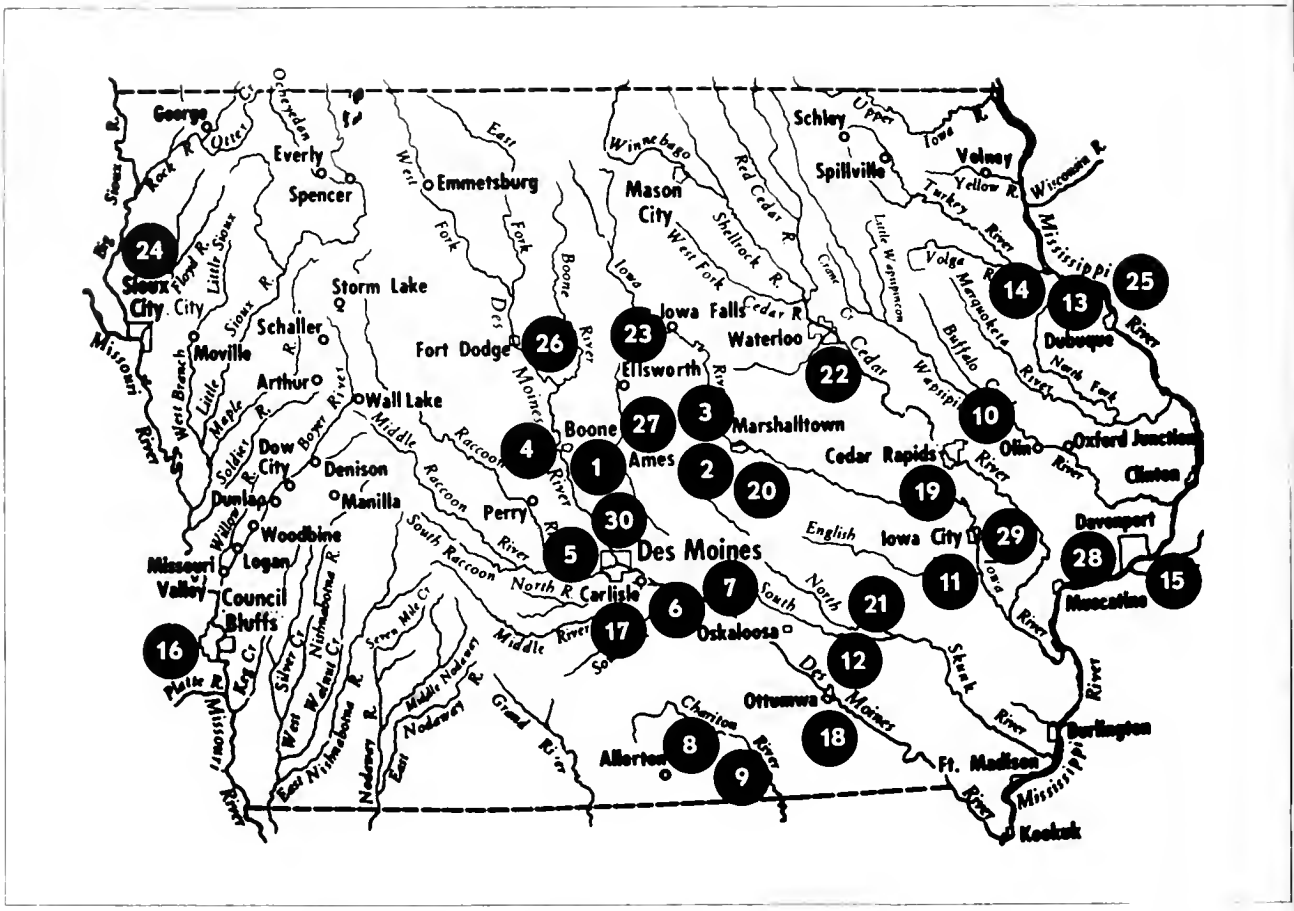

FIGURE 3. *Sites in Iowa watersheds sampled for selected pesticides, 1974*

TABLE 2. *Pesticide concentrations in east branch of Indian Creek near Fernald, Iowa—1974*

Sampling Date	Residues, ng/liter		
	Atrazine	DDE	Dieldrin
6/9	42,000	3,920	25
6/11	3,400	600	7
6/16	870	80	4
6/19	2,000	910	30
6/22	2,400	435	71
6/27	1,075	100	17
7/2	510	6	9
7/9	255	6	8
7/16	210	8	7
7/22	285	4	6
7/30	880	34	24
8/8	163	6	8
8/11	225	5	6
8/19	300	4	4
8/25	300	2	4

NOTE: Samples taken at site No. 2; see map, Figure 3.

TABLE 3. *Pesticide concentrations in drainage ditch near Fernald, Iowa—1974*

Sampling Date	Residues, ng/liter		
	Atrazine	DDE	Dieldrin
6/9	9,000	1,150	20
6/11	1,800	244	10
6/16	440	76	3
6/19	1,500	407	23
6/22	700	200	72
6/27	625	235	8
7/2	190	32	11
7/9	132	10	10
7/16	170	12	9
7/22	250	10	6
7/30	220	20	10
8/8	176	17	4
8/11	353	18	7
8/19	290	19	7
8/25	260	4	8

NOTE: Samples taken at site No. 3; see map, Figure 3.

TABLE 4. *Pesticide concentrations in surface water from Iowa sites sampled on several occasions—1974*

Location	Sampling Site [1]	No. Dates Sampled	Period	Residues, ng/liter [2]		
				Atrazine	DDE	Dieldrin
Des Moines River Boone	4	7	5/21-7/25	211(50-800)	68(1-248)	7(2-14)
Raccoon River Van Meter	5	7	5/30-7/25	814(120-3300)	59(2-250)	7(1-12)
Red Rock Reservoir ~ 10 mi. upstream from dam	6	6	5/19-7/25	813(60-2500)	131(1-373)	11(3-21)
Red Rock Reservoir dam site	7	12	5/21-9/12	921(100-1900)	212(8-350)	18(5-36)
Rathbun Reservoir ~ 10 mi. upstream from dam	8	5	4/21-6/25	4094(207-9400)	420(5-1121)	9(3-22)
Rathbun Reservoir dam site	9	10	4/23-9/22	1285(165-3750)	92(7-325)	3(2-6)

[1] See map, Figure 3.
[2] Figures in parentheses represent ranges.

periods correspond roughly with those in Tables 1-3 in that the concentrations are highest in the spring and decrease gradually during the growing season. This observation agrees with pesticide runoff concepts (*15*) and patterns observed for small watersheds (*3-6*).

Table 5 gives the values obtained for single samples collected at various times from rivers representing other major watersheds of the State; sampling was not coincident with rainfall. These random samples demonstrate the extent of pesticide contamination. That the biocide contamination is not a problem unique to areas adjacent to midwestern agricultural land is attested by results of analyses of water from the Mississippi River at New Orleans (Table 5).

TABLE 5. *Pesticide concentrations in surface water from Iowa and Louisiana sites sampled on one occasion, 1974*

Location	Sampling Site [1]	Sampling Date	Residue, ng/liter		
			Atrazine	DDE	Dieldrin
Cedar River Cedar Rapids, Iowa	10	6/24	6,350	480	42
Iowa River Iowa City, Iowa	11	6/24	3,000	350	22
Skunk River Oskaloosa, Iowa	12	7/29	50	7	1
Mississippi River McGregor, Iowa	13	8/12	100	2	<1
Gremore Lake McGregor, Iowa	14	8/12	190	4	<1
Mississippi River Davenport, Iowa	15	7/30	331	<0.5	<0.5
Mississippi River New Orleans, La.		7/30	1,200	48	7
Missouri River Council Bluffs, Iowa	16	8/15	80	0.5	0.6
Farm Pond southern Iowa	17	7/1	900	20	46
Des Moines River Ottumwa, Iowa	18	7/29	368	74	3

[1] See map, Figure 3.

It is not legitimate to compare amounts of contamination in various watersheds because of numerous variables such as time of sampling, climatic history, soil type, sediment load, and time of pesticide application that influence contamination of a river at any given time (*1, 15*).

FINISHED WATER

The amounts of atrazine, DDE, and dieldrin in finished water samples from cities using wells as their source of raw water are given in Table 6. Water was contaminated

TABLE 6. *Pesticide concentrations in finished waters of Iowa cities which use well systems as raw water source—1974*

Location	Sampling Site [1]	Sampling Date	Residue, ng/liter		
			Atrazine	DDE	Dieldrin
Cedar Rapids [2]	19	7/30	483	28	0
Marshalltown [2]	20	6/24	60	0	0
Oskaloosa [2]	21	7/29	14	<0.5	<0.5
Waterloo [2]	22	8/10	4	<0.5	<0.5
Iowa Falls	23	8/8	<1	<0.5	<0.5
Sioux City	24	8/8	<1	<0.5	<0.5
Dubuque [2]	25	7/4	0	0	0
Fort Dodge	26	8/8	0	<0.5	0
Ames	27	6/19	0	<0.5	0

[1] See map, Figure 3.
[2] Atrazine detected in 1972 survey.

in Cedar Rapids, Marshalltown, Oskaloosa, and Waterloo, cities which use shallow wells in the alluvial plains of the contaminated rivers. Sioux City, Dubuque, Fort Dodge, and Ames use well systems outside the alluvial plain of a contaminated stream; their water showed little or no biocide contamination.

Table 7 gives values obtained for finished waters collected from cities using surface water as their raw water source. Davenport filters Mississippi River water through granular activated carbon in its water purification scheme. The efficiency of activated carbon filtration for removing the pesticide contamination was tested by

TABLE 7. *Pesticide concentrations in finished waters of Iowa cities which use surface waters as raw water source—1974*

Location [1]	Sampling Site [2]	Sampling Date	Residue, ng/liter		
			Atrazine	DDE	Dieldrin
Davenport	28	7/30	405	5	2
Iowa City	29	7/30	200	3	5
Des Moines	30	7/29	29	2	0.4

[1] Atrazine detected in 1972 survey at all three locations.
[2] See map, Figure 3.

monitoring biocides in raw water and in water which had passed through the carbon filter bed. Raw river water contained 331, < 0.5, and < 0.5 ppt atrazine, DDE, and dieldrin, respectively.

Corresponding residues in carbon-filtered water collected the same day were 469, 2, and 1 ppt. This increase in amounts of pesticides after carbon filtration agrees with findings by the U.S. Environmental Protection Agency (EPA) in 1973 (*16*). After monitoring the Davenport activated carbon bed, EPA officials concluded that occasionally the activated carbon treatment may add certain organic chemicals to the water depending upon the history of the activated carbon beds. Experience indicates, however, that odor and taste are removed by activated carbon beds long after they have apparently lost the capacity to remove other organic contaminants.

Des Moines obtains approximately 40 percent of its raw water directly from the Raccoon River and approximately 60 percent from an infiltration gallery that parallels the river for several miles. The amounts of the pesticides in water samples from the Raccoon River, the infiltration gallery, a mixture of the two, and the finished water are given in Table 8. All phases were

TABLE 8. *Pesticide concentrations in Des Moines, Iowa, water supply, raw and finished—1974*

Source [1]	Date	Residues, ng/liter		
		Atrazine	DDE	Dieldrin
Raccoon River	7/29	25	6	2
Infiltration Gallery	7/29	82	5	0.5
Prefilter	7/29	47	4	0.5
Finished Water	7/29	29	2	0.4
Finished Water [2]	8/1	60	2	1
Finished Water [3]	8/1	71	2	2

[1] Sampling sites 5 and 30; see map, Figure 3.
[2] 60-liter composite sample
[3] 16-liter grab sample

sampled the same day and the finished water was sampled again 3 days later. Exact comparisons of finished and raw water are not valid because of uncontrolled mixing which occurs in a large water plant and its distribution system. However, average values over a period of time for finished and raw water should be a valid indicator of the relative purities. For this reason samples of finished water from Des Moines were taken from June 1 to July 25, 1974. Average values for atrazine, DDE, and dieldrin were 515, 21, and 3 ppt, respectively. For approximately the same sampling period, average values of the three biocides in raw water from the Raccoon River were 814, 59, and 7 ppt. These results strongly suggest that current treatment processes do not significantly reduce pesticide contamination.

Conclusions

The pesticides atrazine, DDE, and dieldrin were found in most of the water samples tested. Atrazine concentrations were highest of the three pesticides monitored, which is not surprising; atrazine is used widely on corn, a major product of Iowa, and has relatively high water solubility, 33 ppm. The substantial concentrations of DDE found provide additional evidence of the great persistence of DDT and its metabolites.

Water treatment plants are not removing substantial amounts of pesticides from raw water. Even filtration through activated carbon beds, as employed by one modern treatment plant in this study, is ineffective.

Acknowledgments

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RESIDUES IN FISH, WILDLIFE, AND ESTUARIES

Mirex Residues in Nontarget Organisms after Application of Experimental Baits for Fire Ant Control, Southwest Georgia—1971-72

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ABSTRACT

Mirex, the only compound approved for control of the red imported fire ant (Solenopsis invicta) *and the black imported fire ant* (Solenopsis richteri), *is normally applied at a rate of 1.40 kg/ha. (1.25 lb/acre). Influenced by recent studies showing that low levels of mirex are toxic to certain nontarget organisms, particularly estuarine species, authors report here on a monitoring study of mirex in three large treatment areas of southwest Georgia. Four formulations of bait were applied aerially in 1971-72. Low-level residues were observed in small terrestrial vertebrates and invertebrates and in fresh-water inhabitants. Levels detected were about the same for all baits. Maximum residues were detected 1-3 months after treatment and gradually declined to low levels of 0.02-1.16 ppm 1 year after treatment.*

Introduction

The chlorinated hydrocarbon insecticide mirex is the only compound approved for control of the red imported fire ant, *Solenopsis invicta*, and the black imported fire ant, *S. richteri*. The insecticide, formulated at a concentration of 0.3 percent in a corncob grit/soybean oil bait, is normally applied at a rate of 1.40 kg/ha. (1.25 lb/acre).

Initially, residues were not considered to be a problem because of the very small quantities of mirex used and its low mammalian toxicity (*1*). However, recent laboratory studies have shown that low levels of mirex are toxic to certain nontarget organisms, particularly estuarine species (*2-4*), demonstrating the need for thorough monitoring of mirex residues in nontarget organisms following mirex bait applications. Several studies have been conducted on birds, other large terrestrial vertebrates, and aquatic and estuarine organisms (*5-12*), but very little work has focused on small terrestrial vertebrates and invertebrates or on fresh-water inhabitants.

The present paper reports the results of a monitoring study of mirex in three large treatment areas in southwest Georgia in 1971-72 following applications of a standard bait formulation and of three experimental formulations.

Methods and Procedures

SAMPLE AREAS

Two experimental test sites were selected within each of three larger treatment blocks in Tift, Turner, and Worth Counties in southwest Georgia.

APPLICATION OF MIREX

Baits used in this study were formulated by Allied Chemical Corporation according to the procedures of Banks et al. (*13*). Four formulations of bait (Table 1) were applied in a series of three treatments (Table 2). Baits were dispersed from an altitude of 700 feet by multi-engine commercial aircraft under the supervision of personnel of the Plant Protection Division, Agricul

TABLE 1. *Components of mirex bait applied for fire ant control, Georgia—1971-72*

Formulation	Components of Bait, % log weight			
	Mirex	Soybean Oil	Corncob Grits	Latex Coatin
A	0.3	14.7	85.0	NA
B	0.15	14.85	85.0	NA
C	0.15	18.85	71.0	10.0
D	0.10	18.9	71.0	10.0

NOTE: Treatments A and B represent standard proportions of mirex 0.3 percent and 0.15 percent. Treatments C and D were late coated.

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

Date	County	Formulation: Mirex, %	Area Treated	Bulk Rate [1]
Spring 71	Turner	0.3 (standard)	25,369 ha. (62,640 acres)	1.40 kg/ha. (1.25 lb/acre)
		0.15 (standard)	12,685 ha. (31,390 acres)	1.40 kg/ha. (1.25 lb/acre)
Spring 71	Tift	0.15 (latex coated)	12,150 ha. (30,000 acres)	1.12 kg/ha. (1.0 lb/acre)
		0.10 (latex coated)	14,783 ha. (36,500 acres)	1.12 kg/ha. (1.0 lb/acre)
Fall 71	Worth	0.10 (latex coated)	40,500 ha. (100,000 acres)	1.12 kg/ha. (1.0 lb/acre)
		0.3 (standard)	40,500 ha. (100,000 acres)	1.40 kg/ha. (1.25 lb/acre)

[1] Numbers in parentheses show amount of actual toxicant, i.e., mirex, applied to each hectare.

tural Research Service, U.S. Department of Agriculture (USDA), (now a part of Animal and Plant Health Inspection Service, USDA). All aircraft operated under an electronic guidance system (*14*) and were equipped with auger-fed dispersal systems mounted within the wings of the aircraft.

TREATMENT AND SAMPLING SCHEDULE

Dates of bait application and sample collection were as follows:

Turner County
- Pretreatment samples: May 24-28, 1971
- Baits applied: May 28
- 7-day posttreatment samples: May 31-June 4
- 1-month posttreatment samples: June 21-25
- 3-month posttreatment samples: August 23-26

Tift County
- Pretreatment samples: May 17-21, 1971
- Baits applied: May 25-June 2
- 7-day posttreatment samples: June 14-18
- 1-month posttreatment samples: July 6-9
- 3-month posttreatment samples: September 13-16

Worth County
- Pretreatment samples: September 28-October 5, 1971
- Baits applied: October 5-12
- 1-month posttreatment samples: November 8-12
- 6-month posttreatment samples: April 10-14, 1972
- 1-year posttreatment samples: September 1-8

SAMPLE COLLECTION

Twenty pitfall traps for the collection of invertebrates and small vertebrates (*15*) were placed at sites which had been established randomly in each treatment area. Turner, Tift, and Worth Counties contained 5, 4, and 7 such trap sites, respectively. Hand collections were used to supplement pitfall collections whenever possible. Scientific and common names of species selected appear in Table 3.

Aquatic vertebrates were collected by hand and by seining from farm ponds located in each test area. The areas in Tift County treated with standard 0.15 percent and 0.3 percent baits contained two and one such ponds, respectively; the areas in Turner County treated with latex-coated 0.15 percent and 0.1 percent baits contained four and five collection ponds, respectively. Each of the Worth County test areas contained two collection ponds.

The pretreatment samples from Tift and Turner County and the 7-day posttreatment samples from Turner County were collected in 70 percent isopropanol as described by Markin et al. (*9*). However, authors found that isopropanol leached mirex from trapped specimens and thus distorted the values for mirex residues (*16*); therefore these samples were discarded. Subsequently,

TABLE 3. *Invertebrates and small vertebrates analyzed for mirex residues, Georgia—1971-72*

Scientific Name	Common Name
Insects	
Pictonemobius ambituosus	Ground cricket
Neonemobius near *mormonius*	Ground cricket
Subfamily Neombinae	Immature ground crickets
Gryllus rubens	Southern field cricket
Gryllus firmus	Sand cricket
Gryllus fultoni	Southern wood cricket
Miogryllus verticalis	Stripe-headed cricket
Scapteriscus acletus	Southern mole cricket
Scapteriscus vicinus	Changa
Gryllotalpa hexadactyla	Northern mole cricket
Ceuthophilus spp.	Camel crickets
Parcoblatta spp.	Wood cockroaches
Cariblatta lutea	Small yellow cockroach
Chorisoneura texensis	Small yellow Texas cockroach
Ichnoptera deropeltiformis	Dark wood cockroach
Labidura riparia	Riparian earwig
Euborellia annulipes	Ringlegged earwig
Prosapia bicincta	Twolined spittlebug
Spiders	
Latrodectus mactans	Black widow spider
Isopods	
Armadillidium vulgare	Pillbug
Worms	
	(Mixed unidentified earthworms)
Mammals	
Cryptotis parva	Least shrew
Reptiles	
Cnemidophorus sexlineatus	Sixlined racerunner
Scincella laterale	Brown skink
Eumeces laticeps	Greater fivelined skink
Coluber constrictor priapus	Southern black snake
Natrix sipedon fasciata	Banded water snake
Amphibians	
Rana sphenocephala	Leopard frog
Rana catesbeiana	Bull frog
Gastrophryvne carolinensis	Narrow-mouth toad
Bufo terrestris	Southern toad
Bufo quercicus	Oak toad
Acris gryllus	Cricket frog
Pseudoacris ornata	Ornate chorus frog
Fish	
Gambusia affinis	Mosquito fish
Lepomis macrochirus	Bluegill
Lepomis cyanellus	Green sunfish
Lepomis marginatus	Dollar sunfish
Fundulus lineolatus	Lined topminnow
Notemigonus crysoleucas	Golden shiner
Micropterus salmoides	Largemouth bass

technical crystals of chlorpyrifos were used in small open glass jars as the killing agent for specimens from pitfall traps.

The pitfall traps were checked everyday or every other day during each sampling period. During each collection period the contents of the 20 traps at each site were combined into one glass jar and quick-frozen in the field with dry ice. Aquatic vertebrates were wrapped in aluminum foil and frozen in the same manner. In the laboratory, all samples from a given treatment area and a single collection period were pooled into one composite. The pooled samples were separated by species and delivered to the Pesticide Research Laboratory, University of Florida, for analysis.

Species were selected to represent a cross-sectional sample of the food web. No pitfall or pond samples were collected within a half-mile of the boundaries of the treatment areas, in order to reduce the chance of contamination by other baits or by movement of animals. The limited widths of the treated areas precluded sampling of birds and larger mammals.

Analytical Procedures

EXTRACTION

Samples dried in air to remove surface moisture, condensate, were weighed and then blended in at least 4 ml acetone per gram of sample at high speed for 4 minutes. The extract was filtered through a Buchner funnel, rinsed with fresh solvent, and transferred to a Kuderna-Danish concentrator. The acetone was partly evaporated on a steam bath, and *n*-hexane was added to the concentrator. The evaporation continued until the volume of hexane was reduced substantially. This procedure essentially removed all the acetone. The hexane was then concentrated to a known volume before cleanup.

CLEANUP

The extract, now in hexane, was cleaned by using florisil column chromatography. Three g of 60/100 mesh PR grade florisil was placed in 1-cm-ID glass columns fitted with a fritted glass disk. The florisil was topped with 2-3 cm anhydrous sodium sulfate and placed in a 150°C oven for at least 3 hours. Then the columns were prewashed with 50 ml hexane, and the washings were discarded. The extract, representing up to 1 g of sample, was placed on the column, and the mirex was eluted with 20 ml hexane. The hexane eluate was concentrated to 1.0 ml before gas chromatographic analysis.

QUANTIFICATION

The gas chromatograph used for analysis was a Packard model 7610 equipped with an electron-capture detector. The glass column, 6 ft by ¼ in., was packed with 2 percent OV-101 on 100/120 mesh Gas-Chrom Q and had a nitrogen carrier gas flow rate of 100 cc/min. Injection port, column, and detector temperatures were 215°, 190°, and 208°C, respectively. The method can detect 0.01 ppm mirex in a 1.0-g sample.

Mirex, which had been added to insects and to fat, brain, liver, and muscle of birds at levels of 0.01-1.0 ppm, was recovered at a rate of 90-100 percent. The identity of mirex was confirmed occasionally by determining a p-value.

Results and Discussion

Mirex residues were found in 10 of the 28 species represented by the 49 pretreatment samples taken in Worth County. One year after treatment, residues in six of these same species were equal to or lower than those in pretreatment samples. In the other samples residues were relatively low 1 year after treatment; 62 percent had less than 0.05 ppm mirex and 92 percent had less than 0.5 ppm. Residues in the pretreatment samples probably resulted from treatment of fire ant mounds by landowners, since this area had not received any large-scale treatments. As noted, pretreatment samples from the Turner and Tift County test areas were cross-contaminated by isopropanol collection and were discarded. The pooled findings did not lend themselves to statistical analysis, and none was attempted. The majority of the 248 post-treatment samples, 71.77 percent, contained mirex residues.

As shown in Tables 4-11, maximum levels of mirex were reached 1 month after treatment, though in a few small vertebrates they were noted 3-6 months after treatment. Among the invertebrates, nymphal ground crickets had the highest residues (Table 4). Two specimens of *Pictonemobius ambitiosus* had residues of 13.20 ppm and 10.20 ppm 7 days after treatment and another cricket nymph in the subfamily Nemobinae had residues of 12.87 ppm 3 months after treatment. Residues were generally higher in crickets than in the other arthropods; wood cockroaches had the second-highest residues. Most arthropods analyzed are omnivorous feeders. Crickets and other arthropods were often found in the old mounds after the ants had died; they probably had fed on the dead ants or the remnants of the bait still in the mound.

The *Neonemobius* near *mormonius* (Table 4) and *Gryllus rubens* (Table 5) crickets have at least two generations of young each year in southwest Georgia. Thus the specimens of these two species taken 1 year after treatment almost certainly had not yet hatched at the time of treatment, and the Nemobinae cricket nymph (Table 4) taken 3 months after treatment probably hatched after the bait applications. It seems likely that the residues noted in these cases were acquired by crickets inhabiting the old mounds as previously described.

Labidura riparia has been found to transfer food by trophallaxis to the nymphs (*17*). Such transfer could

TABLE 4. *Mirex residues in crickets of subfamily Nemobinae according to test site, Georgia—1971-72*

County	Month of Application, 1971	Mirex Applied, g/ha.	Residues, ppm					
			Pretreatment	Posttreatment				
				7 Days	1 Mo	3 Mos	6 Mos	1 Yr
Pictonemobius ambitiosus (adult ground crickets)								
Tift	May	1.12	D	0.36 (1)		0.15 (3)		
				1.92 (1)				
				5.40 (1)				
Tift	May	1.68	D	ND (1)	5.73 (1)			
Turner	May-	2.10	D		3.40 (1)	0.15 (10)		
Turner	June	4.20				0.91 (2)		
Worth	October	1.12	1.76 (1)		2.06 (2)			
Worth	October	4.20	ND (4)					ND (1)
Pictonemobius ambitiosus (nymphal ground crickets)								
Tift	May	1.12		13.20 (1)		ND (1)		
Tift	May	1.68		10.20 (1)				
Turner	May-	2.10			1.26 (6)			
Turner	June	4.20			6.08 (5)			
					ND (1)			
Worth	October	1.12	ND (5)		ND (1)		ND (3)	
Worth	October	4.20	ND (4)				0.01 (3)	
Neonemobius near mormonius (adult ground crickets)								
Tift	May	1.12	D			ND (1)		
Tift	May	1.68	D	2.08 (1)	0.59 (2)	2.26 (1)		
				3.11 (1)	1.43 (1)			
					3.90 (2)			
Turner	May-	2.10	D	D	ND (6)	ND (4)		
Turner	June	4.20	D	D				
Worth	October	1.12	ND (5)		1.01 (1)		ND (5)	0.98 (1)
Worth	October	4.20	ND (1)				0.63 (2)	ND (1)
Crickets of subfamily Nemboniae (nymphal ground crickets)								
Tift	May	1.12	D			1.06 (1)		
Tift	May	1.68	D		ND (1)			
Turner	May-	2.10	D	D	ND (1)	ND (4)		
					0.84 (29)	12.87 (1)		
					0.86 (9)			
					1.81 (4)			
Turner	June	4.20	D	D	1.28 (14)	ND (30)		
Worth	October	1.12	ND (7)		1.84 (7)		ND (3)	ND (12)
Worth	October	4.20	ND (45)		ND (5)			ND (3)

NOTE: D = discarded cross-contaminated samples.
ND = no residues detected at 0.01 ppm level.
Figures in parentheses represent number of specimens in pooled sample.

account for the residues of mirex found in samples of earwigs (Table 8) 1 year after treatment. The presence of relatively high residues, 21.50 ppm, in shrews (Table 10) was not surprising, since these mammals are insectivores and would be expected to exhibit some biological concentration of mirex. Authors do not know whether the lower levels noted 3 months and 6 months after treatment are an indication of metabolism and excretion or of population turnover.

The residues found in terrestrial and semiterrestrial reptiles and amphibians (Table 10) probably resulted from biological concentration following consumption of animals that contained lower residues. The highest levels in these organisms were noted in cricket frogs (Table 10); slightly lower levels were found in narrow-mouth toads. Residues in all these animals 1 year after treatment were below 0.5 ppm except in one black snake which had 1.16 ppm mirex.

The semiaquatic and aquatic vertebrates (Table 11) generally contained low levels of residues. The highest levels were detected in mosquito fish (Table 11). The only other aquatic animal that contained more than 0.5 ppm mirex was a single specimen of leopard frog which had 1.08 ppm (Table 11) 3 months after treatment. Residues in all aquatic animals 1 year after treatment were 0.09 ppm or less.

Mirex residues appeared relatively quickly in all levels of the ecosystem studied. However, maximum levels appeared in the various organisms at different intervals after treatment, depending to a large extent on the niche occupied by the organism in the food chain. The levels of mirex detected in the organisms 1 year after treatment were comparable to those found by Baeteke et al. (5) and Collins et al. (7).

All specimens analyzed were taken alive or entered pitfall traps alive, and demonstrated no obvious effects

from mirex residues present. Authors observed no mass mortality of nontarget organisms in the field after treatments nor received reports of such mortality. No substantial differences were noted in the population size of any given species when it was tested before treatment and again 1 year after treatment.

No appreciable differences were noted in the residues in nontarget organisms as a result of applications of the various bait formulations. Indeed, amounts detected in the organisms from the area that received the latex-coated 0.1 percent mirex bait were comparable to those detected in organisms from the area that received the standard 0.3 percent mirex bait. This appears to substantiate the observations of Banks et al. (*13*) that less mirex is bound up in the corncob grits and thus more mirex is available to the ants in the latex-coated baits.

Even though residue levels were comparable, it seems logical to assume that the 75 percent reduction in toxicant load afforded by the 0.1 percent mirex bait must result in less environmental contamination. Since the 0.1 percent mirex bait provides excellent control of the ants (*13*), it should be an environmentally acceptable substitute for the standard mirex formulation.

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TABLE 5. *Mirex residues in crickets of subfamily Gryllinae according to test site, Georgia—1971-72*

County	Month of Application, 1971	Mirex Applied, g/ha.	Residues, ppm					
			Pretreatment	Posttreatment				
				7 Days	1 Mo	3 Mos	6 Mos	1 Yr
Gryllus rubens (adult southern field crickets)								
Tift	May	1.12	D		0.23 (4)			
Tift	May	1.68	D			0.01 (15)		
Turner	May-	2.10	D		0.27 (1)	0.01 (26)		
Turner	June	4.20	D			0.03 (4)		
Worth	October	1.12	0.02 (12)				ND (17)	ND (22)
Worth	October	4.20	ND (8)				0.05 (29)	ND (39)
Gryllus fultoni (adult southern field crickets)								
Tift	May	1.12		1.04 (1)				
Worth	October	1.12	ND (22)					ND (1)
Worth	October	4.20	ND (1)					ND (1)
Gryllus firmus (adult sand crickets)								
Tift	May	1.12				ND (3)		
Tift	May	1.68			0.06 (4)	0.02 (36)		
Turner	May-	2.10	D		0.18 (16)			
Turner	June	4.20	D	D	0.41 (2)			
Worth	October	1.12	ND (15)		0.27 (7)		0.05 (2)	0.04 (10)
Worth	October	4.20	ND (32)				ND (1)	0.03 (21)
Miogryllus verticalis (stripe-headed crickets)								
Worth	October	1.12						ND (2) (adults) ND (8) (nymphs)
Worth	October	4.20						ND (6) (nymphs)

NOTE: D = discarded cross-contaminated samples.
ND = no residues detected at 0.01 ppm level.
Figures in parentheses represent number of specimens in pooled sample

TABLE 6. *Mirex residues in mole crickets according to test site, Georgia—1971-72*

County	Month of Application, 1971	Mirex Applied, g/ha.	Residues, ppm					
			Pretreatment	Posttreatment				
				7 Days	1 Mo	3 Mos	6 Mos	1 Yr
Scapteriscus acletus (adult and nymphal southern mole crickets)								
Tift	May	1.68	D			0.18 (4)		
Turner	May-	2.10	D	D	0.53 (19)	0.04 (6)		
Turner	June	4.20	D	D		0.08 (4)		
Worth	October	1.12	0.10 (13)		0.91 (2)		0.23 (2)	
Worth	October	4.20	ND (32)		ND (3)		0.14 (9)	0.09 (8)
Scapteriscus vicinus (adult and nymphal changas)								
Tift	May	1.68	D		0.05 (1) 1.15 (2)	0.58 (1)		
Turner	May-	2.10	D	D		0.14 (1) 0.34 (2)		
Turner	June	4.20				ND (3)		
Worth	October	4.20	ND (1)				0.06 (9)	ND (2)
Gryllotalpa hexadactyla (adult northern mole crickets)								
Worth	October	1.12	0.10 (6)					0.13 (3)
Worth	October	4.20	ND (1)					ND (1)

NOTE: D = discarded cross-contaminated samples.
ND = no residues detected at 0.01 ppm level.
Figures in parentheses represent number of specimens in pooled sample.

TABLE 7. *Mirex residues in cockroaches according to test site, Georgia—1971-72*

County	Month of Application, 1971	Mirex Applied, g/ha.	Residues, ppm					
			Pretreatment	Posttreatment				
				7 Days	1 Mo	3 Mos	6 Mos	1 Yr
Parcoblatta spp. (adult and nymphal wood cockroaches)								
Tift	May	1.12	D	3.98 (1)	0.78 (8)	ND (1)		
Tift	May	1.68	D	1.50 (2)	3.74 (7)	0.12 (2)		
					6.18 (2)			
Turner	May-June	4.20		D		1.41 (2)		
Worth	October	1.12	ND (3)		4.39 (2)		0.19 (6)	ND (2)
Worth	October	4.20	ND (3)				0.22 (1)	ND (2)
							0.60 (5)	
Cariblatta lutea (adult small yellow cockroaches)								
Tift	May	1.12	D		ND (1)			
Worth	October	4.20					ND (3)	
Chorisoneura texensis (adult small yellow Texas cockroaches)								
Tift	May	1.68			ND (1)			
Ichnoptera deropeltiformis (adult dark wood cockroaches)								
Worth	October	4.20					0.18 (1)	

NOTE: D = discarded cross-contaminated samples.
ND = no residues detected at 0.01 ppm level.
Figures in parentheses represent number of specimens in pooled sample.

TABLE 8. *Mirex residues in earwigs according to test site, Georgia—1971-72*

County	Month of Application, 1971	Mirex Applied, g/ha.	Residues, ppm					
			Pretreatment	Posttreatment				
				7 Days	1 Mo	3 Mos	6 Mos	1 Yr
Labidura riparia (adult and nymphal riparian earwigs)								
Tift	May	1.12				0.19 (29)		
Tift	May	1.68				0.11 (4)		
Turner	May-	2.10	D			ND (1)		
						0.23 (8)		
Turner	June	4.20	D		0.63 (3)	0.08 (11)		
Worth	October	1.12	0.02 (48)		ND (1)			0.03 (33)
Worth	October	4.20	ND (214)		ND (4)		0.85 (4)	0.04 (168)
Euborellia annulipes (adult and nymphal ringlegged earwigs)								
Tift	May	1.12	D		0.43 (15)	0.14 (7)		
Tift	May	1.68	D		2.25 (1)	0.06 (49)		
Turner	May-	2.10	D	D		ND (27)		
Turner	June	4.20	D	D		ND (1)		
						0.37 (2)		
						0.61 (4)		
Worth	October	1.12	0.06 (93)				0.13 (12)	ND (18)
Worth	October	4.20	ND (11)		0.51 (3)		ND (3)	0.04 (27)

NOTE: D = discarded cross-contaminated samples.
ND = no residues detected at 0.01 ppm level.
Figures in parentheses represent number of specimens in pooled sample.

TABLE 9. *Mirex residues in miscellaneous invertebrates according to test site, Georgia—1971-72*

County	Month of Application, 1971	Mirex Applied, g/ha	Residues, ppm					
			Pretreatment	Posttreatment				
				7 Days	1 Mo	3 Mos	6 Mos	1 Yr
Ceuthophilus spp (nymphal camel crickets)								
Tift	May	1.68	D	1.75 (1)	3.60 (1)			
Turner	May-	2.10	D	D	0.40 (1)			
Turner	June	4.20	D	D	0.66 (1)			
					2.88 (2)			
Worth	October	1.12	ND (17)				0.12 (21)	ND (3)
Worth	October	4.20	ND (3)				0.01 (7)	ND (2)
Prosapia bicincta (adult two-lined spittle bugs)								
Tift	May	1.12			ND (22)	ND (7)		
Turner	May-June	4.20				3.23 (1)		
Worth	October	1.12	ND (8)		ND (1)			
Worth	October	4.20	ND (25)		0.58 (1)			
Armadillidium vulgare (adult and immature pillbugs)								
Tift	May	1.12	D		0.04 (16)	0.01 (10)		
Tift	May	1.68	D		0.03 (10)	0.02 (5)		
Turner	May-June	2.10		D	ND (1)	ND (1)		
Worth	October	1.12	ND (1)					
Earthworms								
Tift	May	1.12		0.02 (10)	0.49 (20)	0.04 (25)		
Tift	May	1.68			ND (26)	0.03 (10)		
Turner	May-	2.10	D		0.10 (20)			
Turner	June	4.20		D		0.49 (10)		
Worth	October	1.12	ND (50)		ND (1)		0.02 (10)	ND (18)
Worth	October	4.20	ND (1)		ND (1)		0.03 (10)	
Latrodectus mactans (black widow spider)								
Worth	October	1.12						0.28 (3)

NOTE: D = discarded cross-contaminated samples.
ND = no residues detected at 0.01 ppm level.
Figures in parentheses represent number of specimens in pooled sample.

TABLE 10. *Mirex residues in terrestrial and semiterrestrial vertebrates according to test site, Georgia—1971-72*

County	Month of Application, 1971	Mirex Applied, g/ha.	Residues, ppm					
			Pretreatment	Posttreatment				
				7 Days	1 Mo	3 Mos	6 Mos	1 Yr
Cryptotis parva (least shrews)								
Tift	May	1.12			21.50 (1)			
Tift	May	1.68	D			5.16 (1)		
Worth	October	1.12	ND (1)					
Worth	October	4.20	ND (2)				1.15 (1)	
							0.78 (1)	
Cnemidophorus sexlineatus (6-lined racerunners)								
Turner	May-	2.10	D	D		0.93 (1)		
Turner	June	4.20		D	0.63 (1)	0.07 (1)		
Worth	October	1.12	ND (1)					
Worth	October	4.20	ND (1)					0.40 (1)
Scincella laterale (brown skinks)								
Tift	May	1.12	D			0.34 (1)		
Worth	October	1.12	ND (2)				0.22 (4)	ND (1)
Worth	October	4.20	ND (3)				0.66 (1)	
Eumeces laticeps (greater 5-lined skink)								
Worth	October	1.12					ND (1)	
Coluber constrictor (black snake)								
Worth	October	1.12						1.16 (1)
Natris sipedon fasciata (banded water snake)								
Turner	May-June	4.20		D	0.04 (1)			
Bufo terrestris (southern toads)								
Turner	May-June	2.10	D	D	0.94 (5)			
Turner	May-June	4.20	D		0.10 (1)	0.39 (1)		
Worth	October	1.12	ND (3)		0.24 (5)		0.02 (2)	
Worth	October	4.20					ND (1)	
Gastrophryne carolinensis (narrow-mouth toads)								
Tift	May	1.12	D			0.47 (2)		
Tift	May	1.68	D			3.46 (3)		
Turner	May-	2.10	D	D	2.02 (9)	0.41 (14)		
Turner	June	4.20			0.33 (1)	1.06 (2)		
Worth	Octoher	1.12	ND (16)					0.17 (4)
Worth	October	4.20	0.12 (5)					0.04 (1)
Pseudoacris ornata (ornate chorus frog)								
Worth	October	1.12					0.10 (1)	
Acris gryllus (cricket frogs)								
Worth	October	1.12			9.27 (2)		0.14 (3)	
Worth	October	4.20			3.01 (9)			
Bufo quercicus (oak toads)								
Worth	Octoher	1.12						ND (5)
Worth	Octoher	4.70						0.08 (2)

NOTE: D = discarded cross-contaminated samples.
ND = no residues detected at 0.01 ppm level.
Figures in parentheses represent number of specimens in pooled sample.

TABLE 11. *Mirex residues in semiaquatic and aquatic vertebrates according to test site, Georgia—1971-72*

County	Month of Application, 1971	Mirex Applied, g/ha.	Residues, ppm					
			Pretreatment	Posttreatment				
				7 Days	1 Mo	3 Mos	6 Mos	1 Yr
Rana sphenocephala (leopard frogs)								
Tift	May	1.68				0.08 (1)		
Turner	May-	2.10		D		1.08 (1)		
Turner	June	4.20			0.24 (1)			
Worth	October	1.12				0.56 (1)		
Worth	October	4.20	ND (1)		0.34 (1)			
Rana catesbeiana (bullfrogs)								
Tift	May	1.12			0.05 (1)			
Tift	May	1.68				0.15 (4)		
Turner	May-June	2.10	D		0.43 (1)			
Worth	October	1.12	ND (4)		0.08 (12)			0.03 (6)
Worth	October	4.20			0.25 (3)			0.09 (1)
Gambusia affinis (mosquito fish)								
Tift	May	1.12	D		ND (10)	0.11 (18)		
Tift	May	1.68	D		0.06 (25)	ND (150)		
Turner	May-	2.10	D		0.02 (20)			
					0.08 (25)			
Turner	June	4.20	D		0.08 (20)	0.24 (24)		
Worth	October	1.12	ND (25)		0.25 (3)		2.93 (125)	ND (1)
Worth	October	4.20	0.15 (15)		2.25 (10)		1.75 (105)	ND (6)
								0.03 (30)
Lepomis macrochirus (bluegills)								
Tift	May	1.12	D		ND (69)			
					0.23 (10)			
Tift	May	1.68	D			ND (12)		
Turner	May-June	2.10	D		ND (5)			
Worth	October	1.12					ND (14)	0.05 (4)
Worth	October	4.20	0.03 (7)				0.02 (16)	ND (1)
								0.03 (2)
								0.03 (5)
Fundulus lineolatus (lined topminnows)								
Tift	May	1.12	D		0.05 (9)			
Tift	May	1.68				0.04 (10)		
Turner	May-	2.10			0.21 (5)			
					0.17 (10)			
Turner	June	4.20	D		0.03 (2)			
Worth	October	4.20	0.03 (2)					
Lepomis cyanellus (green sunfish)								
Tift	May	1.12			0.05 (1)			
Worth	October	4.20			0.05 (1)			
Lepomis marginatus (dollar sunfish)								
Turner	May-June	4.20			0.15 (6)			
Notemigonus crysoleucas (golden shiners)								
Worth	October	1.12	ND (7)				0.09 (11)	0.02 (21)
Worth	October	4.20	ND (1)				ND (8)	
Micropterus salmoides								
Worth	October	4.20						ND (5)

NOTE: D = discarded cross-contaminated sample.
ND = no residues detected at 0.01 ppm level.
Figures in parentheses represent number of specimens in pooled sample.

GENERAL

Chlorinated Hydrocarbon Residues in Fish, Crabs, and Shellfish of the Lower Fraser River, Its Estuary, and Selected Locations in Georgia Strait, British Columbia—1972-73

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ABSTRACT

Between August 1972 and September 1973, fish, crabs, and shellfish were collected from the lower Fraser River, its estuary, and selected areas of Georgia Strait in British Columbia. Samples were analyzed for aldrin, dieldrin, α- and γ-chlordane, p,p'-*DDT,* p,p'-*DDE,* p,p'-*DDD, heptachlor, heptachlor epoxide, lindane, and polychlorinated biphenyls (PCB's). Of these,* p,p'-*DDT,* p,p'-*DDE,* p,p'-*DDD, heptachlor epoxide, and one PCB, Aroclor 1254, were detected in samples of many fish, crabs, and shellfish from the lower Fraser River and its estuary. Generally, compounds found in decreasing order of magnitude in samples from the Fraser River and its estuary were: PCB's,* p,p'-*DDE, heptachlor epoxide,* p,p'-*DDT, and* p,p'-*DDD. Greatest concentrations of these compounds occurred in biota from the waters adjacent to the City of Vancouver. With one exception, animals from Georgia Strait and those away from the immediate influence of Fraser River water contained no detectable levels of chlorinated hydrocarbons.*

Introduction

Numerous investigators have found chlorinated hydrocarbon insecticides and their metabolites as well as polychlorinated biphenyls (PCB's) in a variety of aquatic organisms including freshwater and marine fish (*1, 2*), birds (*3, 4*), plankton (*4, 5*), mammals (*4, 6*), and various invertebrates (*7, 8*). Some of these studies have shown that biological matter concentrates chlorinated hydrocarbon residues from the aquatic milieu and magnifies them through the various trophic levels (*4-6*).

The presence and persistence of chlorinated hydrocarbons in various river systems, including their watersheds and estuaries, of the United States (*1, 2, 7*), and to a lesser extent Europe (*9, 10*), have also been demonstrated. However, except for several studies of Ontario Rivers (*11, 12*), such data are generally lacking for many of the watersheds, rivers, and estuaries of Canada, particularly rivers which drain relatively uninhabited areas. Such a river system is the Fraser, which originates in the Rocky Mountains and flows for much of its length through forested or range land. However, this river passes through areas of intense agricultural and industrial use as well as human habitation immediately before terminating in Georgia Strait (Fig. 1). This estuary is adjacent to greater Vancouver, a metropolitan area of approximately one million inhabitants, and receives most of that city's domestic and industrial effluents.

Thus, by studying this river system, one may determine chlorinated hydrocarbon residue levels in water, sediment, and biota in areas adjacent to low habitation, intensive agricultural production, and an urban population. Such data are essential for evaluating the significance of chlorinated hydrocarbons to the aquatic flora and fauna and are relevant in determining the suitability of this water for various uses.

Methods and Materials

Fish were taken from the Fraser River with gill nets and seines and from Georgia Strait with bottom trawls. Most river fish were captured in gill nets set during the day near the river margin at each station (Fig. 1), although some were taken in seine hauls made near the same location. Within a few hours of capture, all fish were frozen.

After a specimen selected for analysis was thawed, measured, and weighed, its dorsolateral surface was scraped clean to remove any debris or slime. Then an area of epaxial white muscle tissue was exposed with a new scalpel which was cleaned with acetone. A block

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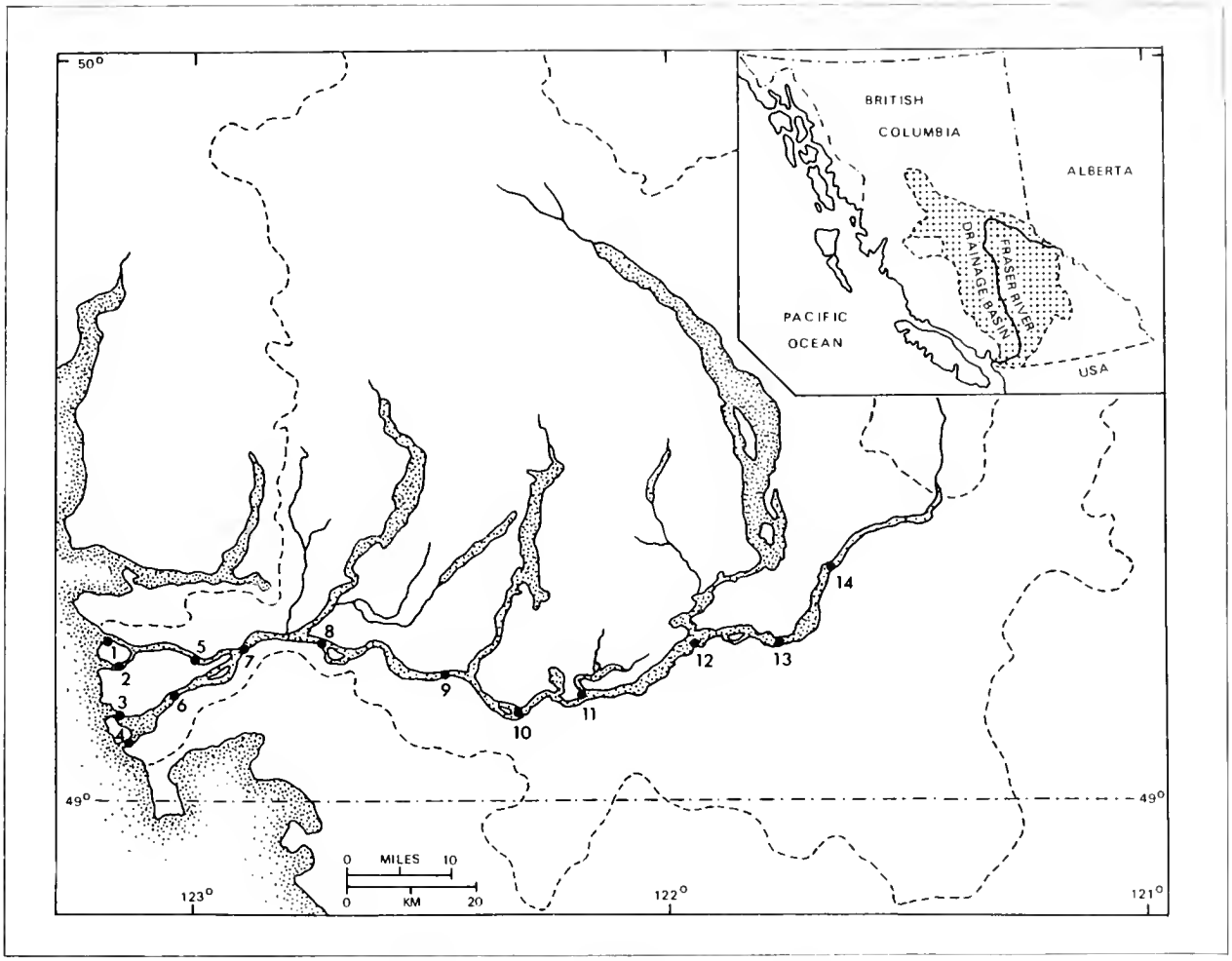

FIGURE 1. *Fraser River with sampling stations*

of approximately 25 g tissue was removed, placed in an externally labeled glass jar, and refrozen. Other animals, including shellfish and crabs, were obtained by scuba divers. Tissue samples were placed into glass jars and frozen. In some cases, entire animals were frozen for future analysis (Table 1). All glass containers were cleaned with redistilled hexane and acetone, then heated to 135°C for 12 hours prior to use.

Tissues were extracted with 50 ml of a 1:1 v/v hexane: acetone mixture for every 25 g sample tissue in a Lourdes homogenizer for 30 minutes. After 15 minutes, 25 g anhydrous Na_2SO_4 was added. Each extract was then filtered through glass wool into a 250-ml separatory funnel and washed twice with 50 ml of an aqueous solution of 2 percent Na_2SO_4.

Aliquots of each extract equivalent to 1 g tissue were then cleaned by a combination of sweep codistillation and column chromatography as described in detail for human adipose tissue extracts by Oloffs et al. (*13*). Finally, PCB's were separated from the other organochlorines according to the method of Armour and Burke (*14*).

The clean extracts were picked up with 2 ml hexane for every 1 g tissue extracted. Gas-liquid chromatographic (GLC) analyses were performed with a Tracor MT 220 and a Tracor 550 equipped with two and one ^{63}Ni electron-capture detectors, respectively. A 183-cm-by-0.64-cm column packed with 2 percent OV-1 and 6 percent OV-210 in 80/100 mesh chromosorb W HP was used. Nitrogen, the carrier gas, had a flow rate of 80 ml/min. The temperatures of the injector, column oven, and detector were 220°, 190°, and 300°C, respectively.

Standard curves were prepared daily before and after sample analyses with reference-grade chemicals in hexane. Residues were quantified to the following concentrations: heptachlor epoxide, 2 ppb; dieldrin, DDD, and DDE, 4 ppb; and DDT, 10 ppb. Aroclor 1254, the only PCB found in these samples, was quantified to 20 ppb standard Aroclor 1254 on the basis of four selected peaks as described and critically discussed by Iwata et al. (*15*).

If an injection of 8 μl of the 2 ml hexane : 1 g tissue extract gave a response for one of the compounds which

TABLE 1. *Chlorinated hydrocarbon concentrations in muscle tissue of fish, Fraser River, British Columbia—1972-73*

Station No.	Species [1]	Fork Length, mm		Heptachlor Epoxide					DDE					PCB's [5]				No. Samples
		Mean	Range	Mean, ppb	Range, ppb	N [2]	N [3]	N [4]	Mean, ppb	Range, ppb	N [2]	N [3]	N [4]	Mean, ppb	Range, ppb	N [2]	N [3]	N [4]	
14	SQUAW	337.5	262-440	ND		0	0	17	56.2	T -164.3	16	1	0	32.7	ND- 234.7	5	5	7	17
14	LSS [6]	389.1	346-453	4.1	ND-26.5	5	0	11	10.7	ND- 55.3	8	1	7	138.0	ND- 589.7	9	0	7	16
14	RT	279.0	256-302	ND		0	0	2	5.9	ND- 11.7	1	0	1	37.2	T - 72.4	1	1	0	2
14	CTT	308		ND		0	0	1	ND		0	0	1	T		0	1	0	1
14	MW	275.3	245-297	ND		0	0	4	56.3	7.0-100.3	4	0	0	ND		0	0	4	4
14	CHUB	255.5	254-257	ND		0	0	2	106.0	57.5-154.4	2	0	0	ND		0	0	2	2
14	ST	434.0	363-475	ND		0	0	4	37.6	31.9- 40.0	4	0	0	41.7	ND- 164.7	1	1	2	4
13	SQUAW	301.0	264-359	1.7	ND-5.0	1	0	2	9.9	T - 17.6	2	1	0	204.2	ND- 526.7	2	0	1	3
13	LSS	335		ND		0	0	1	9.6		1	0	0	349.8		1	0	0	1
13	BBH	246		ND		0	0	1	3.5		1	0	0	235.3		1	0	0	1
13	CARP	492		ND		0	0	1	53.5		1	0	0	ND		0	0	1	1
13	RT [7]	316.5	245-394	ND		0	0	8	20.3	ND- 48.8	6	0	2	58.9	ND- 229.2	3	4	1	8
13	CHUB	260.3	242-277	ND		0	0	3	44.4	26.7- 62.8	3	0	0	ND		0	0	3	3
12	SQUAW	286.3	261-355	ND		0	0	6	48.2	ND-144.7	5	0	1	0.3	ND-T	0	1	5	6
12	LSS	320		ND		0	0	1	ND		0	0	1	ND		0	0	1	1
12	MW	258.5	252-265	ND		0	0	2	28.9	27.5- 30.3	2	0	0	ND		0	0	2	2
12	CHUB	258		ND		0	0	1	49.6		1	0	0	ND		0	0	1	1
12	ST	400.7	356-464	ND		0	0	3	18.1	15.0- 22.9	3	0	0	1.3	ND-T	0	2	1	3
11	LSS	330		ND		0	0	1	ND		0	0	1	ND		0	0	1	1
11	SQUAW	325.0	286-364	ND		0	0	2	37.2	4.9- 59.4	2	0	0	ND		0	0	2	2
11	RT	356.5	276-442	ND		0	0	4	32.1	6.9- 59.5	4	0	0	0.5	ND-T	0	1	3	4
11	CTT	311		ND		0	0	1	14.4		1	0	0	ND		0	0	1	1
11	MW	253		ND		0	0	1	20.3		1	0	0	ND		0	0	1	1
11	CHUB	257.5	249-266	ND		0	0	2	32.1	22.1- 42.1	2	0	0	ND		0	0	2	2
10	SQUAW	320.5	313-328	ND		0	0	2	36.4	11.5- 61.3	2	0	0	83.8	ND- 167.5	1	0	1	2
10	RT [8]	293.3	253-418	2.3	ND-10.7	3	0	9	7.3	ND- 29.4	8	2	2	61.7	ND- 106.2	9	0	3	12
10	ST	438		ND		0	0	1	ND		0	0	1	ND		0	0	1	1
10	LSS	317.5	275-360	4.6	ND- 9.1	1	0	1	7.5	ND- 14.9	1	0	1	147	ND- 294.0	1	0	1	2
10	DV	337		ND		0	0	1	19.5		0	0	1	164.3		1	0	0	1
9	RT	283.3	275-288	ND		0	0	3	8.9	ND- 14.5	2	0	1	ND		0	0	3	3
9	LSS	368		ND		0	0	1	ND		0	0	1	3694.9		1	0	0	1
9	CHUB	263		ND		0	0	1	37.3		1	0	0	ND		0	0	1	1
8	MW	192		ND		0	0	1	T		0	1	0	ND		0	0	1	1
8	ST	355		ND		0	0	1	21.8		1	0	0	ND		0	0	1	1
8	LSS	364		ND		0	0	1	ND		0	0	1	623.4		1	0	0	1
8	SQUAW	288		ND		0	0	1	329.3		1	0	0	ND		0	0	1	1
8	CHUB	233		ND		0	0	1	34.7		1	0	0	ND		0	0	1	1
7	ST	455		ND		0	0	1	10.6		1	0	0	ND		0	0	1	1
7	CHUB	247		ND		0	0	1	33.4		1	0	0	ND		0	0	1	1
7	RT [9]	344.4	273-400	12.4	ND-44.9	3	0	2	34.9	ND- 50.1	4	0	1	143.2	58.2- 192.8	5	0	0	5
7	CTT [10]	423.7	319-565	4.7	ND-13.7	2	0	2	19.8	ND- 43.5	3	0	1	128.2	77.1- 208.5	4	0	0	4
6	LSS	308.7	302-314	ND		0	0	3	ND		0	0	3	171.2	ND- 259.4	2	0	1	3
6	SQUAW [7]	279.8	183-340	ND		0	0	5	85.0	8.8-151.7	5	0	0	748.4	204.1-1894.4	5	0	0	5
6	ST	413.0	390-436	ND		0	0	2	11.8	ND- 23.5	1	0	1	143.4	ND- 286.7	1	0	1	2
5	LSS	417.8	374-453	ND		0	0	4	7.2	T - 16.9	3	1	0	90.6	T - 198.7	2	1	1	4
5	DV	422		ND		0	0	1	17.5		1	0	0	ND		0	0	1	1
5	ST	438.5	419-458	4.2	ND- 8.3	1	0	1	22.9	3.4- 42.3	2	0	0	167.4	136.9- 197.8	2	0	0	2
5	RT [11]	282.5	282-283	3.3	ND- 6.5	1	0	1	7.4	6.8- 8.0	2	0	0	128.9	64.8- 192.9	2	0	0	2
5	SQUAW [12]	351.5	344-359	4.3	ND- 8.6	1	0	1	238.3	39.5-437.1	2	0	0	1039.8	426.7-1652.9	2	0	0	2
5	CARP [13]	557		ND		0	0	1	1739.6		1	0	0	933.9		1	0	0	1
4	RT	283		ND		0	0	1	20.0		1	0	0	138.8		1	0	0	1
4	SQUAW	217.8	153-367	ND		0	0	4	36.4	3.8- 99.9	4	0	0	121.8	ND- 483.2	1	2	1	4
3	SOCK-EYE	595.8	561-633	ND		0	0	5	ND		0	0	5	ND		0	0	5	5
3	CTT [13]	362.5	344-381	4.5	ND- 9.0	1	0	1	25.3	21.1- 29.4	2	0	0	118.6	101.7- 135.4	2	0	0	2
3	CHUB	225.3	211-253	ND		0	0	3	43.4	T - 69.9	2	1	0	90.8	ND- 272.4	1	0	2	3
3	CHI-NOOK	394.5	389-400	2.2	ND- 4.3	1	0	1	12.3	9.0- 15.5	2	0	0	86.8	83.5- 90.1	2	0	0	2
3	SQUAW	359.5	325-394	47.0	7.4-86.6	2	0	0	73.3	51.4- 95.2	2	0	0	755.4	607.6- 903.2	2	0	0	2
3	LSS	331.7	302-370	ND		0	0	3	12.2	ND- 36.5	1	0	2	153.9	ND- 250.6	2	0	1	3
3	ST [14]	510.9	391-635	3.9	ND- 7.1	3	0	6	14.9	ND- 47.4	7	0	2	165.4	ND- 317.7	7	0	2	9
2	RT	303.0	267-345	4.2	ND-12.6	1	0	2	34.5	T - 54.9	2	1	0	116.5	T - 314.1	2	1	0	3
1	CHUB	237		ND		0	0	1	85.9		1	0	0	527.3		1	0	0	1

NOTE: ND = not detectable; T = trace.

[1] SQUAW = northern squawfish; LSS = large scale sucker; RT = rainbow trout; CTT = cutthroat trout; MW = mountain whitefish; CHUB = peamouth chub; ST = sturgeon; BBH = bullhead; DV = dolly varden.

[2] No. samples with concentrations > 4 ppb (> 20 ppb for Aroclor 1254).

[3] No. samples with a trace of residue.

[4] No. samples with no detectable residue.

[5] Similar to Aroclor 1254.

[6] One sample had a trace of DDT, four had a trace of DDD, and one had a trace of dieldrin.

[7] One sample had a trace of DDT.

[8] Three samples had a trace of DDT, five had a trace of DDD.

[9] Two samples had a trace of DDT, two had a trace of DDD, and one had traces of DDT and DDD.

[10] Three samples had a trace of DDT, three had a trace of DDD, and two had a trace of dieldrin.

[11] One sample had a trace of DDD.

[12] Two samples had a trace of DDT; one sample had a trace of DDD

[13] One sample had traces of DDT and DDD

[14] Three samples had a trace of DDT, three had a trace of DDD, and one had 9.7 ppb dieldrin.

was below the lowest amount of standard injected, approximately 5 percent chart deflection, it was designated a trace amount. If no response was observed, it was considered to be not detectable. For quantification of compounds with higher concentrations, hexane extracts were appropriately diluted to yield responses within the range of the injected standards.

Samples containing sufficiently high concentrations of DDE and Aroclor 1254 were checked by mass spectrometry. These spectra resembled those of the corresponding reference-grade compounds. The instrument was a Varian gas chromatograph series 1400 with an attached Hitachi Perkin-Elmer RMV-6E spectrometer. The column and packing remained the same for this study. A 183-cm-by-0.64-cm column packed with 2 percent OV-1 and 6 percent OV-210 was employed for confirmation.

Recoveries and the efficiency of separating Aroclor 1254 from the other compounds were checked periodically with tissue samples spiked with standards at concentrations near the lower limits of quantification. Average percentages of recovery were Aroclor 1254, 85.2; DDD, 89.2; dieldrin, 91.3; DDT, 91.4; DDE, 92.8; heptachlor epoxide, 93.9; aldrin, 94.3; lindane, 97.5; and heptachlor, 99.0. Recovery studies were occasionally done so that the person analyzing the samples did not know they were spiked.

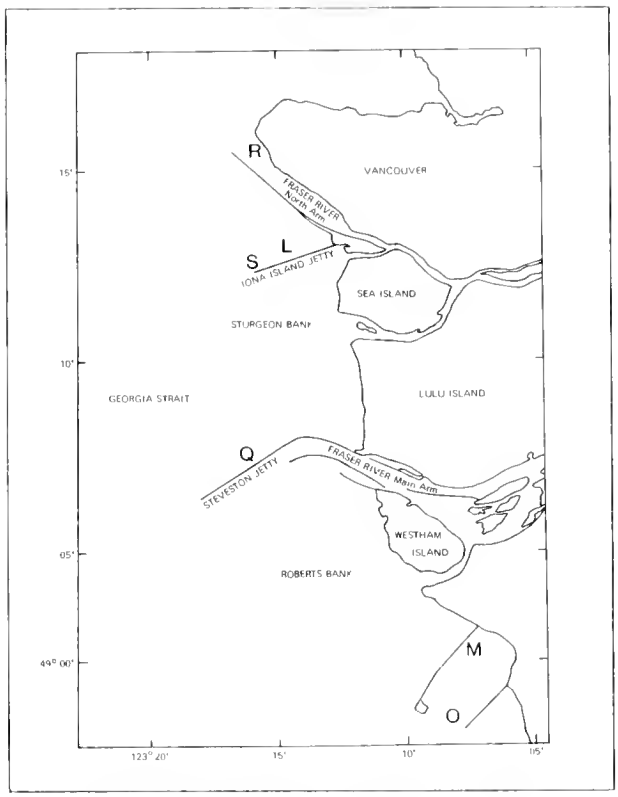

FIGURE 2. *Georgia Strait with sampling stations*

Results and Discussion

Eichelberger and Lichtenberg (*16*) have shown that of 28 common pesticides including 12 organochlorines, 9 organophosphates, and 7 carbamates placed in raw river water for up to 8 weeks, all were degraded except chlorinated hydrocarbons BHC, heptachlor epoxide, dieldrin, *p,p'*-DDT, *p,p'*-DDE, *p,p'*-DDD, and endrin, as well as the organophosphate monocrotophos. In addition to their greater resistance to degradation, these compounds also tend to accumulate in both plant and animal biota (*5*).

Data in Tables 1 and 2 indicate this as well. Although chlorinated hydrocarbons were not detected in waters or sediments of the lower Fraser River, its estuary, or Georgia Strait (*17-19*), dieldrin, *p,p'*-DDT, *p,p'*-DDD, *p,p'*-DDE, heptachlor epoxide, and PCB's were found in many fish and benthic animal samples of the Fraser River and its estuary (Tables 1, 2). However, except for a very low mean level of *p,p'*-DDE in three of seven *Cancer magister* samples from station C (mean of 2.1 ppb), no chlorinated hydrocarbons were found in fish and crab samples from Georgia Strait and in an area away from the immediate influence of Fraser River water (Fig. 2, stations A, B, and C). Table 3 lists the fish and crabs analyzed. Chlordane, lindane, endrin, and aldrin were not detected in any of these samples.

Analysis of the data in Table 1 indicates that several chlorinated hydrocarbons were present to a greater extent than others in fish. Compounds in Fraser River estuary fish were found in the following order of decreasing concentrations: PCB's, *p,p*-DDE, heptachlor epoxide, *p,p'*-DDD, and *p,p'*-DDT (stations 1-7, Fig. 1, Table 1). Analysis of the relative concentrations of chlorinated hydrocarbons in other fauna of this estuary indicates a similar pattern (Fig. 3, Table 2). The order of decreasing concentrations of compounds in fish from the upper reaches (stations 13, 14, Fig. 1, Table 1) was PCB's, *p,p'*-DDE, heptachlor epoxide, *p,p'*-DDD, *p,p'*-DDT, and dieldrin. A similar pattern was noted for fish from the middle reaches (stations 8-12, Fig. 1, Table 1).

Clearly, PCB's and *p,p'*-DDE are the chlorinated hydrocarbons of major importance in the biota sampled within this aquatic system. Further analysis of the data in Table 1 indicates that the average PCB and *p,p'*-DDT residues in fish species from the estuary (stations 1-7) were significantly greater than those from the upper portion (stations 13, 14) of the Fraser River. These patterns of concentrations may reflect the uses of land adjacent to the river at each station. Most of the upper and middle reaches are adjacent to agricultural regions whereas the estuary is next to the urban and industrial region of greater Vancouver as well as agricultural land. Hence the relatively greater concentrations of chlori-

TABLE 2. *Chlorinated hydrocarbon concentrations in various faunal species, Fraser River estuary, British Columbia—1972-73*

Station No.	Species [1]	Shell size, mm		Heptachlor Epoxide					*p,p'* - D D E					PCB's [5]					PCB's [6]				
		Mean	Range	Mean, ppb	Range, ppb	N [2]	N [3]	N [4]	Mean, ppb	Range, ppb	N [2]	N [3]	N [4]	Mean, ppb	Range, ppb	N [2]	N [3]	N [4]	Mean, ppb	N [2]	N [3]	N [4]	No. Samples
M	CC	8 [7]		ND		0	0	1	ND		0	0	1	ND		0	0	1	11.9	1	0	0	1
M	CG	11 [7]		ND		0	0	1	T		0	1	0	2724.1		1	0	0	ND	0	0	1	1
R	CM	10.8 [8]		ND		0	0	1	82.0		1	0	0	105.3		1	0	0	ND	0	0	1	1
Q	CM	13.1 [8,9]	9.5-16.1	7.7	ND-22.0	2	0	3	95.6	23.0-295.8	5	0	0	781.8	234.2-2100.3	5	0	0	ND	0	0	5	5
L	CC	all [7,10] sizes		23.0		1	0	0	32.0		1	0	0	295.0		1	0	0	ND	0	0	1	1
L	ME	4 [10,11]		ND		0	0	1	ND		0	0	1	T		0	1	0	ND	0	0	1	1
L	CS	3 [7,10,12]		ND		0	0	1	T		0	1	0	214.0		1	0	0	ND	0	0	1	1
O	CCO	9.5 [11,13]		ND		0	0	1	ND		0	0	1	193.0		1	0	0	ND	0	0	1	1
O	CM	13.5 [8]	11.9-15.5	3.3	ND-18.9	2	0	5	36.8	ND-141.1	5	1	1	559.3	170.1-1375.4	7	0	0	ND	0	0	7	7
S	CM	15.4 [8,9]	14.8-16.1	3.7	ND-11.4	2	0	3	101.4	23.1-176.9	5	0	0	839.7	154.3-1607.1	5	0	0	ND	0	0	5	5
S	CG	13 [7,14]		ND		0	0	1	T		0	1	0	322.3		1	0	0	ND	0	0	1	1

NOTE: ND = not detectable; T = trace.

[1] CC = *Callianassa californiensis;* CG = *Crassostrea gigas;* CM = *Cancer magister;* ME = *Mytilus edulis;* CS = *Citharichthyes stigmaeus;* and CCO = *Cardium corbis.*
[2] No. samples with concentrations > 4 ppb.
[3] No. samples with trace of residue.
[4] No. samples with no detectable residue.
[5] Similar to Aroclor 1254.
[6] Similar to Aroclor 1242.
[7] Entire animal assayed.
[8] Hepatopancreas assayed.
[9] One sample had a trace of dieldrin.
[10] More than one individual in this sample.
[11] Soft tissue assayed.
[12] Body length.
[13] Two samples had traces of *p,p'*-DDD.
[14] One sample had a trace of *p,p'*-DDT.

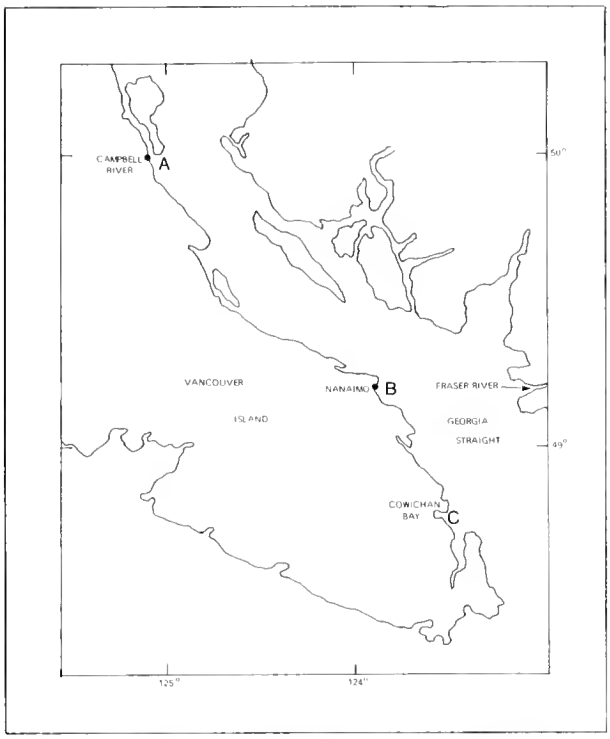

FIGURE 3. *Fraser River estuary with sampling stations*

nated hydrocarbons in estuarine fish may reflect increased residue levels in estuarine water compared to water from the upper reaches of the Fraser River.

Chlorinated hydrocarbons are believed to enter water bodies, including rivers, via rainfall, surface runoff, aerial sprays, ground water, direct application for insect control, and domestic and industrial effluents. However, the most probable pathways by which PCB's enter the Fraser River and its estuary are by surface runoff and domestic and industrial effluents from the Vancouver region. The storm and sewage lines of the city of Vancouver combine and terminate in an outfall near station L (Fig. 3). PCB residues in fauna were highest in animals from this estuary; their concentration appears to be proportional to the distance of the sampled benthic animals from the outfall. Exemplary are levels of *C. magister* at stations O, Q, S, and R, and *Callinanassa*

TABLE 3. *Fish and crabs sampled from Georgia Strait and areas away from the immediate influence of Fraser River water, British Columbia—1972-73*

Species	Station	Fork Length or Shell Width, cm	No. Individuals Analyzed
Red snapper	A	36	1
Sole	A	24	1
Ratfish	A	37	1
Tomcod	A	36	1
Skate	A	62	1
Rockfish	A	37.5	2
Coho salmon	B	46	3
Ratfish	C	30.6	5
Rockfish	C	23.5	2
Cancer magister	C	11.2	7

californiensis at stations L and M (Table 2). It is thus possible that one major route through which PCB's, and possibly other chlorinated hydrocarbons, enter this water and are taken up by fish and other biota, is the Iona Island sewage outfall adjacent to station L.

The two species of salmon adults sampled from the Fraser River estuary contained either low chlorinated hydrocarbon levels (chinook salmon) or none at all (sockeye salmon, Table 1). Because chinook are only in the river as juvenile migrants and are only temporarily near the estuary and sockeye are present only as juvenile migrants before they return as adults, the general low levels in these species seem reasonable.

Henderson et al. (*1*) have shown that of 147 fish removed from 50 sampling locations on various rivers across the United States, all contained *p,p'*-DDT and its metabolite *p,p'*-DDE. Dieldrin was present in 137 of these 147 samples whereas BHC was reported in fish from 15 stations only. Heptachlor epoxide residues were present in six samples at three stations whereas chlordane was present in samples from six stations. A calculation of mean *p,p'*-DDE, *p,p'*-DDT, and PCB concentrations in fish from levels reported by these authors revealed values of 692.9, 289.6, and 1,254.8 ppb, respectively. Mean values of *p,p'*-DDE, *p,p'*-DDT, and PCB's reported in this investigation of Fraser River fish were very much lower at 40.5, 0.3, and 140.8 ppb, respectively.

Henderson et al. (*1*) have further shown that *p,p'*-DDT levels in fish vary widely, depending upon the river in question. However, reported values for *p,p'*-DDT and *p,p'*-DDE in the 50 United States rivers sampled were all greater than values in fish from the Fraser River.

Studies of Long Island estuaries (*7*) and several California estuaries (*2*) revealed that shellfish and fish sampled from these waters also tended to concentrate chlorinated hydrocarbons in their tissues. In both areas levels of *p,p'*-DDT, *p,p'*-DDD, *p,p'*-DDE, and dieldrin were determined in animal tissue. In addition, many fish and shellfish removed from the California marine estuaries contained endrin (*2*).

Authors' analyses indicated the presence of only *p,p'*-DDE, heptachlor epoxide, and PCB's in fish and other benthic animals from the Fraser River estuary although several samples contained trace residues of *p,p'*-DDT, *p,p'*-DDD, and dieldrin. However, concentrations of *p,p'*-DDE were approximately equivalent to those reported by Modin (*2*) for *C. magister* removed from the California coast in the vicinity of San Francisco.

Miles and Harris (*12*), working with agricultural, urban-agricultural, and resort rivers in Ontario, found a more extensive pattern of chlorinated hydrocarbon insecticides than authors have noted for the lower Fraser River system. In addition to *p,p'*-DDE, heptachlor

epoxide, *p,p'*-DDT, *o,p'*-DDE, and *p,p'*-TDE, they detected *o,p'*-DDT, *o,p'*-TDE, *p,p'*-TDE, α-chlordane, and endrin in sampled fish whereas the authors of the present study did not. The one river in which they detected PCB's in fish was the Thames River, which is urban-agricultural as is the lower part of the Fraser River. PCB contamination of water, and hence fish and other aquatic fauna, appears to be more closely associated with rivers adjacent to urban areas than with agricultural or forested land.

Acknowledgments

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Mirex Residues in Wildlife and Soils, Hawaiian Pineapple-Growing Areas—1972-74 [1,2]

Arthur Bevenue, James N. Ogata, Lester S. Tengan, and John W. Hylin

ABSTRACT

A monitoring program was conducted in the pineapple-growing areas of Hawaii from 1972 to 1974 to survey mirex residues in sediments, soils, and aquatic and terrestrial wildlife. Residues in pineapple field soils ranged from 3 to 18 ppb 9 months after mirex had been applied. No residues were found in the sediments. Only 8 fish of 110 aquatic animals sampled contained mirex; these levels were low and ranged from 3 to 7 ppb. Mirex residues in birds ranged from undetectable to 10 ppm; residues in rodents were quite variable, but in terms of the geometric mean, the amounts in the Polynesian rat decreased with time from 1,270 to 56 ppb. Similarly, values for the roof rat ranged from 666 to 17 ppb. The geometric mean for residues in mongooses decreased from 2,200 ppb immediately after application to 238 ppb 39 weeks later. Aerial application of mirex to the pineapple fields did not contaminate the marine environment of Hawaii and no evidence of mirex residue buildup in the aquatic food chain was apparent. Mirex accumulation in terrestrial biota was temporary; there was no definitive indication of permanent accumulation in the wildlife of the areas studied.

Introduction

Successful pineapple production requires the control of several insect-transmitted diseases, the most serious of which is mealybug wilt caused by the pineapple mealybug (*Dysmicoccus brevipes*). Direct control of this organism is not feasible, but because it is transported and protected by the bigheaded ant (*Pheidole megacephala*), the disease can be controlled by reducing the ant population in pineapple fields. Mirex has been successfully used for ant control in pineapple production in Hawaii since 1970. It was used on about 30,000 acres in 1972 when about 76,000 lb bait containing 220 lb mirex (0.29 percent active ingredient) was applied. The use of mirex in Hawaii was temporarily suspended in 1972 when the U.S. Environmental Protection Agency (EPA) permitted an exception to their Notice of Cancellation of registrations of pesticides containing mirex (March 18, 1971, and amended by two Determination and Orders on May 3, 1972, and June 30, 1972), provided that aerial application of mirex in the Hawaiian pineapple fields would be subjected to EPA approval. Monitoring procedures used for the 1972-74 pineapple-growing seasons and the analytical results of mirex residues in environmental specimens obtained from pineapple-growing areas are described in this report.

Sampling

State areas pertinent to mirex monitoring are indicated in Figures 1-3. The 1972-73 samples included aquatic specimens, sediments, and soils; sampling was confined to two coastal areas on the island of Maui and one each on the islands of Molokai and Oahu. Samples were taken quarterly for 1 year.

The 1973-74 samples were primarily terrestrial vertebrates with some additional aquatic and soil samples. The second-year sampling program for soil and terrestrial biota was confined to the Maliko watershed area on the island of Maui, an area which contained 4,962 acres under pineapple production. Aquatic specimens were collected at both the Maliko and Honokohau areas. Soil and sediment samples were selected from sites where mirex would most likely be transported by streams from the fields to coastal areas. Sediment samples were taken near the shoreline areas at an approximate depth of 1 cm and placed in 1-quart cans which had been baked at 200°C. Topsoil samples were removed to a depth of about 1 cm from 9-ft² areas and were also stored in heat-treated cans. At least two samples were taken during each round of monitoring from two pineapple fields in an area where surface water runoff converged after exiting each field. Most

[1] Presented in part at the Third International Congress of Pesticide Chemistry, Helsinki, Finland, July 3-9, 1974. Journal Series No. 1858, Hawaii Agricultural Experiment Station

[2] University of Hawaii, Honolulu, Hawaii 96822.

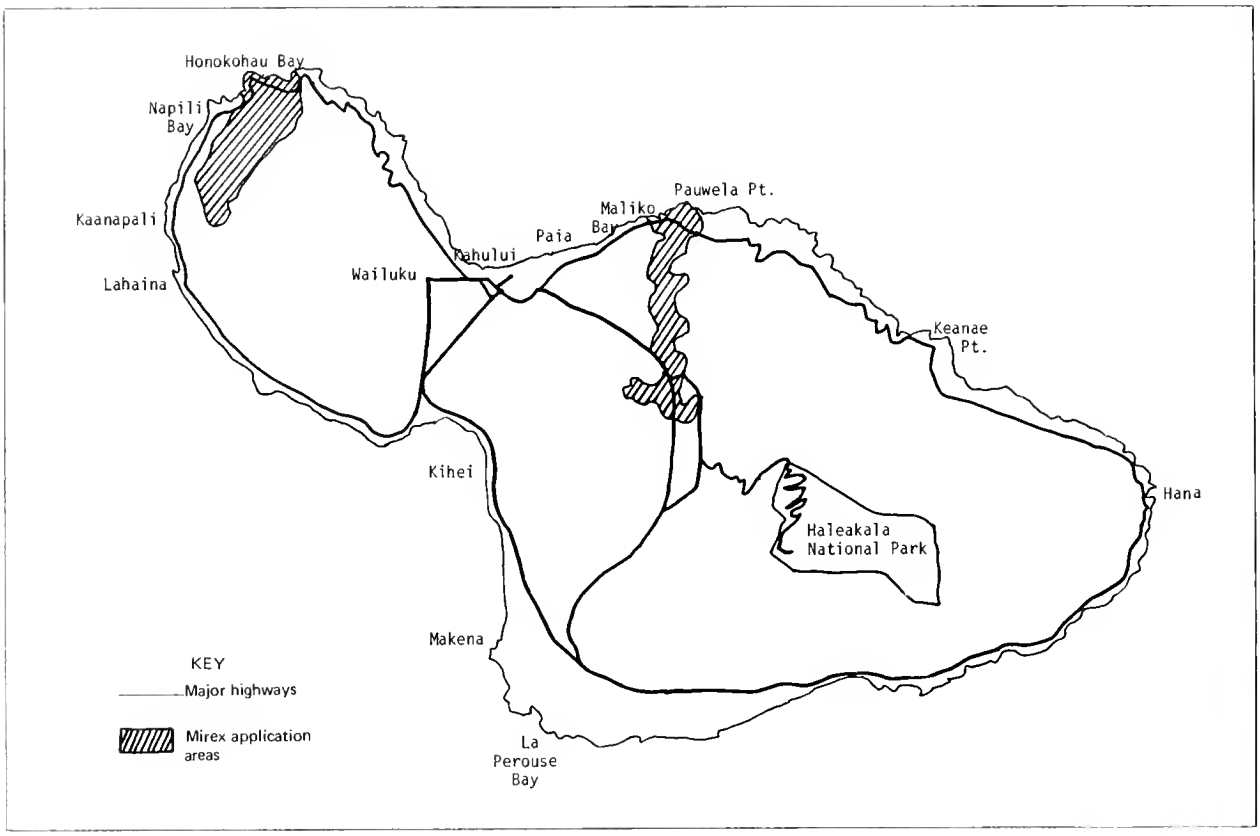

FIGURE 1. *Pineapple-growing areas treated with mirex, Maui, Hawaii—1972-74*

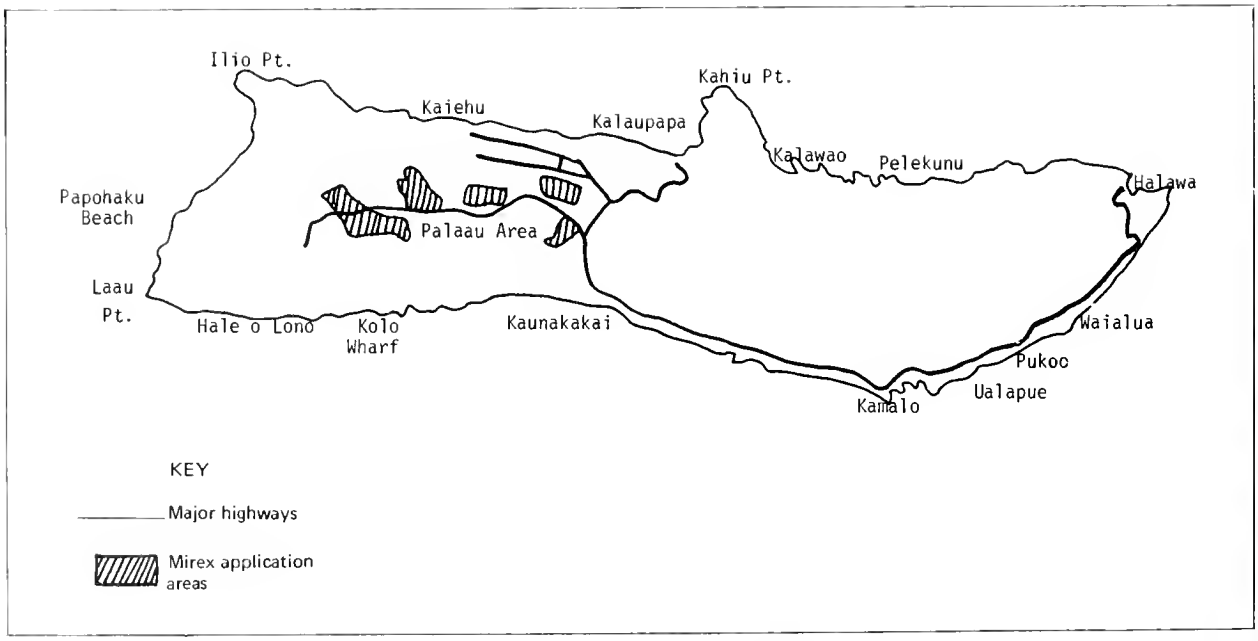

FIGURE 2. *Pineapple-growing areas treated with mirex, Molokai, Hawaii—1972-73*

of the fish, shrimp, and crabs were caught by either throw or scoop nets. Occasionally, spearfishing was substituted for netting. Algae and oysters were gathered by hand; birds were shot; and rodents and mongooses were obtained with snap and live traps, respectively. All animals were taken within the confines of a mirex-treated field.

Specimens were obtained 1 week before and 1-2 weeks after mirex application. Additional samples were taken at approximately 1-month intervals for a period of 9 months. All specimens were labelled and packaged separately, packed in ice in chilled insulated containers, and transported to the analytical laboratory within 24 hours of collection. Upon arrival, samples were immediately prepared for analysis.

A total of 27 sediment, 4 soil, and 89 aquatic biota samples were analyzed for the 1972-73 period. In 1973-74, 10 soil and 23 aquatic biota samples were collected; other samples include 20 birds, 6 mice, 41 rats, and 22 mongooses. Table 1 lists all species collected.

Analytical Procedures

The analytical method used for mirex residues was essentially the same as the method recommended by Wilson (*1*). In the present study the method was applied to certain types of biological species not heretofore examined by this procedure.

Equipment included a Waring blendor; a Sorvall Omnimixer; a Buchi rotary vacuum evaporator; a Soxhlet apparatus, size 23; 400-mm-by-20-mm-ID chromatographic columns with 200-ml reservoir fitted with teflon ultramax valves; and glass wool rinsed with acetone and hexane, air-dried, and heated at 200°C for 16 hours before use. All glassware was soaked in a sulfuric acid:

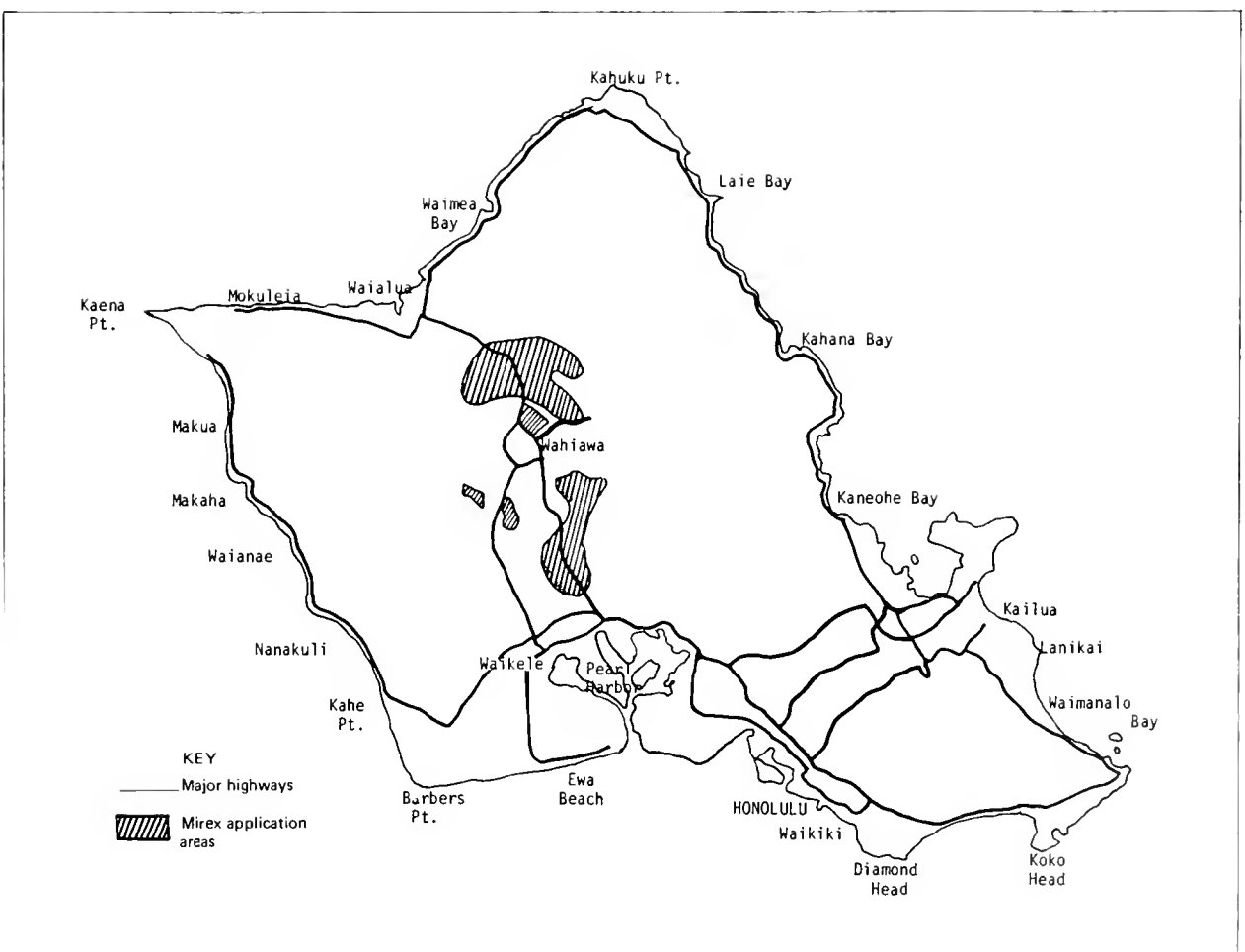

FIGURE 3. *Pineapple-growing areas treated with mirex, Oahu, Hawaii—1972-73*

TABLE 1. *Species sampled for mirex residues, Hawaiian pineapple-growing areas—1972-74*

Common Name	Scientific Name
Algae	
	Chnaspora sp.
	Acanthophora specifera
	Sargassum sp.
Crustaceae	
Crab	*Portunus sanguinolentus*
Crab	*Grapsus grapsus*
Crenate swimming crab	*Thalamita crenata*
Long-eyed swimming crab	*Podophthalmus vigil*
Shrimp	*Palaemon debilis*
Echinoderm	
Sea cucumber	*Halothuria atra*
Sea urchin	*Tripneustes gratilla*
Flat sea urchin	*Colobacentratus atratus*
Fish	
Aholehole	*Kuhlia sandvicensis*
Great barracuda	*Sphraena barracuda*
Largemouth bass	*Micropterus salmoides*
Damselfish	*Abudefduf abdominalis*
Goatfish	*Parupeneus multifasciatus*
Goatfish	*Parupeneus porphyreus*
Halibut	*Bothus pantherinus*
Molhe	*Mollienisia latipinna*
Striped mullet	*Mugil cephalus*
False mullet	*Neomyxus chaptalii*
Parrotfish	*Scarus dubius*
Pompano	*Caranx ignobilis*
Surgeonfish	*Acanthurus candvicensis*
Mozambique tilapia	*Tilapia mossambica*
Wrasse	*Anampses godeffroyi*
Wrasse	*Thalassoma duperreyi*
Wrasse	*Thalassoma fuscum*
Mollusk	
Clam	*Quadrans palatam*
Mussel	*Isognomon californicum*
Oyster	*Crassostrea virginica*
Limpet	*Cellana calcosa*
Limpet	*Cellana exerata*
Rough periwinkle	*Littorina scabra*
Open dye shell	*Purpura aperta*
Nerita (pitchy sea snail)	*Nerita picea*
Birds	
Golden Pacific plover	*Pluvialis dominica fulva*
Barred dove	*Geopelia striata*
Spotted dove	*Streptopelia chinensis*
Mynah	*Acridotheres tristis*
Ruddy turnstone	*Arenaria interpres*
Mammals	
Mouse	*Mus musculus*
Polynesian rat	*Rattus exulans*
Roof rat	*Rattus rattus*
Small Indian mongoose	*Herpestus auropunctatus*

potassium dichromate solution, rinsed thoroughly with distilled water and then with acetone and hexane. The dry glassware was heated at 200°C for 16 hours prior to use.

Operating conditions for the gas chromatograph were:

Instrument:	Hewlett-Packard model 5750
Columns:	Glass, ¼ in. by 4 ft OD, packed with 2 percent OV-101 on 100/120 mesh Gas Chrom Q
For confirmation:	Glass, ¼ in by 4 ft OD, packed with 0.75 percent OV-17 and 0.97 percent OV-210 on 100/120 mesh Gas Chrom Q
Detector:	Electron-capture, with 200 mCi tritium as ionizing source
Temperatures:	Column 196°C Injector 212°C Detector 207°C
Carrier Gas:	Argon:methane (90:10) flowing at 60 ml/min

The following reagents were employed:

Sodium sulfate: anhydrous powder, J. T. Baker No. 3898

QUSO-G30: precipitated silica (Philadelphia Quartz Co., Philadelphia, Pa.)

Desiccant mix: 10 percent QUSO, 90 percent anhydrous sodium sulfate

Acetone, acetonitrile, hexane, petroleum ether: all redistilled

Ethyl ether: Mallinckrodt No. 0844

Florisil: Regular grade (Floridin Co., Berkeley Springs, W. Va.), heated 5 hours at 130 C

Eluting solvents

A: 100 ml distilled water made to 1000 ml volume with acetonitrile

B: 60 ml ethyl ether made to 1000 ml volume with petroleum ether

SAMPLE PREPARATION

Soil and Sediments: Samples were air-dried at room temperature, 20°-25°C, for 72 hours, then mixed for 1 minute in a Waring blendor and stored in pint-size Mason jars for subsequent analysis. A separate 10-g portion of each soil or sediment sample was weighed in a tared aluminum dish. The sample was dried for 16 hours at room temperature and then for 16 hours at 110°C in an air oven. After cooling in a desiccator, samples were reweighed and the percent solids was calculated.

Aquatic Biota: Initially, all samples were blotted dry and weighed. Shells were removed and discarded from all mollusk samples except the Nerita specimens. The operculum of the snails and the carapace of the crabs were also removed and discarded. The remainder of each of these species was homogenized in a Waring blendor. Sea cucumbers, sea urchins, shrimp, algae, and small fish less than 4 cm were prepared for whole-body analysis by homogenization in a blendor. Larger fish weighing less than 150 g were scaled; the head, tail, and viscera were removed and discarded; and the remainder of each fish was homogenized. Fish weighing more than 150 g were scaled and fillet samples were homogenized.

Birds: Breast and wing muscles of the dressed birds were composited and homogenized.

Mice and Rats: The head, feet, skin, and viscera, including kidney, heart, and lungs, were removed from each specimen and discarded. The remainder of the

mice was homogenized for analysis. Samples of tissue were removed from the back and legs of the rats and homogenized for analysis.

Mongooses: Samples of tissue from the two hind legs and lower back were removed from each skinned mongoose and homogenized for analysis. A 30-g sample of each homogenized specimen was weighed into a pint-size Mason jar and chilled at −10°C for 30 minutes. A quantity of the desiccant mix was added to the chilled sample and mixed thoroughly with a spatula. The amount of desiccant mix added to each sample varied from two to four times the weight of the specimen and was governed by the wetness of the sample. The mixture was frozen and then pulverized in a Sorvall Omni-mixer. It was necessary to refreeze and regrind the samples several times to obtain a free-flowing powdery mixture. Prepared samples were stored in the freezer until analysis.

SAMPLE EXTRACTION

The biota sample was packed between two 1-inch layers of glass wool and Soxhlet-extracted for 4 hours with petroleum ether at a solvent cycle rate of 6-7 minutes. The extraction procedure for sediment and soil was similar except that the extract mixture was composed of acetone : petroleum ether (1:9).

SAMPLE CLEANUP

Extracts were concentrated to approximately 10 ml in a rotary evaporator. The biota concentrates were transferred with petroleum ether in 3-4-ml portions to chromatographic columns containing 3 inches of unheated florisil. A gentle vacuum was applied to the columns after the addition of each portion to evaporate the solvent from the column. Residues were then eluted from the columns with 70 ml eluting solvent A and the eluate was evaporated to dryness in a rotary evaporator.

Biota residues obtained from this cleanup procedure were dissolved in petroleum ether and the sediment and soil concentrated extracts were transferred to chromatographic columns containing 4 inches of heat-treated florisil and topped with ½ inch anhydrous sodium sulfate. Columns had been previously washed with petroleum ether. Residues were eluted from the columns with 200 ml eluting solvent B. Eluates were evaporated to approximately 1 ml in a rotary evaporator, transferred to volumetric flasks, and made to volume with hexane. Suitable aliquots of the sample extracts and standardized solutions of mirex were applied to the gas chromatograph. Peak heights were compared and mirex residues were calculated and recorded. Samples of sediment, soil, and aquatic and terrestrial biota were fortified with mirex at the 0.1-0.5 ppm level to substantiate the efficiency and reliability of the analytical procedure (Table 2). Residue data reported have not been corrected for recovery. Analytical specificity was confirmed by examination of mirex residues found in mongooses and rats by mass spectrometry/gas chromatography with the utilization of a Finnigan Model 3000 GC Quadropole Mass Spectrometer Peak Identifier.

TABLE 2. *Percent recovery of mirex from soils and biota, Hawaiian pineapple-growing areas—1972-74* [1]

SAMPLE	PERCENT RECOVERY
Sediment	96
	91
	75
	87
	94
Soil	80
	91
Barracuda	90
Goatfish	86
Mollie	90
Wrasse	98
Crenate crab	94
	90
Limpet	98
	92
	91
Nerita	76
Sea cucumber	96
Sea urchin	92
Flat sea urchin	93
Rat	77

[1] All samples were spiked with 0.1 ppm mirex except the Nerita which received 0.5 ppm.

Results

Mirex bait is aerially applied once each year at the rate of 2.5 lb (1,134 g)/acre in the pineapple fields. The active insecticide ingredient in this amount is 3.29 g. To comprehend the significance of this small amount of insecticide per acre in terms of potential environmental contamination, several physical properties of the bait were measured in the laboratory (Table 3).

TABLE 3. *Properties of mirex bait formulation applied, Hawaiian pineapple-growing areas—1972-74*

Mirex content, %	0.29
Average mass of individual bait grains, mg	0.783
Range	0.1-3.0
Settling rate of bait grains in water, cm/sec [1]	
Majority of grains	5.9
Fastest rate	11.8
Solubility of mirex in water at 25°C: 3 trials, ppm [2]	0.048
	0.093
	0.073
Average solubility, ppm	0.071

[1] Less than 1% of the bait floats.
[2] One bait was agitated gently in tap water for 2 hr, then allowed to soak overnight or 22 hr. The filtrate, passed through Whatman No. 42 analytical grade paper, was analyzed for mirex.

Only 5 fish and 3 soil samples of the 120 samples collected for the 1972-73 season contained mirex residues and all residues were near the level of analytical detectability (Table 4). The five fish samples originated from the Maui estuaries. The limit of detection for mirex ranged from 3 to 6 ppb. Fish species similar to

TABLE 4. *Mirex residues in environmental samples, Hawaiian pineapple-growing areas—1972-74*

SPECIMEN [1]	COLLECTION SITE	MIREX RESIDUE, μG/KG
Goatfish (1)	Maliko Bay, Maui	3
Wrasse (1)	Maliko Bay, Maui	3
Aholehole (1)	Honokohau Bay, Maui	3
Aholehole (2)	Maliko Bay, Maui	4
Aholehole (18)	Honokohau Bay, Maui	7
Soil [2]	Palaau Field, Molokai	
	September 8, 1972	ND
	December 8, 1972	18
	March 15, 1973	10
	June 15, 1973	15
Control Series, Fish [3]		
Goatfish (2)	Makua, Oahu	ND
Goatfish (2)	Kaneohe Bay, Oahu	ND
Aholehole (1)	Kaneohe Bay, Oahu	ND

NOTE: ND = not detected.

[1] Number in parentheses indicates number of samples; residues in fish reported on fresh-tissue basis.
[2] Soil sampled from edge of field treated with mirex October 30, 1972; residues reported on air-dried basis.
[3] Specimens obtained in areas remote from mirex usage.

the specimens which contained residues were obtained far from mirex usage areas and were analyzed for mirex residue to make certain that the residue observed in the fish had indeed been contributed by mirex and not by an inherent gas-chromatographic-sensitive component characteristic of these species. These samples did not positively show mirex residues. It is possible for a fish to have randomly ingested one bait particle which would contribute a residue in the fish and it would be commensurate with the amounts of mirex in Table 3. Analytical residue results for the first season's monitoring program did not indicate any environmental problem resulting from the use of mirex in the pineapple fields, at least not in terms of aquatic biota and sediment contamination. However, the random finding of very low amounts of residue in the aforementioned fish and the apparent small but persistent residue found in the soil of one field (Table 4) prompted a second sample collection which was confined to the island of Maui and included a terrestrial vertebrate sampling program.

EPA permitted aerial application of mirex to the Hawaiian pineapple fields during the 1973-74 season provided that a monitoring program be continued as set forth in the Agency's Determination and Order dated August 31, 1973.

In the second season, top soil samples were obtained from two treated fields at a point where surface runoff would converge after leaving the fields. Areas from which the samples were taken consisted of well-drained soils with gentle to moderate slopes. Two samples from field No. 233 obtained within 3 months after mirex application contained 3-4 ppb mirex. Samples obtained from the same field 6-8 months later contained no detectable mirex residues. Samples obtained from field No. 234 during the same period of time contained mirex residues in the range of 5-9 ppb (Table 5).

TABLE 5. *Mirex residues in soil and fish samples, Hawaiian pineapple-growing areas—1973-74*

SAMPLE [1,2]	DATE	MIREX RESIDUE, μG/KG
Soil, Maui field 233	October 6, 1973 [3]	ND
	November 3, 1973	3
	January 19, 1974	4
	April 21, 1974	ND
	July 13, 1974	ND
Soil, Maui field 234	October 6, 1973	ND
	November 2, 1973	9
	January 19, 1974	5
	April 21, 1974	9
	July 13, 1974	9
Fish		
Wrasse (1)	October 6, 1973	3
Aholehole (1)	October 6, 1973	3
Aholehole (1)	April 21, 1974	3

NOTE: ND = not detected.

[1] Soil samples taken adjacent to fields where surface runoff converged after exiting the field. Soil residues reported on dry-weight basis.
[2] Analyses of only 3 fish of 23 aquatic biota indicated the presence of a low level of mirex residue. Number in parentheses indicates number of samples; residues in fish reported on fresh-tissue basis.
[3] October 6, 1973, was 1 week before mirex application.

A total of 11 marine fish, 5 mollusk, 3 echinoderm, and 2 seaweed samples were collected from the Maliko and Honokohau areas. Only three of the marine fish contained mirex residues (Table 5); each residue was at the minimum detectable level. Freshwater fauna sampled near the end of the second collection to determine whether mirex was accumulating in this area of the local environment contained no mirex residues.

Discussion

Markin et al. (*2*) published data from an island near Gulfport, Miss., which had been treated with mirex three times in 1 year. Residues appeared in practically all marine life examined in the area 3 weeks after the third mirex treatment. Residues decreased to either undetectable or trace amounts in the subsequent 3-year period. Breteke et al. (*3*) found residues in most of the fish examined in certain areas of Mississippi where mirex had been used extensively for at least 5 years before the sampling program. Borthwick et al. (*4*) examined estuarine wildlife in an area of South Carolina 24 months after treatment of the area with mirex and found residues greater than 0.01 ppm in only 10 percent of the specimens examined.

In a study of a crawfish-growing area of Louisiana Markin et al. (*5*) found, in most instances, no mirex residues in crawfish, some of which had been obtained from areas treated five times during the year prior to the sampling program. The absence of mirex residues in the aquatic areas of Hawaii may be attributed to

several factors: in some areas reservoirs and irrigation canals receive all runoff water because there are no large rivers or streams in the pineapple-producing areas of the State; normal rainfall is quickly absorbed by the volcanic soils; and soil and water conservation measures, including contour plowing, diking, and grassing of water courses, are constantly practiced to contain the soil and water within the pineapple fields so that runoff is limited to roadways and newly planted fields.

Bird samples were predominantly from golden Pacific plover. This bird and the ruddy turnstone are migratory and reside in Hawaii from September to May. Both species feed principally on insects and larvae, preferably in newly plowed and planted fields. Mirex residues in plovers varied considerably between samples from 80 to 10,400 ppb (Table 6); no definitive cumulative or diminutive trend of residues with time was apparent. It is reasonable to assume that the plover which weighed 127 g and contained 10.4 ppm mirex in its body tissue could have randomly acquired these residues from less than 0.5 g bait (Table 3) or from insects which had ingested the bait (*2*). Yet plover data (Table 6) indicate that these levels were exceptionally high. Furthermore, bait deteriorates rapidly in the field, becoming unacceptable to the birds as a feedstuff. Similarly, residue data obtained from a limited number of samples of the ruddy turnstone and the mynah were inconclusive.

Difficulty in acquiring definite time-related data on a migratory species over a period of 7 months is readily apparent in the data in Table 6. Except for one specimen which had a trace of mirex, less than 10 ppb, no residues were found in the doves.

TABLE 6. *Mirex residues in birds, Hawaiian pineapple-growing areas—1973-74*

Date	Mirex Residue, μg/kg				
	Barred Dove	Lace-Necked Dove	Mynah	Golden Pacific Plover	Ruddy Turnstone
October 11, 1973 [1]	6 (1)			118 (2)	
October 31, 1973				1,955 (4)	
November 20, 1973				440 (1)	210 (1)
November 20, 1973				310 (1)	
January 17, 1974	ND (1)		325 (1)	625 (1)	810 (1)
February 27, 1974			30 (1)	10,400 (1)	
" " "				1,250 (1)	
" " "				180 (1)	
" " "				330 (1)	
April 17,1974				80 (1)	200 (1)
July 10, 1974		ND (1)			

NOTE: ND = not detected.

[1] October 11, 1973, was 1 week before seasonal mirex application. Number in parentheses indicates number of samples, residues in birds reported on fresh whole-tissue basis.

Oberheu (*6*) examined starlings, which are also migratory birds. Samples were obtained from mirex-treated areas of seven southeastern States. Oberheu concluded that mirex residues found in the birds (80-1,666 ppb) related directly to the exposure potential but admitted that the significance of the levels was not explainable. Ivie et al. (*7*) noted that mirex residue levels in birds varied appreciably in different species. Their controlled study with mirex-treated quail indicated that mirex was

TABLE 7. *Mirex residues in mice and rats, Hawaiian pineapple-growing areas—1973-74*

Date	Weeks after Application	Mirex Residues, μg/kg				
		Mouse	Polynesian Rat	Geometric Mean	Roof Rat	Geometric Mean
10-11-73 [1]		281 (4)	67 (5)		13 (4)	
11-01-73	3	379 (1)	8,435 (5)		1,060 (5)	
11-21-73	6		1,570 (1)		1,850 (1)	
			890 (1)		110 (1)	
			1,470 (1)	1,270	770 (1)	666
			1,280 (1)		500 (1)	
					1,670 (1)	
01-17-74	14	890 (1)	9,410 (1)		295 (1)	
			790 (1)		925 (1)	
			125 (1)	976	830 (1)	683
					960 (1)	
02-28-74	20		350 (1)	388	95 (1)	149
			430 (1)		235 (1)	
04-17-74	27		890 (1)		120 (1)	
			50 (1)		85 (1)	
			150 (1)	188	135 (1)	212
					715 (1)	
					435 (1)	
07-10-74	39		133 (1)		13 (1)	
			47 (1)		5 (1)	
			68 (1)	56	24 (1)	17
			24 (1)		21 (1)	
					49 (1)	

NOTE: Number in parentheses indicates number of samples; residues in specimens reported on fresh whole-tissue basis.

[1] October 11, 1973, was 1 week before seasonal mirex application.

rapidly absorbed by body fat, particularly in males. Residue levels in female quail declined rapidly because the residue was transferred to the eggs. Residues in the male declined more slowly; 50 percent of the administered mirex was still present in the male tissue 84 days after treatment. Markin et al. (*2*) reported residues of mirex in sandpipers and snowy egrets in the range of 440-1,320 ppb 1 year after the last of three mirex applications. Residues decreased to about 35 ppb in both species 2 years later. However, authors of that study observed no effect on the overall population of the area.

All samples of mice and rats were obtained from the same pineapple field. The Polynesian rat, which is limited to a diametral feeding range of about 100 feet, feeds on pineapple stumps, arthropods, and seeds. The roof rat has a feeding range of about 200 feet; its indiscriminate food selection includes grass, fruits, birds, and bird eggs.

Mirex residues in mice samples (Table 7) ranged from 281 to 890 ppb; data were insufficient to indicate a trend in accumulation or excretion. Residues in the Polynesian rat ranged from 24 to 9,410 ppb. (Table 7). Levels dropped markedly after the 13th week after mirex application. Residues in the roof rat ranged from 5 to 1,850 ppb and, similarly, residue levels decreased with time.

Gibson et al. (*8*) and Mehendale et al. (*9*) noted differences in excretion patterns after feeding mirex to laboratory-controlled rats. Gibson's group noted that 18 percent of the mirex was eliminated from rats within a 7-day period, whereas Mehendale et al. reported that about 59 percent was eliminated during the same time period. Both groups noted that the remainder of the pesticide would be eliminated slowly from the body tissue of the rats. Obviously, controlled laboratory studies cannot be readily or easily correlated to the rodent living in the wild.

The small Indian mongoose was included in the sampling program because it represented the highest trophic level of the food chain in the pineapple fields. The only true carnivore that frequents the fields, the Hawaiian or Pueo owl, may be classed as an endangered species; thus specimens were not taken, nor were any observed during the program. The mongoose eats birds, small mammals, plant material, detritus, garbage, or any other organic material available. They have a feeding range of about one-fourth mile. The 22 mongooses trapped in field No. 235 had mirex residues ranging from 30 to 11,760 ppb (Table 8). Mongooses trapped about 1 mile from the treated area (Table 8) contained average mirex residues of 126 ppb, somewhat lower than the average value of the samples obtained in the treated area on the same sampling date.

These latter data may be misleading. If the one high residue value of 1,250 ppb from field No. 235 on April 16, 1974, were excluded, the average mirex residues in the mongoose from the two areas would be 114 ppb and 126 ppb, respectively, indicating no tangible difference in the values for the two areas. However, residue concentrations in the mongoose species did decrease with time. This was markedly apparent 27-39 weeks after mirex application. An examination of six mongoose fetuses and the respective mothers indicated that mirex residues in the fetuses were about 14 percent of the amount found in the mothers (Table 9).

TABLE 8. *Mirex residues in small Indian mongoose, Hawaiian pineapple-growing areas—1973-74*

DATE	WEEKS AFTER APPLICATION	COLLECTION SITE	RESIDUE, µG/KG	GEOMETRIC MEAN, PPB
11-21-73 [1]	6	Field 235	430	
			6,190	
			3,930	
			9,820	
			500	2,200
01-17-74	14	Field 235	11,760	
			2,080	
			6,665	5,460
02-27-74	20	Field 235	2,940	
			4,120	
			1,730	
			470	1,770
04-16-74	27	Field 235	1,250	
			30	
			70	
			305	
			50	132
07-10-74	39	Field 235	576	
			200	
			533	
			333	
			37	238
04-16-74	27	1 mile seaward from fields 233-234	35	
			370	
			90	
			105	
			30	82

NOTE: Each of above residue values represents the residue in one mongoose specimen; residues reported on fresh whole-tissue basis.

[1] Mirex had been applied to the field during the week of October 19, 1973.

TABLE 9. *Comparison of mirex residues in the fetus and related mother of small Indian mongooses, Hawaiian pineapple-growing area—1972-74*

COLLECTION SITE	RESIDUE, µG/KG		
	Mother	Fetus	Fetus/Mother
Edge of mirex-treated field No. 235	4,120	625	0.15
1 mile from mirex-treated field No. 233, 234	350	15	0.04
"	145	20	0.14
"	20	6	0.30
"	480	60	0.13

NOTE: Samples obtained February 27, 1974, about 4.5 months after mirex application. Each residue value represents the residue in one mongoose specimen except for the fetus value of 625, which was obtained from a composite sample of two fetuses. Residues reported on fresh whole-tissue basis.

In summation, aerial application of mirex to the pineapple fields did not contaminate the Hawaiian marine environment. During the monitoring period of 1972-74, only 8 fish of 112 aquatic biota samples contained mirex residues, and these 8 samples contained only negligible amounts less than 10 ppb. No evidence of food web pesticide residue accumulation was apparent in the local aquatic biota. Mirex residue levels in pineapple field soils were very low (3-18 ppb) but persistent for the 6- to 9-month period after mirex application. Residue levels in the mongoose, the highest member of the food web examined from the pineapple fields, were at a maximum amount 6-14 weeks after mirex application. A marked drop in residue levels in this species was observed in the subsequent time period, 27-40 weeks after mirex application. A similar trend was observed in the rats. Data indicated that mirex accumulation in terrestrial biota of the mirex-treated pineapple fields was temporary and no permanent buildup or food web accumulation of residue was evident, with the possible exception of the Pacific golden plover.

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Exposure and Contamination of the Air and Employees of a Pentachlorophenol Plant, Idaho—1972 [1,2]

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ABSTRACT

A pentachlorophenol (PCP) wood treatment plant was studied to determine PCP exposure to people by occupation and to the plant by work area. This plant operates on a year-round basis with a 25 percent increase in production from May through October. Approximately 2.5 million board feet of timber are processed annually. Samples were taken in the morning of the second work week of each month for 5 consecutive months. Samples consisted of serum and urine from the employees and air from locations throughout the plant work area. All samples were analyzed for PCP residue. Peripheral blood was used to culture cells to investigate possible chromosomal aberrations.

Introduction

Pentachlorophenol (PCP) has been used to treat wood products for preservation and control of insects and fungus since the late 1930's (*1-4*).

A study of a small wood treatment plant and its six full-time employees was conducted to determine their exposure by air and environmental contact to PCP and how this exposure possibly affected chromosomes.

Sampling and Analysis

Blood and urine samples were collected monthly from January through May. The ages of the employees ranged from 20 to 54 years. Employee work stations and their length of employment and/or exposure are shown in Table 1. The main tasks of the employees are listed, but as is typical in a plant of this size, all are trained in each capacity and often function accordingly. Respirators and rubber gloves are worn when working inside the treatment chamber and while mixing concentrates. Other than at these times, no protective gear is worn.

The method of analysis for serum and urine was that of Rivers (*5*). Two ml serum or urine was added to a culture tube along with 6 ml benzene and two drops of concentrated sulfuric acid. The tube and contents were then rotated for 2 hours at 50 rpm on a roto-rack. Three ml of the benzene was transferred to a centrifuge tube and methylated with 0.2 ml diazomethane. The sample was then ready for dilution and gas chromatography. Recovery data were collected by running samples in duplicate spike at 0.1, 0.5, 5, and 50 ppm (Table 2). Reagent blanks were run with each set of samples.

Air samples were taken from the 11 sites shown in Figure 1. A series of three MSA Monitaire midget impingers were used to collect the first test samples, but after the first analysis two impingers were dropped because results showed all the PCP was trapped in the first impinger. Ten ml ethylene glycol was placed in each impinger. Air samples were collected for an average of 6 hours during the working day. Two ml ethylene glycol from each impinger was then extracted using the Rivers method for blood and urine.

Chromosome work was done using a slight modification of the technique of Difco Laboratories (*6*). Peripheral blood cultures were incubated at 38°C and samples were cultured for 48 hours to obtain cells in the first mitotic division (*7*). Slides were stained with Giemsa and rearranged and coded by a person other than the scorer to avoid bias. Twenty-five cells were scored as to chromosome number, abnormal configurations, breaks, and gaps. Photographs were taken of all abnormal bursts and karyotypes were done when there was evidence of loss of material. Gebhart's criteria were used to differentiate breaks and gaps from achromatic lesions (*8*). Gaps were considered abnormal because they vary in

[1] Idaho Epidemiologic Studies Project, Department of Health and Welfare, Statehouse, Boise, Idaho 83720

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TABLE 1. *PCP residues in serum, whole blood, and urine of workers in a PCP plant and a control, Idaho—1972*

Subject	Occupation	Age, Years	Exposure, Years	Residues, ppb									
				January		February		March		April		May	
				Serum	Urine	Serum	Urine	Serum	Urine	Serum	Urine	Serum	Urine
1	Office Manager	48	10	643.8	112.2	417.9	63.4	749.1	41.3	702.5	42.0	705.0	61.3
2	Outside Loader	29	2	372.9	132.5	348.4	111.1	610.0	124.6	1203.0	157.2	1630.0	151.2
3	Welder and Laborer	20	6 summers and 2 full years	1236.0	245.5	1246.0	130.0	1580.0	80.9	1791.0	148.8	3963.0	262.3
4	Pressure Treater	54	5	1979.0	760.0	1508.0	121.8	1746.0	93.6	3550.0	188.6	2675.0	315.1
5	Owner: Office and Yard	47	11	1036.0	470.1	688.5	109.5	1110.0	107.2	1664.0	334.8	3001.0	179.5
6	Outside Laborer	44	2	540.0	151.1	405.7	44.4	737.5	56.3	2011.0	63.2	1321.0	53.0
MEAN				967.9	312.0	769.1	96.7	1088.8	84.0	1820.2	155.8	2215.8	170.4
1 Control: Chemist				47.8	4.2	42.4	2.8	68.0	2.9	42.5	4.3	38.0	2.6

TABLE 2. *Recovery data, PCP analyses*

Sample	Spiking Level, ng/g	Recovery of Duplicate Samples, %
Urine	.1	102
	.5	107
	5.0	103
	50.0	99
Serum	.1	98
	.5	96
	5.0	93
	50.0	97
Air	.1	93
	.5	95
	5.0	100
	50.0	100

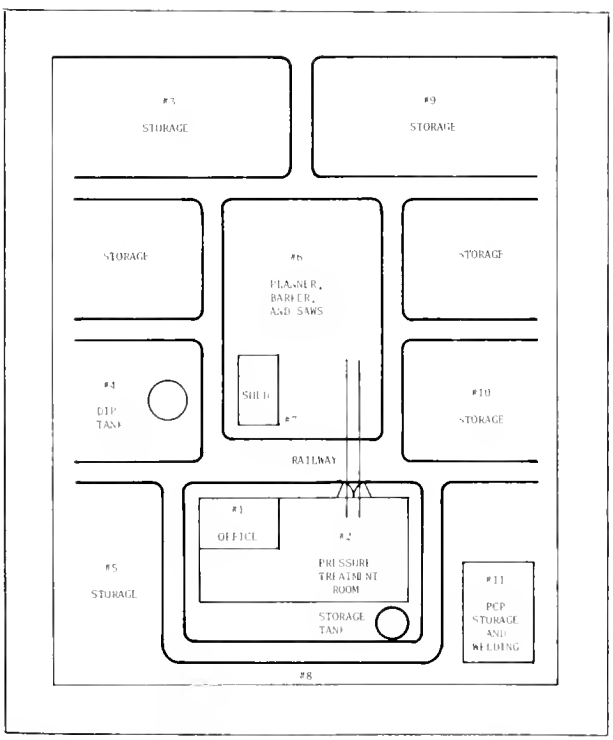

FIGURE 1. *Map of pentachlorophenol plant showing air sampling sites*

number due to the concentration and length of exposure (*8*). Six exposed and four control samples were used for the study. Background data on the control group of the cytogenetic study are listed in Table 3.

TABLE 3. *Background data on control group members of cytogenic studies*

Subject	Sex	Age, years	Occupation	Exposure, years
1X	M	50	Chemist	30
2X	M	31	Chemist	8
3X	M	26	Medical Technologist	4
4X	M	20	Laboratory Technician	2

All samples analyzed for PCP concentrations were injected into a Micro-Tek 220 gas chromatograph fitted with electron-capture detectors. Two columns were used, one as the working column and the other for confirmation. Parameters for the gas-liquid chromatography are listed below:

Columns: (A) Pyrex, u-shaped, 6 ft by ¼ in., packed with 100/120 mesh 4 percent SE-30/6 percent QF-1
(B) Pyrex, u-shaped, 6 ft by ¼ in., packed with 80/100 mesh 1.5 percent OV-17/1.95 percent QF-1

Temperatures: Oven 200°C
Detector 205°C
Inlet 215°C
Transfer 245°C

Carrier Gas: Nitrogen

Flow Rate: 4 percent SE-30/6 percent QF-1: 100 ml/min
1.4 percent OV-17/1.95 percent QF-1: 70 ml/min

Results and Discussion

Serum PCP levels (Table 2) of all subjects decreased during February and rose slightly in March and again in April with the exception of subject number 1, the office manager. Residue in his serum stayed at approxi-

mately the same level throughout the study. In May subjects 3, 5, and 2 had increased serum levels; those of subjects 4 and 6 returned to a lower level. This phenomenon cannot be explained by the investigator.

Serum PCP levels ranged from 348.4 to 3,963.0 ppb for the exposed group and from 38.0 to 68.0 ppb for the control group. The average levels for the exposed and control groups were 1,372.1 ppb and 47.7 ppb, respectively.

PCP levels in urine were quite a bit lower than those in serum (Table 2). Levels started at a high average (312 ppb) in January, plunged to a low (96.7 ppb) in February, stayed nearly the same in March (84.0 ppb), and then increased (155.8 ppb) in April. Levels in subjects 5, 6, and 2 dropped in May, although those of subjects 4, 3, and 1 continued to increase. Urine levels for the exposed group ranged from 41.3 to 760.6 ppb PCP. Levels in urine averaged 163.8 ppb for the exposed group and 3.4 ppb for the control group.

Results of the present study are comparable to those of urine analyses done by Cranmer and Freal in Florida. They analyzed six control urine samples in which PCP levels ranged from 2.2 to 10.8 ppb with a mean of 4.85 ppb. Levels in four urine samples from occupationally exposed individuals ranged from 24.1 to 265 ppb with a mean of 119.8 ppb PCP (*9*).

Bevenue et al. found PCP in urine in Hawaii. Levels ranged from 3 to 357,000 ppb with a mean value of 1,244 ppb for 211 samples of occupationally exposed individuals (*10*). They also reported on PCP in the urine of 290 individuals who were not exposed; levels ranged from 0 to 1,840 ppb with a mean of 40 ppb (*11*).

PCP residues in the urine of exposed workers studied by Bevenue et al. were 7.6 times higher than levels found in the urine of exposed workers in this study and 10.4 times higher than residues in the urine of exposed workers studied by Cranmer and Freal. Levels in the urine of the Hawaiian control group were 11.8 times higher than those of this study and 8.2 times higher than those taken in Florida. These discrepancies may be caused by the heavy use of PCP-treated products in Hawaii (*12, 13*) where PCP is used on wood products to control mold, mildew, and termites, on pineapple and in sugarcane fields (*10, 13*), and in many homes to control spot infestations of insects (*10*).

Air samples were collected during the middle of the work week on the same basis as the serum and urine samples (Table 4). Air samples 1 and 2 cannot be compared to the others because they were taken inside the pressure treatment building. Depending on which systems were working, levels would elevate and regress. Air sampling at all sites except 1 and 2 started in January. Levels were below 300 ng PCP/m^3 and dropped slightly in February. Residues at sites 7, 9, 10, and 11 increased in March to levels over 300 ng/m^3 while those at sites 3, 4, 5, and 6 stayed about the same. In April residues at all but two sites fell below 300 ng/m^3. In May levels rose at all stations except site 10. Residues at sites 1, 2, 6, and 11 rose dramatically to an average 3,546.9 ng/m^3 in May.

TABLE 4. *PCP residues in the air of a PCP plant, Idaho—1972*

Site	Residues, ng/m^3				
	January	February	March	April	May
1	1688.6	3189.8	571.1	187.9	3453.3
2	4854.2	15275.1	517.4	2206.8	7010.4
3	64.6	58.9	56.0	45.9	331.1
4	106.2	21.9	18.7	12.2	801.9
5	54.8	11.5	10.6	8.3	533.6
6	169.7	26.9	90.1	5.1	2581.5
7	61.9	30.1	561.4	42.9	739.7
8	87.3	79.7	86.5	87.5	1127.3
9	144.0	86.8	932.6	172.8	190.8
10	34.1	9.1	367.8	48.7	79.6
11	241.2	230.4	495.4	75.3	3917.6
TOTAL	7506.6	19020.2	3707.6	2893.4	20766.8
AVERAGE	682.4	1729.1	337.0	263.0	1887.9

Work done in Russia by Tabakova established a maximum permissible concentration of 40 ng/m^3 PCP in the air (*14*). Using this criterion as a maximum allowable limit, one can see that residues in the air of the general work areas throughout the plant are over the suggested tolerance a good portion of the time.

Statistical analyses of the exposed and control groups for the incidence of chromosomal aberrations (breaks and gaps) show that the difference in the means is not significant at the 0.05 level of confidence. This does not mean that PCP does not cause chromosome damage, only that the exposed and control groups studied were too small to permit significant generalizations and that there were no extreme differences in chromosomal aberrations between the exposed and control groups. Aberrations found are listed in Table 5.

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TABLE 5. *Chromosomal aberrations in workers in a PCP plant, Idaho—1972*

Subject	January		February		March		April		May	
	No. Breaks	No. Gaps	No. Breaks	No. Gaps	No. Breaks	No. Gaps	No. Breaks	No. Gaps	No. Breaks	No. Gaps
Exposed Group										
1	0	0	1	1	0	0	0	0	0	1
2	0	0	0	2	0	1	1	2	1	0
3	2	2	0	3	3	0	0	0	0	0
4	0	1	0	1	0	2	0	1	0	1
5	0	0	0	1	0	0	0	0	0	3
6	0	0	3	0	1	3	0	0	0	0
Subjects with aberrations, %	17	33	33	83	17	66	17	33	17	33
Average aberrations per 150 cells, %	1.3	2.0	2.6	5.3	0.6	6.0	0.6	0.6	0.6	3.3
Control Group										
1X	0	1	0	1	0	2	0	1	0	2
2X	0	0	0	0	0	1	0	0	0	0
3X	0	1	0	0	0	1	0	0	0	1
4X	0	0	0	1	1	1	0	1	0	0
Subjects with aberrations, %	0	50	0	50	25	100	0	50	0	50
Average aberrations per 150 cells, %	0	2.0	0	2.0	0.1	5.0	0	2.0	0	3.0

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
ATRAZINE	2-Chloro-4-ethylamino-6-isopropylamino-*s*-triazine
BHC (BENZENE HEXACHLORIDE)	1,2,3,4,5,6-Hexachlorocyclohexane (mixture of isomers). Commercial product contains several isomers of which *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.
CHLORPYRIFOS	*O,O*-Diethyl *O*-(3,5,6-trichloro-2-pyridyl) phosphorothioate
DDD	See TDE.
DDE	Dichlorodiphenyl dichloro-ethylene (degradation product of DDT) *o,p'*-DDE: 1,1-Dichloro-2-(*o*-chlorophenyl)-2-(*p*-chlorophenyl) ethylene *p,p'*-DDE: 1,1-Dichloro-2,2-bis(*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
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
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
LINDANE	*Gamma* isomer of benzene hexachloride (1,2,3,4,5,6-hexachlorocyclohexane) of 99+% purity
MIREX	Dodecachlorooctahydro-1,3,4-metheno-2H-cyclobuta[cd]pentalene
MONOCROTOPHOS	*Cis*-3-(dimethoxyphosphinyloxy)-*N*-methylcrotonamide
PCB'S (POLYCHLORINATED BIPHENYLS)	Mixtures of chlorinated byphenyl compounds having various percentages of chlorine
PCP	Pentachlorophenol
TDE	2,2-Bis(*p*-chlorophenyl)-1,1-dichloroethane

Information for Contributors

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CONTENTS

Volume 9 March 1976 Number 4

BRIEF

Residues of Organochlorines and Heavy Metals in Ruddy Ducks from the Delaware River, 1973 [1]

Donald H. White and T. Earl Kaiser

ABSTRACT

In December 1973, eight ruddy ducks killed in an oil spill on the Delaware River were collected to be analyzed for residues of environmental pollutants. Whole carcasses were analyzed for organochlorine pesticides and livers were examined for lead, cadmium, and mercury. Residues of polychlorinated biphenyls and DDT and/or its metabolites were present in all carcasses. Dieldrin and hexachlorobenzene were present in seven of the eight samples. All livers contained detectable levels of lead, cadmium, and mercury.

Introduction

Ruddy ducks feed primarily on benthic organisms (*1*) in estuaries that may be contaminated with various environmental pollutants. In December 1973 approximately 2,000 ruddy ducks (*Oxyura jamaicensis*) died following an oil spill on the Delaware River near Paulsboro, New Jersey. Many of these birds were brought to the Patuxent Wildlife Research Center for analysis of gizzard contents. Because little is known about environmental pollutants in ruddy ducks, authors analyzed tissues from some of these birds to identify and quantify toxic chemicals present.

Analytical Methods

Eight ruddy ducks including two adults and two immatures of each sex were selected at random for analysis of organochlorine pesticides in the carcasses and heavy metals in the livers. The skin, beak, feet, gastrointestinal tract, and liver were removed and the carcass was homogenized with a Hobart food cutter. A 10-g aliquot was blended with sodium sulfate and extracted for 7 hours with hexane on a Soxhlet apparatus. An aliquot of the extract, equivalent to 4 g of the carcass, was placed on a florisil column to remove lipids. Pesticides and polychlorinated biphenyls (PCB's) were separated into three fractions on a Silicar column. The organochlorine pesticides and PCB's were identified and quantified by gas chromatography on a 4 percent SE-30/6 percent QF-1 column. Limits of sensitivity were 0.1 ppm for pesticides and 0.5 ppm for PCB's on a wet-weight basis. Residues in 25 percent of the samples were confirmed with a gas chromatograph/mass spectrometer. These procedures are described in detail by Cromartie et al. (*2*).

Livers were analyzed for lead, cadmium, and mercury at the Environmental Trace Substances Center, Columbia, Mo. Samples for lead and cadmium analysis were ashed using a nitric and perchloric acid mixture and the metals were solubilized in an acidic solution. Samples for mercury analysis were digested under reflux conditions with concentrated nitric acid. Stannous chloride was added to reduce the ionic mercury to elemental mercury. Samples and standards were aspirated into an appropriate flame of an atomic absorption spectrophotometer. A hollow cathode lamp for each metal of interest provided the characteristic line for the particular metal. Limits of sensitivity were 0.1 ppm for lead, 0.01 ppm for cadmium, and 0.02 ppm for mercury on a wet-weight basis.

Results and Discussion

Levels of organochlorine residues in carcasses are presented in Table 1. DDE was present in all samples at levels ranging from 1.1 to 4.5 ppm. PCB's equivalent to Aroclor 1260 also were detected in all samples ranging from 2.8 to 10 ppm. DDT and/or DDD levels were below 0.34 ppm in all but one sample. Dieldrin and hexachlorobenzene occurred in all but one sample, but neither exceeded 0.36 ppm.

All livers contained detectable levels of lead, cadmium, and mercury (Table 2). Heavy metals were detected in the following concentrations: lead, 0.19-0.61 ppm; cadmium, 0.27-1.60 ppm; and mercury, 0.06-0.74 ppm.

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

TABLE 1. *Organochlorine residues in ruddy duck carcasses, Delaware River, 1973*

Age	Sex	Residues, ppm wet weight					
		p,p'-DDE	*p,p'*-DDD	*p,p'*-DDT	dieldrin	HCB	PCB's [1]
Adult	M	4.5	0.10	0.23	0.33	0.07	10.0
Adult	M	3.3	0.14	0.14	0.18	0.08	6.5
Adult	F	2.3	0.23	0.33	0.35	0.08	7.0
Adult	F	1.1	0.17	ND	0.30	0.24	2.8
Immature	M	2.4	0.21	ND	0.19	ND	3.5
Immature	M	3.5	0.13	0.28	0.35	0.22	8.0
Immature	F	1.3	ND	ND	ND	0.24	2.8
Immature	F	2.1	0.18	0.20	0.20	0.06	4.8
Mean ± S. E.		2.6±0.41	0.15±0.03	0.15±0.05	0.24±0.04	0.13±0.03	5.7±0.93

NOTE: ND = not detected.
[1] PCB's are equivalent to Aroclor 1260.

TABLE 2. *Residues of lead, cadmium, and mercury in ruddy duck livers, Delaware River, 1973*

Age	Sex	Residues, ppm wet weight		
		Lead	Cadmium	Mercury
Adult	M	0.61	1.60	0.09
Adult	M	0.40	0.70	0.15
Adult	F	0.59	0.56	0.12
Adult	F	0.19	0.51	0.74
Immature	M	0.25	0.38	0.08
Immature	M	0.24	0.41	0.10
Immature	F	0.21	0.27	0.06
Immature	F	0.32	0.41	0.10
Mean ± S.E.		0.35±0.06	0.61±0.15	0.18±0.08

Residue levels of these metals were similar to those found in livers of canvasbacks from the Chesapeake Bay region (*3*). Lead levels appear to be somewhat higher in ruddy duck livers based on experimental studies with mallards at Patuxent Wildlife Research Center (*4*). The ruddy duck livers contained levels of lead similar to those in livers of mallards dosed with a single shot and sacrificed after 1 month.

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RESIDUES IN FOOD AND FEED

Pesticide Residues in Total Diet Samples (IX)

R. D. Johnson and D. D. Manske [1]

ABSTRACT

During the ninth year of the Total Diet Study, pesticide residues remained at the relatively low levels reported previously. 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 found are reported for the period August 1972 through July 1973 by food class. Lead, selenium, and zinc data are included for the first time. During this period, the individual items used in making up the dairy and meat composites in four market baskets were analyzed for pesticides and the results are included. Results of recovery studies within various classes of residues are also presented.

Introduction

This report presents the results obtained in the Total Diet Program (*1*) of the Food and Drug Administration (FDA), U.S. Department of Health, Education, and Welfare, from August 1972 through July 1973. Amounts and types of residues found from June 1964 through July 1972 have been described in earlier reports (*2-9*). Samples were collected in 30 different grocery markets in 30 different cities. Conditions, procedures, methodology (*10-15*), and the limits of quantitation were the same as those described in the last report (*8, 10-15*. Also: H. K. Hundley and J. C. Underwood, Food and Drug Administration, 1970: personal communication). Lead and selenium were added to the program because of the increased awareness of the hazards presented by these elements. Zinc, while not recognized as a toxic metal, has been included in this program because of its apparent neutralizing effect on the toxicity of cadmium. These new methodologies and their quantitative limits are: lead by atomic absorption spectroscopy (*16*): 0.1 parts per million (ppm); selenium by fluorometry (*17*): 0.1 ppm; and zinc by atomic absorption spectroscopy (*18*): 0.5 ppm. This year for the first time individual items used in making up the dairy and meat food group composites of four market baskets were analyzed for pesticides.

[1] Kansas City Field Office Laboratory, Food and Drug Administration, U.S. Department of Health, Education, and Welfare, Kansas City, Mo. 64106.

Results

During the current reporting period, 1,729 residues of 40 different compounds were found. Excluding lead, zinc, and selenium, the new elements which were added during this period, 988 residues of 37 different materials were found. In the previous reporting period, 1,003 residues of 35 different compounds were found in 35 market baskets. The 40 different residues found are listed in decreasing order of frequency in Table 1. Table 2 lists various chemical residues found, according to food class. Table 3 gives the levels of chemical residues found, according to food class. The average stated in Table 3 is based on 30 composites examined and does not include any trace values found in its calculation. 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 for each of the 12 food composites are discussed below; maximum levels appear in parentheses. None of the reported findings have been corrected for recoveries obtained in recovery experiments. A summary of recovery studies is given in Table 4.

DAIRY PRODUCTS

All 30 composites of dairy products contained pesticide residues. Organochlorine residues were the most common and they appeared in all 30 composites. The most common organochlorines and their maximum concentrations were dieldrin, 0.005 ppm; BHC, 0.004 ppm; DDE, 0.012 ppm; and heptachlor epoxide, 0.002 ppm. Also present in this composite were DDT, TDE, lindane, methoxychlor, polychlorinated biphenyls (PCB's), PCP, HCB, and diazinon. Zinc, ranging from 3.1 to 8.2 ppm, appeared in all 30 composites. Selenium, lead,

cadmium, and arsenic were occasionally found in this composite.

MEAT, FISH, AND POULTRY

Ten organochlorine residues were found in varying combinations in all 30 composites. The most common organochlorine residues and their maximum concentrations were DDE, 0.114 ppm; dieldrin, 0.010 ppm; DDT, 0.015 ppm; heptachlor epoxide, 0.002 ppm; BHC, 0.003 ppm; and TDE, 0.011 ppm. Other residues found were lindane, PCB's, diazinon, HCB, TCNB, and ethion. Selenium and zinc, ranging from trace to 0.3 ppm and from 5.1 to 33.4 ppm, respectively, were found in all 30 composites. Mercury appeared in 29 of the 30 composites with a high value of 0.04 ppm. Lead, cadmium, and arsenic were also observed.

GRAIN AND CEREAL PRODUCTS

Malathion, ranging from 0.004 to 0.099 ppm, appeared in all 30 composites examined. Additional organophosphorus residues were diazinon and Dursban. Other residues found were DDT, dieldrin, lindane, PCB's, DDE, TDE, TCNB, methoxychlor, ronnel, and orthophenylphenol. Zinc and cadmium, ranging from 4.7 to 10.4 ppm and from 0.02 to 0.05 ppm, respectively, were found in all 30 composites. Selenium, ranging from 0.1 to 0.4 ppm, was found in 29 composites. Lead, arsenic, and mercury were also found.

POTATOES

Cadmium and zinc, ranging from 0.02 to 0.12 ppm and from 1.7 to 5.7 ppm, respectively, were found in all 30 composites. Lead occurred at levels up to 0.1 ppm in 17 composites. Selenium and arsenic were also found. Eleven organochlorine residues were observed in 24 of the 30 composites examined. The most common and their maximum values were dieldrin, 0.007 ppm; CIPC, 1.36 ppm; DDE, 0.005 ppm; DDT, 0.005 ppm; and endosulfan, 0.015 ppm. Other residues found were TCNB, TDE, diazinon, heptachlor epoxide, lindane, PCB's, parathion, carbaryl, endrin, and 2,4-D.

LEAFY VEGETABLES

Seven organochlorine residues were observed in varying combinations in 24 of the 30 composites. Organophosphorus residues were found in 20 of these composites. The most common of these compounds and their maximum levels were endosulfan, 0.439 ppm; DDE, 0.006 ppm; parathion, 0.017; and diazinon, 0.009 ppm; Cadmium and zinc ranging from 0.01 to 0.28 ppm and from 0.5 to 4.0 ppm, respectively, were found in all 30 composites. Lead occurred in 25 composites ranging from trace levels to 0.5 ppm. Other residues found were selenium, methyl parathion, dieldrin, TDE, arsenic, DDT, carbaryl, Perthane, and DCPA.

LEGUME VEGETABLES

Zinc and lead, ranging from 3.7 to 10.5 ppm and from trace to 0.7 ppm, respectively, were found in all 30 composites. Other residues were selenium, cadmium, parathion, dieldrin, arsenic, TDE, carbaryl, PCP, an Strobane.

ROOT VEGETABLES

Zinc, ranging from 0.6 to 4.2 ppm, was found in all 3 composites. Lead appeared in 25 composites at a max mum level of 1.0 ppm. Cadmium occurred at levels u to 0.06 ppm in 24 composites. Other residues foun were selenium, DDE, arsenic, DDT, diazinon, mercury parathion, ethion, carbaryl, and HCB.

GARDEN FRUITS

Ten organochlorine residues were detected in 22 of 3 composites. The most common and their maximur levels were dieldrin, 0.012 ppm; TDE, 0.009 ppm; an endosulfan, 0.002 ppm. Zinc, ranging from 0.8 to 5. ppm, occurred in all 30 composites. Lead was found i 27 composites at levels up to 0.3 ppm and cadmiun was found in 25 composites at levels up to 0.06 ppm Other residues found were selenium, diazinon, DDE BHC, DDT, carbaryl, parathion, lindane, TCNB, aldrin and chlordane.

FRUITS

Six organophosphorus residues were found in variou combinations in 16 of 30 composites. The most commo and the highest levels found were ethion, 0.099 ppm diazinon, 0.016 ppm; and malathion, 0.073 ppm. Zinc ranging from 0.1 to 3.2 ppm, was found in all 3 composites. Lead was found in 21 of the composites the highest level observed was 0.4 ppm. Other residue found were carbaryl, selenium, cadmium, endosulfan Perthane, dicofol, dieldrin, arsenic, parathion, TCNB ronnel, Dursban, and phosalone.

OILS, FATS, AND SHORTENING

Ten organochlorine residues appeared in 14 of the 3 composites. The most common and their maximun levels were dieldrin, 0.004 ppm; HCB, 0.006 ppm; PCA 0.032 ppm; and PCNB, 0.002 ppm. Malathion, rangin from trace to 0.101 ppm, was found in 18 composites Zinc occurred in 30 composites at levels up to 9.1 ppn and cadmium appeared in 29 composites at levels u to 0.06 ppm. Other residues found were lead, selenium diazinon, DDE, BHC, TDE, arsenic, DDT, mercury PCB, and TCNB.

SUGARS AND ADJUNCTS

Five organochlorine residues were observed in 14 com posites. The most common and their maximum level were lindane, 0.002 ppm; BHC, 0.005 ppm; and PCP 0.02 ppm. Zinc, ranging from 1.0 to 5.1 ppm, wa found in 30 composites. Lead occurred in 19 composite and cadmium in 13 composites at levels up to 0.1 ppm and 0.06 ppm, respectively. Other residues found wer malathion, selenium, DDT, TDE, and arsenic.

BEVERAGES

Metal residues were the only ones found in beverages Zinc was the most common; it occurred in 29 of th 30 composites at levels up to 5.4 ppm. Lead, cadmium and selenium were also observed.

Discussion

Organochlorine residues appeared in 187 of the 360 composites examined, or 52 percent of total. Corresponding quantities in previous years were 54 percent in 1971-72, 61.4 percent in 1970-71, and 74.2 percent in 1969-70. Organophosphorus residues in the current reporting period were found in 113 composites, or 31 percent. Corresponding percentages in previous years were 27.8, 21.4, and 20.6, respectively.

Carbaryl was found in 12 composites during the present reporting period; 10 of these findings were at the trace level. This is a higher incidence than the 6 findings of the previous reporting period but still below the 20 occurrences in 1970-71. Orthophenylphenol, which is detected with carbaryl, occurred in only one composite and that residue was at the trace level. In the previous reporting period, orthophenylphenol was detected seven times.

Only one composite containing a chlorophenoxy acid herbicide was found in this reporting period. Pentachlorophenol, which is detected by the method for chlorophenoxy acid, was found nine times.

Zinc was detected in all but one composite examined, ranging from 0.1 to 33.4 ppm. The second most commonly occurring metal, lead, was found in all 12 food classes and was encountered in 242 of the 360 composites examined, at levels ranging from trace to 1.0 ppm. Cadmium and selenium were also found in all 12 composites. The highest of the 217 findings of cadmium was 0.28 ppm and the highest of the 140 findings of selenium was 0.40 ppm.

Mercury appeared in 32 composites and, as in the past, the meat, fish, and poultry class was the source of most findings. The highest value was 0.04 ppm.

The program was expanded this year to include individual commodity analysis for chlorinated, organophosphate, and PCP residues in food groups I (dairy) and II (meats) on 4 of the 30 Total Diet samples. Composites I and II were selected because of past data showing that most significant chlorinated residues occurred in these two groups (*2-9, 19*). Individual commodity analysis results are shown in Table 5 (dairy group) and Table 6 (meat group). 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, occasionally the fortification level 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, the recovery improves. Recovery data demonstrate that individual, low-level residues may vary from the so-called true value but overall findings are useful in appraising the national residue picture.

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TABLE 1. *Pesticide residues found in food composites, August 1972–July 1973*

Chemical	No. Composites With Residues	No. Positive Composites With Residues Reported As Trace [1]	Range, ppm
ZINC	359	0	0.1-33.4
LEAD	242	152	0.1-1.0
CADMIUM	217	0	0.01-0.28
SELENIUM	140	80	0.1-0.40
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	107	29	0.0002-0.012
DDE 1,1-dichloro-2,2-bis (*p*-chlorophenyl) ethylene (all isomers are included in reportings)	81	27	0.0004-0.114
BHC 1,2,3,4,5,6-hexachlorocyclohexane, mixed isomers except gamma	59	15	0.0002-0.005
DDT 1,1,1-trichloro-2,2-bis (*p*-chlorophenyl) ethane (all isomers are included in reportings)	54	25	0.0004-0.015
DIAZINON *O,O*-diethyl *o*-(2-isopropyl-6-methyl-4-pyrimidyl) phosphorothioate	54	24	0.001-0.044
MALATHION diethylmercaptosuccinate, *S*-ester with *O,O*-dimethyl phosphorodithioate	54	4	0.003-0.101
TDE 1,1-dichloro-2,2-bis (*p*-chlorophenyl) ethane (all isomers are included in reportings)	48	24	0.001-0.021
HEPTACHLOR EPOXIDE 1,4,5,6,7,8,8-heptachloro-2,3-epoxy-3a, 4,7,7a-tetrahydro-4,7-methanoindan	46	26	0.0006-0.002
LINDANE 1,2,3,4,5,6-hexachlorocyclohexane, 99% or more gamma isomer	39	13	0.0003-0.006
MERCURY	32	20	0.02-0.04
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 iclude isomers I, II, and the sulfate)	29	13	0.002-0.439
ARSENIC (As_2O_3)	22	14	0.1-0.2
PCB'S (polychlorinated biphenyls) calculated as Aroclor with varied chlorine content	20	19	0.073
PARATHION *O,O*-diethyl *o-p*-nitrophenyl phosphorothioate	19	8	0.004-0.017
ETHION *O,O,O',O'*-tetraethyl *S,S'*-methylene bisphosphorodithioate	14	10	0.004-0.099
CIPC isopropyl *n*-(3-chlorophenyl) carbamate	13	0	0.027-1.36
CARBARYL 1-naphthyl methyl carbamate	12	10	0.05-0.10
HCB hexachlorobenzene	10	3	0.0006-0.041
PCP pentachlorophenol	9	1	0.01-0.02
TCNB 1,2,4,5-tetrachloro-3-nitrobenzene	7	1	0.001-0.173
PCA pentachloroaniline	6	0	0.003-0.032
METHOXYCHLOR 1,1,1-trichloro-2,2-bis (*p*-methoxyphenyl) ethane	6	5	0.005
PCNB pentachloronitrobenzene	5	3	0.0008-0.002
METHYL PARATHION *O,O*-dimethyl *o-p*-nitrophenyl phosphorothioate	5	2	0.002-0.003
PERTHANE 1,1-dichloro-2,2-bis (*p*-ethylphenyl) ethane	4	0	0.013-1.32
DICOFOL (KELTHANE) 4,4'-dichloro-α-(trichloromethyl) benzhydrol	3	1	0.018-0.044
RONNEL *O,O*-dimethyl (*o*-2,4,5-trichlorophenyl) phosphorothioate	2	2	T
DURSBAN *O,O*-diethyl-*o*-(3,5,6-trichloro-2-pyridyl) phosphorothioate	2	0	0.003-0.005
PHOSALONE *O,O*-diethyl *S*-(6-chloro-2-oxobenzoxazolin-3-yl) methyl phosphorodithioate	1	0	0.015
STROBANE terpene polychlorinates (65-66% chlorine)	1	1	T
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	1	0	0.005
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	0.002
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

(Continued next page)

TABLE 1 (cont'd). *Pesticide residues found in food composites, August 1972–July 1973*

Chemical	No. Composites With Residues	No. Positive Composites With Residues Reported As Trace [1]	Range, ppm
ORTHOPHENYLPHENOL 2-hydroxydiphenyl	1	1	T
2,4-D 2,4-dichlorophenoxyacetic acid	1	0	0.014
DCPA (DACTHAL) 2,3,5,6-tetrachloroterephthalic acid dimethyl ester	1	0	0.013

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

TABLE 2. *Occurrence frequency of chemical residues by food class, August 1972–July 1973*

	Number of Occurrences											
	Food Class [1]											
Chemical	I	II	III	IV	V	VI	VII	VIII	IX	X	XI	XII
Zinc	30	30	30	30	30	30	30	30	30	30	30	29
Lead	10	23	23	17	25	30	25	27	21	16	19	6
Cadmium	5	12	30	30	30	10	24	25	4	29	13	5
Selenium	13	30	29	7	10	12	6	10	5	12	3	3
Dieldrin	26	29	3	11	5	2		22	1	8		
DDE	21	30	1	9	12		3	2		3		
BHC	24	22						2		3	8	
DDT	10	28	4	6	1		1	2		1	1	
Diazinon	2	3	21	2	9		1	6	5	5		
Malathion			30						3	18	3	
TDE	10	21	1	2	3	1		6		3	1	
Heptachlor Epoxide	21	24		1								
Lindane	7	16	3	1				1			11	
Mercury		29	1				1			1		
Endosulfan				4	17			4	4			
Arsenic	1	8	2	1	2	2	2		1	2	1	
PCB's	3	10	5	1						1		
Parathion				1	11	3	1	2	1			
Ethion		1					1		12			
CIPC				13								
Carbaryl				1		1	1	2	7			
HCB	1	2					1			6		
PCP	2					1					6	
TCNB		1	1	2				1	1	1		
PCA										6		
Methoxychlor	5		1									
PCNB										5		
Methyl Parathion					5							
Perthane					1				3			
Dicofol									3			
Ronnell			1						1			
Dursban			1						1			
Phosalone									1			
Strobane						1						
Endrin				1								
Aldrin								1				
Chlordane								1				
Orthophenylphenol			1									
2,4-D				1								
DCPA					1							

[1] See Table 3 for identification of the 12 food classes.

TABLE 3. *Levels of chemical residues found by food class, August 1972–July 1973*

I. Dairy Products
Residues, ppm

ZINC	
Average	5.0
Positive Composites	
Total No.	30
No. Reported as Trace	0
Range	3.1-8.2
DIELDRIN	
Average	0.002
Positive Composites	
Total No.	26
No. Reported as Trace	4
Range	T-0.005
BHC	
Average	0.001
Positive Composites	
Total No.	24
No. Reported as Trace	4
Range	T-0.004
DDE	
Average	0.002
Positive Composites	
Total No.	21
No. Reported as Trace	8
Range	T-0.012
HEPTACHLOR EPOXIDE	
Average	T
Positive Composites	
Total No.	21
No. Reported as Trace	13
Range	T-0.002
SELENIUM	
Average	T
Positive Composites	
Total No.	13
No. Reported as Trace	13
Range	T
DDT	
Average	T
Positive Composites	
Total No.	10
No. Reported as Trace	10
Range	T
LEAD	
Average	T
Positive Composites	
Total No.	10
No. Reported as Trace	10
Range	T
TDE	
Average	T
Positive Composites	
Total No.	10
No. Reported as Trace	9
Range	T-0.001
LINDANE	
Average	T
Positive Composites	
Total No.	7
No. Reported as Trace	4
Range	T-0.0006
CADMIUM	
Average	T
Positive Composites	
Total No.	5
No. Reported as Trace	0
Range	0.01-0.06
METHOXYCHLOR	
Average	T
Positive Composites	
Total No.	5
No. Reported as Trace	4
Range	T-0.005
PCB's	
Average	T
Positive Composites	
Total No.	3
No. Reported as Trace	3
Range	T
DIAZINON	
Average	T
Positive Composites	
Total No.	2
No. Reported as Trace	1
Range	T-0.006
PCP	
Average	T
Positive Composites	
Total No.	2
No. Reported as Trace	1
Range	T-0.010
ARSENIC	
Average	T
Positive Composites	
Total No.	1
No. Reported as Trace	0
Range	0.1
HCB	
Average	T
Positive Composites	
Total No.	1
No. Reported as Trace	0
Range	0.0006

II. Meat, Fish, and Poultry
Residues, ppm

DDE	
Average	0.012
Positive Composites	
Total No.	30
No. Reported as Trace	3
Range	T-0.114
ZINC	
Average	26.4
Positive Composites	
Total No.	30
No. Reported as Trace	0
Range	5.1-33.4
SELENIUM	
Average	0.2
Positive Composites	
Total No.	30
No. Reported as Trace	1
Range	T-0.3
DIELDRIN	
Average	0.004
Positive Composites	
Total No.	29
No. Reported as Trace	0
Range	0.001-0.010
MERCURY	
Average	0.01
Positive Composites	
Total No.	29
No. Reported as Trace	17
Range	T-0.04
DDT	
Average	0.006
Positive Composites	
Total No.	28
No. Reported as Trace	3
Range	T-0.015
HEPTACHLOR EPOXIDE	
Average	T
Positive Composites	
Total No.	24
No. Reported as Trace	12
Range	T-0.002
LEAD	
Average	T
Positive Composites	
Total No.	23
No. Reported as Trace	20
Range	T-0.2
BHC	
Average	T
Positive Composites	
Total No.	22
No. Reported as Trace	5
Range	T-0.003
TDE	
Average	0.002
Positive Composites	
Total No.	21
No. Reported as Trace	4
Range	T-0.011
LINDANE	
Average	T
Positive Composites	
Total No.	16
No. Reported as Trace	4
Range	T-0.003
CADMIUM	
Average	0.01
Positive Composites	
Total No.	12
No. Reported as Trace	0
Range	0.01-0.06
PCB's	
Average	T
Positive Composites	
Total No.	10
No. Reported as Trace	10
Range	T
ARSENIC	
Average	T
Positive Composites	
Total No.	8
No. Reported as Trace	3
Range	T-0.2
DIAZINON	
Average	T
Positive Composites	
Total No.	3
No. Reported as Trace	1
Range	T-0.003
HCB	
Average	0.001
Positive Composites	
Total No.	2
No. Reported as Trace	1
Range	T-0.041
ETHION	
Average	T
Positive Composites	
Total No.	1
No. Reported as Trace	1
Range	T
TCNB	
Average	T
Positive Composites	
Total No.	1
No. Reported as Trace	0
Range	0.0011

(Continued next page)

TABLE 3 (cont'd). *Levels of chemical residues found by food class, August 1972–July 1973*

III. Grain and Cereal
Residues, ppm

CADMIUM		ZINC		TCNB	
Average	0.03	Average	8.1	Average	T
Positive Composites		Positive Composites		Positive Composites	
Total No.	30	Total No.	30	Total No.	1
No. Reported as Trace	0	No. Reported as Trace	0	No. Reported as Trace	0
Range	0.02-0.05	Range	4.7-10.4	Range	0.005
MALATHION		SELENIUM			
Average	0.024	Average	0.2		
Positive Composites		Positive Composites			
Total No.	30	Total No.	29		
No. Reported as Trace	0	No. Reported as Trace	0		
Range	0.004-0.099	Range	0.1-0.4		

IV. Potatoes
Residues, ppm

CADMIUM		DDT		2,4-D	
Average	0.05	Average	T	Average	T
Positive Composites		Positive Composites		Positive Composites	
Total No.	30	Total No.	6	Total No.	1
No. Reported as Trace	0	No. Reported as Trace	4	No. Reported as Trace	0
Range	0.02-0.12	Range	T-0.005	Range	0.014
ZINC		ENDOSULFAN		ENDRIN	
Average	3.7	Average	0.001	Average	T
Positive Composites		Positive Composites		Positive Composites	
Total No.	30	Total No.	4	Total No.	1
No. Reported as Trace	0	No. Reported as Trace	1	No. Reported as Trace	0
Range	1.7-5.7	Range	T-0.015	Range	0.005
LEAD		DIAZINON		HEPTACHLOR EPOXIDE	
Average	T	Average	T	Average	T
Positive Composites		Positive Composites		Positive Composites	
Total No.	17	Total No.	2	Total No.	1
No. Reported as Trace	16	No. Reported as Trace	2	No. Reported as Trace	1
Range	T-0.1	Range	T	Range	T
CIPC		TDE		LINDANE	
Average	0.143	Average	T	Average	T
Positive Composites		Positive Composites		Positive Composites	
Total No.	13	Total No.	2	Total No.	1
No. Reported as Trace	0	No. Reported as Trace	2	No. Reported as Trace	0
Range	0.027-1.36	Range	T	Range	0.001
DIELDRIN		TCNB		PARATHION	
Average	0.001	Average	0.007	Average	T
Positive Composites		Positive Composites		Positive Composites	
Total No.	11	Total No.	2	Total No.	1
No. Reported as Trace	4	No. Reported as Trace	0	No. Reported as Trace	1
Range	T-0.007	Range	0.032-0.173	Range	T
DDE		ARSENIC		PCB's	
Average	0.001	Average	T	Average	T
Positive Composites		Positive Composites		Positive Composites	
Total No.	9	Total No.	1	Total No.	1
No. Reported as Trace	4	No. Reported as Trace	1	No. Reported as Trace	1
Range	T-0.005	Range	T	Range	T
SELENIUM		CARBARYL			
Average	T	Average	T		
Positive Composites		Positive Composites			
Total No.	7	Total No.	1		
No. Reported as Trace	6	No. Reported as Trace	1		
Range	T-0.1	Range	T		

V. Leafy Vegetables
Residues, ppm

CADMIUM		PARATHION		TDE	
Average	0.05	Average	0.003	Average	T
Positive Composites		Positive Composites		Positive Composites	
Total No.	30	Total No.	11	Total No.	3
No. Reported as Trace	0	No. Reported as Trace	3	No. Reported as Trace	3
Range	0.01-0.28	Range	T-0.017	Range	T
ZINC		SELENIUM		ARSENIC	
Average	2.2	Average	T	Average	T
Positive Composites		Positive Composites		Positive Composites	
Total No.	30	Total No.	10	Total No.	2
No. Reported as Trace	0	No. Reported as Trace	10	No. Reported as Trace	2
Range	0.5-4.0	Range	T	Range	T

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TABLE 3 (cont'd). *Levels of chemical residues found by food class, August 1972–July 1973*

LEAD		DIAZINON		DCPA	
Average	T	Average	0.001	Average	T
Positive Composites		Positive Composites		Positive Composites	
Total No.	25	Total No.	9	Total No.	1
No. Reported as Trace	17	No. Reported as Trace	2	No. Reported as Trace	0
Range	T-0.5	Range	T-0.009	Range	0.0130
ENDOSULFAN		DIELDRIN		DDT	
Average	0.019	Average	T	Average	T
Positive Composites		Positive Composites		Positive Composites	
Total No.	17	Total No.	5	Total No.	1
No. Reported as Trace	7	No. Reported as Trace	5	No. Reported as Trace	1
Range	T-0.439	Range	T	Range	T
DDE		METHYL PARATHION		PERTHANE	
Average	0.001	Average	T	Average	0.044
Positive Composites		Positive Composites		Positive Composites	
Total No.	12	Total No.	5	Total No.	1
No. Reported as Trace	7	No. Reported as Trace	2	No. Reported as Trace	0
Range	T-0.006	Range	T-0.003	Range	1.32

VI. Legume Vegetables
Residues, ppm

LEAD		PARATHION		PCP	
Average	0.3	Average	T	Average	T
Positive Composites		Positive Composites		Positive Composites	
Total No.	30	Total No.	3	Total No.	1
No. Reported as Trace	1	No. Reported as Trace	1	No. Reported as Trace	0
Range	T-0.7	Range	T-0.005	Range	0.010
ZINC		ARSENIC		STROBANE	
Average	7.6	Average	T	Average	T
Positive Composites		Positive Composites		Positive Composites	
Total No.	30	Total No.	2	Total No.	1
No. Reported as Trace	0	No. Reported as Trace	2	No. Reported as Trace	1
Range	3.7-10.5	Range	T	Range	T
SELENIUM		DIELDRIN		TDE	
Average	T	Average	T	Average	T
Positive Composites		Positive Composites		Positive Composites	
Total No.	12	Total No.	2	Total No.	1
No. Reported as Trace	12	No. Reported as Trace	2	No. Reported as Trace	1
Range	T	Range	T	Range	T
CADMIUM		CARBARYL			
Average	T	Average	T		
Positive Composites		Positive Composites			
Total No.	10	Total No.	1		
No. Reported as Trace	0	No. Reported as Trace	1		
Range	0.01-0.03	Range	T		

VII. Root Vegetables
Residues, ppm

ZINC		ARSENIC		HCB	
Average	2.3	Average	T	Average	T
Positive Composites		Positive Composites		Positive Composites	
Total No.	30	Total No.	2	Total No.	1
No. Reported as Trace	0	No. Reported as Trace	2	No. Reported as Trace	1
Range	0.6-4.2	Range	T	Range	T
LEAD		CARBARYL		MERCURY	
Average	0.1	Average	0.002	Average	T
Positive Composites		Positive Composites		Positive Composites	
Total No.	25	Total No.	1	Total No.	1
No. Reported as Trace	13	No. Reported as Trace	0	No. Reported as Trace	1
Range	T-1.0	Range	0.050	Range	T
CADMIUM		DDT		PARATHION	
Average	0.02	Average	T	Average	T
Positive Composites		Positive Composites		Positive Composites	
Total No.	24	Total No.	1	Total No.	1
No. Reported as Trace	0	No. Reported as Trace	0	No. Reported as Trace	1
Range	0.01-0.06	Range	0.006	Range	T
SELENIUM		DIAZINON			
Average	T	Average	T		
Positive Composites		Positive Composites			
Total No.	6	Total No.	1		
No. Reported as Trace	5	No. Reported as Trace	0		
Range	T-0.2	Range	0.002		
DDE		ETHION			
Average	0.001	Average	T		
Positive Composites		Positive Composites			
Total No.	3	Total No.	1		
No. Reported as Trace	0	No. Reported as Trace	1		
Range	0.002-0.014	Range	T		

(Continued next page)

TABLE 3 (cont'd). *Levels of chemical residues found by food class, August 1972–July 1973*

VIII. GARDEN FRUITS
RESIDUES, PPM

ZINC	
Average	3.1
Positive Composites	
Total No.	30
No. Reported as Trace	0
Range	0.8-5.3
LEAD	
Average	0.1
Positive Composites	
Total No.	27
No. Reported as Trace	7
Range	T-0.3
CADMIUM	
Average	0.02
Positive Composites	
Total No.	25
No. Reported as Trace	0
Range	0.01-0.06
DIELDRIN	
Average	0.003
Positive Composites	
Total No.	22
No. Reported as Trace	5
Range	T-0.012
SELENIUM	
Average	T
Positive Composites	
Total No.	10
No. Reported as Trace	10
Range	T
DIAZINON	
Average	0.001
Positive Composites	
Total No.	6
No. Reported as Trace	5
Range	T-0.023
TDE	
Average	0.001
Positive Composites	
Total No.	6
No. Reported as Trace	1
Range	T-0.009
ENDOSULFAN	
Average	T
Positive Composites	
Total No.	4
No. Reported as Trace	3
Range	T-0.002
BHC	
Average	T
Positive Composites	
Total No.	2
No. Reported as Trace	0
Range	0.001-0.002
CARBARYL	
Average	T
Positive Composites	
Total No.	2
No Reported as Trace	2
Range	T
DDE	
Average	T
Positive Composites	
Total No.	2
No. Reported as Trace	2
Range	T
DDT	
Average	T
Positive Composites	
Total No.	2
No. Reported as Trace	2
Range	T
PARATHION	
Average	T
Positive Composites	
Total No.	2
No. Reported as Trace	1
Range	T-0.009
ALDRIN	
Average	T
Positive Composites	
Total No.	1
No. Reported as Trace	0
Range	0.002
CHLORDANE	
Average	T
Positive Composites	
Total No.	1
No. Reported as Trace	1
Range	T
LINDANE	
Average	T
Positive Composites	
Total No.	1
No. Reported as Trace	0
Range	0.006
TCNB	
Average	T
Positive Composites	
Total No.	1
No. Reported as Trace	0
Range	0.005

IX. FRUITS
RESIDUES, PPM

ZINC	
Average	1.0
Positive Composites	
Total No.	30
No. Reported as Trace	0
Range	0.1-3.2
LEAD	
Average	T
Positive Composites	
Total No.	21
No. Reported as Trace	13
Range	T-0.4
ETHION	
Average	0.004
Positive Composites	
Total No.	12
No. Reported as Trace	8
Range	T-0.099
CARBARYL	
Average	T
Positive Composites	
Total No.	7
No. Reported as Trace	7
Range	T-0.10
DIAZINON	
Average	0.001
Positive Composites	
Total No.	5
No. Reported as Trace	3
Range	T-0.016
SELENIUM	
Average	T
Positive Composites	
Total No.	5
No. Reported as Trace	5
Range	T
CADMIUM	
Average	T
Positive Composites	
Total No.	4
No. Reported as Trace	0
Range	0.01-0.02
ENDOSULFAN	
Average	T
Positive Composites	
Total No.	4
No. Reported as Trace	2
Range	T-0.007
DICOFOL	
Average	0.002
Positive Composites	
Total No.	3
No. Reported as Trace	1
Range	T-0.044
MALATHION	
Average	0.003
Positive Composites	
Total No.	3
No. Reported as Trace	0
Range	0.003-0.073
PERTHANE	
Average	0.002
Positive Composites	
Total No.	3
No. Reported as Trace	0
Range	0.013-0.020
ARSENIC	
Average	T
Positive Composites	
Total No.	1
No. Reported as Trace	1
Range	T
DIELDRIN	
Average	T
Positive Composites	
Total No.	1
No. Reported as Trace	1
Range	T
DURSBAN	
Average	T
Positive Composites	
Total No.	1
No. Reported as Trace	0
Range	0.005
PARATHION	
Average	T
Positive Composites	
Total No.	1
No. Reported as Trace	1
Range	T
PHOSALONE	
Average	T
Positive Composites	
Total No.	1
No. Reported as Trace	0
Range	0.015
RONNEL	
Average	T
Positive Composites	
Total No.	1
No. Reported as Trace	1
Range	T
TCNB	
Average	T
Positive Composites	
Total No.	1
No. Reported as Trace	0
Range	0.001

(Continued next page)

TABLE 3 (cont'd). *Levels of chemical residues found by food class, August 1972–July 1973*

X. Oils, Fats, and Shortening
Residues, ppm

ZINC		HCB		TDE	
Average	6.2	Average	0.001	Average	0.001
Positive Composites		Positive Composites		Positive Composites	
Total No.	30	Total No.	6	Total No.	3
No. Reported as Trace	0	No. Reported as Trace	1	No. Reported as Trace	2
Range	3.4-9.1	Range	T-0.006	Range	T-0.021
CADMIUM		PCA		ARSENIC	
Average	0.03	Average	0.003	Average	T
Positive Composites		Positive Composites		Positive Composites	
Total No.	29	Total No.	6	Total No.	2
No. Reported as Trace	0	No. Reported as Trace	0	No. Reported as Trace	1
Range	0.01-0.06	Range	0.003-0.032	Range	T-0.1
MALATHION		DIAZINON		DDT	
Average	0.023	Average	0.003	Average	T
Positive Composites		Positive Composites		Positive Composites	
Total No.	18	Total No.	5	Total No.	1
No. Reported as Trace	3	No. Reported as Trace	1	No. Reported as Trace	1
Range	T-0.101	Range	T-0.044	Range	T
LEAD		PCNB		MERCURY	
Average	T	Average	T	Average	T
Positive Composites		Positive Composites		Positive Composites	
Total No.	16	Total No.	5	Total No.	1
No. Reported as Trace	13	No. Reported as Trace	3	No. Reported as Trace	1
Range	T-0.2	Range	T-0.002	Range	T
SELENIUM		BHC		PCB's	
Average	T	Average	T	Average	T
Positive Composites		Positive Composites		Positive Composites	
Total No.	12	Total No.	3	Total No.	1
No. Reported as Trace	12	No. Reported as Trace	1	No. Reported as Trace	1
Range	T	Range	T-0.005	Range	T
DIELDRIN		DDE		TCNB	
Average	T	Average	T	Average	T
Positive Composites		Positive Composites		Positive Composites	
Total No.	8	Total No.	3	Total No.	1
No. Reported as Trace	7	No. Reported as Trace	2	No. Reported as Trace	1
Range	T-0.004	Range	T-0.012	Range	T

XI. Sugars and Adjuncts
Residues, ppm

ZINC		BHC		ARSENIC	
Average	2.7	Average	T	Average	T
Positive Composites		Positive Composites		Positive Composites	
Total No.	30	Total No.	8	Total No.	1
No. Reported as Trace	0	No. Reported as Trace	5	No. Reported as Trace	1
Range	1.0-5.1	Range	T-0.005	Range	T
LEAD		PCP		DDT	
Average	T	Average	0.003	Average	T
Positive Composites		Positive Composites		Positive Composites	
Total No.	19	Total No.	6	Total No.	1
No. Reported as Trace	17	No. Reported as Trace	0	No. Reported as Trace	1
Range	T-0.1	Range	0.01-0.02	Range	T
CADMIUM		MALATHION		TDE	
Average	0.01	Average	0.001	Average	T
Positive Composites		Positive Composites		Positive Composites	
Total No.	13	Total No.	3	Total No.	1
No. Reported as Trace	0	No. Reported as Trace	1	No. Reported as Trace	1
Range	0.01-0.06	Range	T-0.012	Range	T
LINDANE		SELENIUM			
Average	T	Average	T		
Positive Composites		Positive Composites			
Total No.	11	Total No.	3		
No. Reported as Trace	5	No. Reported as Trace	3		
Range	T-0.002	Range	T		

XII. Beverages
Residues, ppm

ZINC		CADMIUM	
Average	0.9	Average	T
Positive Composites		Positive Composites	
Total No.	29	Total No.	5
No. Reported as Trace	0	No. Reported as Trace	0
Range	0.2-5.4	Range	0.01-0.08
LEAD		SELENIUM	
Average	T	Average	T
Positive Composites		Positive Composites	
Total No.	6	Total No.	3
No. Reported as Trace	5	No. Reported as Trace	3
Range	T-0.1	Range	T

NOTE: T = trace; see definition, Table 1.

TABLE 4. *Recovery experiments on residues in total diet samples, August 1972–July 1973*

Residue	Type of Food Composite	Spike Level, ppm	Range of Blank Level, ppm [1]	Range of Total Recovered, ppm	No. of Recovery Experiments
DDE	Fatty	0.005	0.0004-0.0078 (0.0038)	0.0042-0.0116 (0.0077)	5
	Nonfatty	0.005	0-0.0024 (0.0003)	0.0032-0.0091 (0.0057)	9
DDT	Fatty	0.01	0-0.0095 (0.0037)	0.0064-0.0182 (0.0130)	5
	Nonfatty	0.01	0-0.0031 (0.0004)	0.0069-0.0181 (0.0118)	8
Dieldrin	Fatty	0.005	0-0.0105 (0.0042)	0.0035-0.0162 (0.0084)	5
	Nonfatty	0.005	0-0.0024 (0.0007)	0.0042-0.0081 (0.0058)	10
Strobane	Fatty	0.20	0	0.108-0.263 (0.176)	6
	Nonfatty	0.20	0	0.169-0.280 (0.186)	9
Ronnel	Fatty	0.005	0	0.0035-0.0045 (0.0039)	5
	Nonfatty	0.005	0	0.0036-0.0046 (0.0042)	10
Endrin	Fatty	0.005	0-0.0016 (0.0003)	0.0034-0.0061 (0.0045)	5
	Nonfatty	0.005	0	0.0036-0.0058 (0.0047)	10
Kelthane	Fatty	0.02	0	0.010-0.023 (0.018)	4
	Nonfatty	0.02	0	0.015-0.025 (0.018)	10
Methyl Parathion	Fatty	0.01	0	0.0062-0.0133 (0.0099)	5
	Nonfatty	0.01	0	0.0064-0.0150 (0.0097)	10
Parathion	Fatty	0.005	0	0.0041-0.0055 (0.0046)	5
	Nonfatty	0.005	0	0.0026-0.0076 (0.0050)	10
Ethion	Fatty	0.005	0	0.0037-0.0050 (0.0045)	5
	Nonfatty	0.005	0	0-0.0058 (0.0040)	10
2, 4, 5-T	Fatty	0.03	0	0-0.048 (0.020)	15
	Nonfatty	0.03	0	0.014-0.047 (0.032)	26
2, 4-D	Fatty	0.02	0	0-0.017 (0.010)	4
	Nonfatty	0.02	0	0-0.024 (0.015)	15
MCP	Fatty	0.04	0	0-0.042 (0.025)	9
	Nonfatty	0.04	0	0.008-0.048 (0.034)	14
2, 4-DB	Fatty	0.02	0	0-0.017 (0.011)	6
	Nonfatty	0.02	0	0-0.022 (0.016)	19
Carbaryl	Nonfatty	0.20	0	T-0.20 (0.18)	60
Orthophenyl-phenol	Nonfatty	0.4	0	0-0.40 (0.30)	59
Cadmium	Fatty	0.1	0-0.037 (0.010)	0.077-0.127 (0.108)	30
	Nonfatty	0.1	0-0.152 (0.045)	0.080-0.221 (0.119)	60
Lead	Fatty	0.2	0-0.090 (0.034)	0.080-0.300 (0.182)	36
	Nonfatty	0.2	0-0.336 (0.082)	0.060-0.880 (0.262)	84
Mercury	Fatty	0.064	0-0.036 (0.006)	0.034-0.104 (0.067)	29
	Nonfatty	0.064	0-0.009 (0.001)	0.035-0.090 (0.063)	60
Arsenic	Fatty	0.2	0-0.160 (0.030)	0.090-0.310 (0.169)	28
	Nonfatty	0.2	0-0.072 (0.016)	0.035-0.240 (0.172)	60
Selenium	Fatty	0.2	0-0.340 (0.093)	0.120-0.850 (0.299)	32
	Nonfatty	0.1	0-0.220 (0.020)	0.040-0.390 (0.299)	30
	Nonfatty	0.2	0-0.405 (0.034)	0.100-0.575 (0.206)	37

[1] Numbers in parentheses represent average residue levels.

TABLE 5. *Pesticide residues in individual commodities of dairy composite of four market basket samples*

Pesticide	Commodity [1,2]								
	Whole Fluid Milk (4)	Evaporated Milk (4)	Ice Cream (4)	Cottage Cheese (4)	Processed Cheese (4)	Natural Cheese (4)	Butter (4)	Margarine (4)	Ice Milk (3)
DDE									
No. occurrences	2	2	3	2	4	3	4		2
Range, ppm	0.001-0.003	0.013-0.016	T-0.019	0.012-0.015	T-0.008	0.003-0.008	0.005-0.154		T-0.009
DIELDRIN									
No. occurrences	1	3	3	3	4	4	4	1	2
Range, ppm	T	0.002-0.003	T-0.007	T	0.005-0.010	0.005-0.014	0.014-0.056	T	T
HCB									
No. occurrences	1	1							
Range, ppm	T	T							
BHC									
No. occurrences	1	2	3	1	4	3	3		1
Range, ppm	T	T-0.001	T-0.001	T	0.004-0.011	0.002-0.005	0.009-0.018		T
HEPTACHLOR EPOXIDE									
No. occurrences		2	2		4	2	3		
Range, ppm		T	T-0.002		T-0.004	0.003-0.012	0.005-0.007		
METHOXYCHLOR									
No. occurrences		1			1	2	1		
Range, ppm		T			0.031	0.029-0.040	0.090		
LINDANE									
No. occurrences			1			1			
Range, ppm			0.001			0.001			
p,p'-DDT									
No. occurrences			2		2	3	3	1	1
Range, ppm			T		T	T-0.006	T-0.011	T	T
TDE									
No. occurrences			2		3	3	3	1	
Range, ppm			T		T	T-0.005	T	T	
PCB's									
No. occurrences		1					2		
Range, ppm		T					T		
MALATHION									
No. occurrences								1	
Range, ppm								0.013	

[1] Buttermilk, skim milk, and nonfat dry milk not shown because no residues were found.

[2] Figures in parentheses represent number of replicates.

TABLE 6. *Pesticide residues in individual commodities of meat composite of four market basket samples*

Pesticide	Commodity [1,2]															
	Roast Beef (4)	Ground Beef (4)	Pork Chops (4)	Bacon (4)	Chicken (4)	Fish Fillet (4)	Tuna or Salmon (4)	Lunch-Meat (4)	Frank-furters (4)	Beef Liver (4)	Eggs (4)	Ham (4)	Round Steak (4)	Veal (2)	Lamb (3)
DDE															
No. occurrences	3	4	2	3	4	2	4	4	4	1	2	2	4	1	3
Range, ppm	0.008-0.559	0.006-0.083	T-0.012	0.003-0.018	T-0.018	0.018-0.095	T-0.018	0.010-0.038	0.014-0.036	0.020	0.005-0.046	T	0.008-0.010	0.014	T-0.003
DIELDRIN															
No. occurrences	4	3	4	2	4			4	4		1	2	4	1	1
Range, ppm	0.002-0.019	0.003-0.009	T-0.007	0.002-0.003	T-0.004			0.003-0.011	0.004-0.009		T	0.002-0.009	0.003-0.010	T	0.008
p,p'-DDT															
No. occurrences	2	1	2	3	1	2		4	4	1	1	2	2	1	1
Range, ppm	0.005-0.022	T	T-0.030	0.008-0.030	T	0.018-0.039		T-0.041	T-0.038	0.008	0.006	T	T-0.091	0.011	T
TDE															
No. occurrences	2		1	1		1	2	2	2			1	1	1	1
Range, ppm	0.007-0.013		0.032	T		0.014	0.006-0.010	T-0.010	0.005-0.010			T	0.019	0.006	T
HCB															
No. occurrences	2					1				1			1		1
Range, ppm	0.002-0.007					0.002				0.002			0.001		0.001
PCB's															
No. occurrences	1	1	2			1	1			1		1	2	1	1
Range, ppm	T	T	T			T	T			T		T	0.050-0.051	0.053	0.060
HEPTACHLOR EPOXIDE															
No. occurrences	1	2	2	1	2			3	1				1		
Range, ppm	T	T-0.004	T	T	T			T-0.005	0.005				T		
BHC															
No. occurrences	1	1	1			1	2	2	1			1			2
Range, ppm	0.002	0.003	T			0.002	T-0.004	T-0.004	0.004			0.006			0.003-0.006
LINDANE															
No. occurrences	1	1				1		2	1			1			1
Range, ppm	0.004	0.004				0.027		T-0.002	0.003			T			T
RONNEL															
No. occurrences		1													
Range, ppm		0.006													

[1] Shrimp not shown because no residues found.
[2] Figures in parentheses represent number of replicates.

RESIDUES IN FISH, WILDLIFE, AND ESTUARIES

Chlorinated Hydrocarbon Pesticides and Mercury in Coastal Young-of-the-Year Finfish, South Carolina and Georgia—1972-74 [1]

Robert J. Reimold [2] and Malcolm H. Shealy, Jr.[3]

ABSTRACT

Pesticides and heavy metals were monitored in fish collected from 11 estuaries representing all the Atlantic drainage basins in Georgia and South Carolina. Part of the U.S. Environmental Protection Agency National Estuarine Monitoring Program, the semiannual survey of young-of-the-year fishes, was conducted from 1972 to 1974. Data are intended to provide an initial base line for residue levels in the fish studied in these waters. Dieldrin was found in 2 percent of the samples, DDT and metabolites were in 33 percent, polychlorinated biphenyls were in 4 percent, and mercury was in 47 percent. Noticeably absent were any measureable residues of toxaphene even though there is a toxaphene manufacturing plant in Brunswick, Ga.

Introduction

The presence of chlorinated hydrocarbons in continental United States marine and estuarine molluscs was monitored from 1965 to 1972 by the U.S. Environmental Protection Agency (EPA) (*1,2*). Nevertheless there is a paucity of data concerning the concentrations of these compounds and total mercury in estuarine finfish from coastal Georgia and South Carolina.

As part of the EPA National Estuarine Monitoring Program, a semiannual survey of selected Georgia and South Carolina estuaries was initiated in October 1972. This paper reports base line chlorinated hydrocarbon and total mercury concentrations, including negative results, in young-of-the-year finfish from the Georgia and South Carolina estuaries of the Atlantic coast from fall 1972 through spring 1974.

Methods

The study area included coastal Georgia and South Carolina. Collection sites in six South Carolina estuaries and five Georgia estuaries are depicted in Figures 1 and 2. At each location, samples were collected during fall 1972, spring 1973, fall 1973, and spring 1974. Specimens for residue analysis were restricted to young-of-the-year fish. Consequently, residues reflect the accumulation over a period of not more than 1 year preceding sample collection. Each sample consisted of a 25-g aliquot from a composite sample of at least 25 fish. South Carolina fish were collected with a 6-m semi-balloon otter trawl described by Shealy (*3*). Georgia specimens were collected with an otter trawl described by Reimold and Durant (*4*). Georgia samples were placed on ice and were processed for analysis within 4 hours of collection according to techniques of Reimold and Durant (*4*) and Durant and Reimold (*5*). South Carolina samples were frozen immediately upon collection and were processed later for analysis by the techniques noted above.

All samples were analyzed by the EPA Pesticide Monitoring Laboratory, Bay St. Louis, Miss., using the techniques of Butler (*2*) for pesticides and of Uthe et al. (*6*) and Brandenberger and Bader (*7,8*) for total mercury. Specific chlorinated hydrocarbons for which analyses were conducted were: DDT, DDE, TDE, dieldrin, endrin, polychlorinated biphenyls (PCB's), toxaphene, mirex, and chlordane. Phenoxy-herbicides, and carbamate and organophosphorus pesticides were also monitored but are not discussed in this report because their residues were not detected. PCB's were quantified by matching residues with an Aroclor 1254 standard. Recovery of pesticides was between 85 and 90 percent; data have not been corrected. Concentrations of all pesticides and mercury are reported on a whole-body, wet-weight basis. Pesticide concentrations

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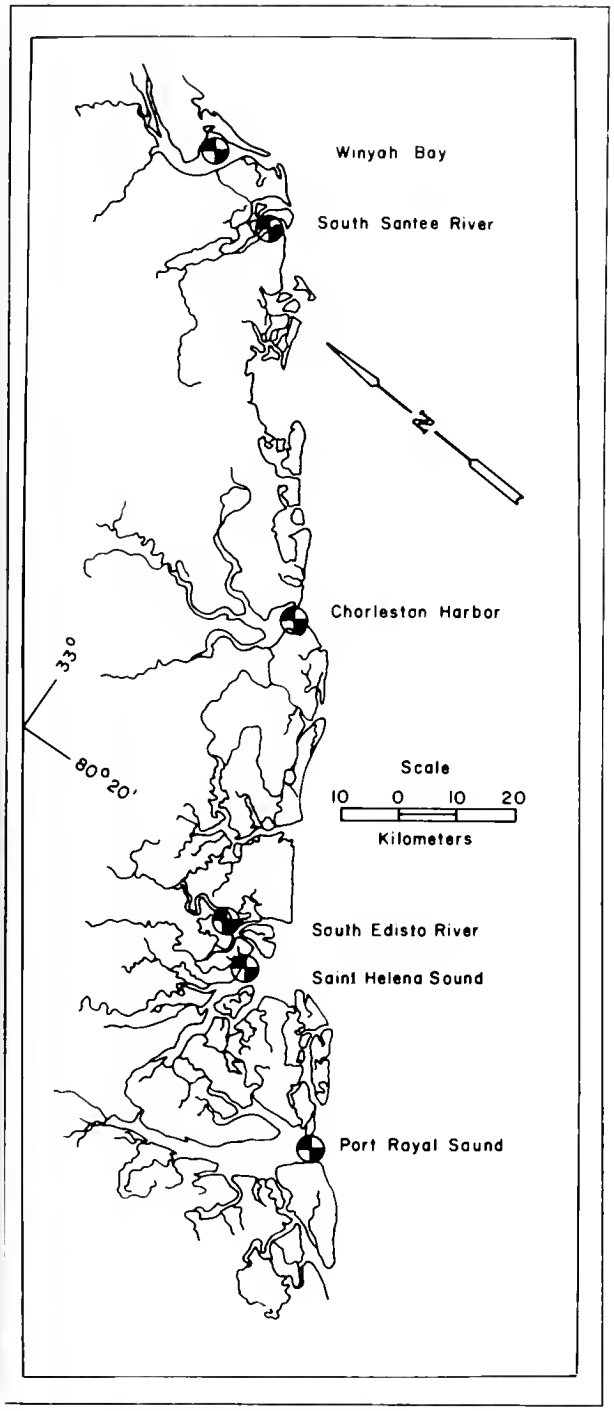

FIGURE 1. *Estuarine collection sites in coastal South Carolina, 1972-74*

less than 10 μg/kg and mercury concentrations less than 20.0 μg/kg are not reported.

Results

Table 1 lists scientific names and collection locations of all fishes analyzed. Scientific and common names are those accepted by the American Fisheries Society (*9*). Quantifiable concentrations of chlorinated hydrocarbons and mercury in coastal sites of South Carolina and Georgia are summarized in Table 2.

Dieldrin was detected only in Atlantic croaker collected in the Savannah River, Ga., in spring 1973, and in star drum from St. Andrews Sound, Ga., in fall 1972. DDT was detected in star drum (33 μg/kg) collected from Port Royal Sound, S.C., in spring 1973. All other samples containing detectable concentrations of DDT were collected during the fall of 1972. DDE was found in ichthyofauna from all collection sites. The maximum concentration (40 μg/kg) was measured in spot from the Savannah River, Ga., in fall 1972. TDE was found at all collection locations except the south Edisto River, S.C.; St. Helena Sound, Ga., and St. Catherines Sound, Ga. The maximum concentration of 43 μg/kg TDE was in star drum collected in fall 1972 from St. Andrews Sound. PCB's equivalent to Aroclor 1254 were detected in silver perch from Port Royal Sound (182 μg/kg, fall 1972), star drum from the Savannah River (137 μg/kg, spring 1974), and star drum from St. Andrews Sound (508 μg/kg, fall 1972). No other pesticides were detected in any samples during the monitoring period. Mercury was detected at all geographic locations with highest values in Winyah Bay, S.C. (797 μg/kg in At-

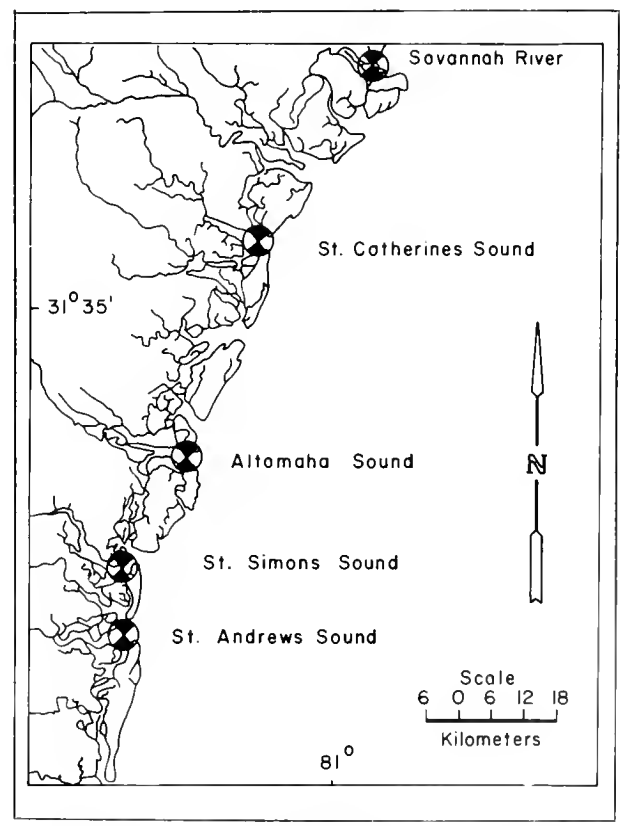

FIGURE 2. *Estuarine collection sites in coastal Georgia, 1972-74*

TABLE 1. *List of coastal young-of-the-year fishes sampled from fall 1972 through spring 1974, South Carolina and Georgia*

Scientific Name	Common Name	South Carolina						Georgia				
		WB	SS	CH	SE	SHS	PRS	SR	SCS	AS	SSS	SAS
Anchoa mitchilli	Bay anchovy								X		X	X
Arius felis	Sea catfish							X	X	X		
Bairdiella chrysura	Silver perch		X	X	X		X				X	
Brevoortia tyrannus	Atlantic menhaden									X		X
Cynoscion regalis	Weakfish					X			X			
Etropus crossotus	Fringed flounder								X			X
Leiostomus xanthurus	Spot		X					X	X			
Menticirrhus americanus	Southern kingfish							X	X	X		
Micropogon undulatus	Atlantic croaker	X						X		X		
Peprilus alepidotus	Harvestfish											X
Rissola marginata	Striped cusk-eel										X	
Stellifer lanceolatus	Star drum	X		X	X	X	X	X		X	X	X
Symphurus plagiusa	Blackcheek tonguefish							X				X

NOTE: WB = Winyah Bay, SS = South Santee River, CH = Charleston Harbor, SE = South Edisto River, SHS = St. Helena Sound, PRS = Port Royal Sound, SR = Savannah River, SCS = St. Catherines Sound, AS = Altamaha Sound, SSS = St. Simons Sound, and SAS = St. Andrews Sound.

lantic croaker, spring 1973), and the South Santee River, S.C. (3,059 μg/kg in silver perch, spring 1973).

Discussion

When combined, levels in ichthyofauna in the two States represent an array of indicator finfish species and chlorinated hydrocarbon and mercury residues in a large number of fishes common to estuaries of the southeastern United States. Thirteen species, representing eight families from five orders, are included.

The five fish species reported for the South Carolina coast, all in the family Sciaenidae, were selected because they are among the most abundant and ubiquitous bottom fishes in these estuaries (*10*). The eight Georgia species reported represent various diets and several additional important families, including the Engraulidae, Clupeidae, Ariidae, Bothidae, Cynoglossidae, Ophidiidae, and Stromateidae.

Eleven estuaries representing all the Atlantic drainage basins in the two States were monitored, allowing comparison of contaminant residue levels between various locations over much of the portion of the southeastern Atlantic coast known as the Georgia Embayment.

Total mercury values listed do not differentiate between inorganic mercury and the much more harmful organomercurials. For further information on organic mercury, the reader is referred to D'Itri (*11*) and Lepple (*12*).

During spring 1973, the 797 μg/kg mercury in Atlantic croaker from Winyah Bay, S.C., represented a level slightly above the 500 μg/kg legal maximum concentration of mercury in food set by the Food and Drug Administration, U.S. Department of Health, Education, and Welfare (*12*). The 3,059 μg/kg in silver perch from South Santee, S.C. is six times above this level. In both estuaries, mercury levels were considerably lower both before and after spring 1973. The cause of the singularly high total mercury values in the two estuaries during this sampling period has not been ascertained.

The data establish base line conditions by which future comparisons of chlorinated hydrocarbon and total mercury residue levels can be made for selected ichthyofauna of coastal South Carolina and Georgia. During this study detectable concentrations were measured and reported for dieldrin, DDT, DDE, TDE, PCB's, and total mercury (i.e., concentrations greater than or equal to 10 μg/kg for chlorinated hydrocarbons and 20 μg/kg for mercury). Dieldrin was never detected after spring 1973. Similarly, DDT was found only prior to spring 1973, which may reflect the 1972 ban by EPA. The metabolites of DDT, namely DDE and TDE, were seasonally and spatially ubiquitous throughout the monitoring period. The PCB detected may represent isolated instances associated with industrial activities adjacent to Beaufort and Port Royal Sound in South Carolina, the Savannah River in Savannah, Ga., and St. Andrews Sound. The chlorinated hydrocarbons toxaphene, chlordane, endrin, and mirex, and phenoxyherbicides, carbamates, and organophosphorus pesticides were never detected in concentrations greater than or equal to 10 μg/kg.

The absence of toxaphene is extremely interesting because a toxaphene manufacturing plant at Brunswick, Ga., was in operation throughout the monitoring program and agricultural use of toxaphene has continued in the watersheds of South Carolina and Georgia. Earlier studies (*13*) evaluated effluents from a toxaphene manufacturing plant in Georgia and found detectable quantities of toxaphene in estuarine biota during 1971-72, including salt marsh cordgrass, *Spartina alterniflora;* white shrimp, *Penalus setiferus;* American oyster, *Crassostrea virginica;* spot, *Leiostomus xanthurus;* mummichog, *Fundulus heteroclitus;* striped mullet, *Mugil cephalus;* lesser scaup, *Aythya affinis;* and ped-billed grebe, *Podilymbus podiceps.* This discrepancy between toxaphene residues in the two studies, and the fact that analytical precision of the studies was similar,

suggest that a pollution abatement program initiated by the toxaphene manufacturing plant effectively removed toxaphene during the present study.

Residues of dieldrin, DDT, DDE, and TDE were found in 2, 10, 33, and 16 percent of the samples, respectively. The PCB equivalent to Aroclor 1254 was found in only 4 percent of the samples; mercury was found in 47 percent. The distribution of DDT and its metabolites and mercury was similar in coastal areas of both Georgia and South Carolina. Aroclor 1254 was found more frequently in the Caribbean sites than in those along the southeastern coastline of the United States. Concentration ranges were also generally lower in samples from the southeastern United States; maximum residue levels were: dieldrin, 98 μg/kg; DDT, 33 μg/kg; DDE, 40 μg/kg; PCB's (Aroclor 1254), 508 μg/kg; and mercury, 3,059 μg/kg.

Future monitoring activities should include sampling of different trophic levels in each geographic location where significant concentrations are detected. Finfish monitoring should be continued and compared periodically to the base line residue levels of the current study to determine whether these pollutants are increasing, decreasing, or maintaining a steady state in these estuaries and indicator finfish species.

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TABLE 2. *Chlorinated hydrocarbon and mercury concentrations in young-of-the-year ichthyofauna, South Carolina and Georgia—1972-74*

Date	Common Name	Whole-body wet weight, μg/kg					
		Dieldrin	DDT	DDE	TDE	PCB's	Mercury
		Winyah Bay, S.C.					
Fall 1972	Atlantic croaker	—	18	17	17	—	—
Fall 1972	Star drum	—	10	—	—	—	—
Spring 1973	Atlantic croaker	—	—	—	—	—	797
Spring 1973	Star drum	—	—	10	—	—	286
Fall 1973	Atlantic croaker	—	—	16	10	—	64
Fall 1973	Star drum	—	—	10	—	—	80
Spring 1974	Atlantic croaker	—	—	—	—	—	<20
Spring 1974	Star drum	—	—	13	—	—	<20

(Continued next page)

TABLE 2 (cont'd). *Chlorinated hydrocarbon and mercury concentrations in young-of-the-year ichthyofauna, South Carolina and Georgia—1972-74*

Date	Common Name	Whole-body wet weight, µg/kg					
		Dieldrin	DDT	DDE	TDE	PCB's	Mercury
South Santee River, S.C.							
Fall 1972	Spot	—	16	21	17	—	67
Fall 1972	Silver perch	—	14	23	17	—	—
Spring 1973	Spot	—	—	—	—	—	114
Spring 1973	Silver perch	—	—	12	—	—	3059
Fall 1973	Spot	—	—	19	11	—	—
Fall 1973	Silver perch	—	—	—	—	—	48
Spring 1974	Spot	—	—	13	—	—	—
Spring 1974	Silver perch	—	—	19	10	—	50
Charleston Harbor, S.C.							
Fall 1972	Silver perch	—	19	21	20	—	22
Fall 1972	Star drum	—	—	—	—	—	—
Spring 1973	Silver perch			sample not available			
Spring 1973	Star drum	—	—	14	—	—	157
Fall 1973	Silver perch	—	—	12	—	—	<20
Fall 1973	Star drum	—	—	—	—	—	32
Spring 1974	Silver perch			sample not available			
Spring 1974	Star drum	—	—	13	10	—	—
South Edisto River, S.C.							
Fall 1972	Star drum	—	—	—	—	—	111
Fall 1972	Silver perch	—	—	16	—	—	111
Spring 1973	Star drum	—	—	—	—	—	140
Spring 1973	Silver perch	—	—	—	—	—	200
Fall 1973	Star drum	—	—	—	—	—	—
Fall 1973	Silver perch	—	—	10	—	—	32
Spring 1974	Star drum	—	—	—	—	—	—
Spring 1974	Silver perch	—	—	—	—	—	138
St. Helena Sound, S.C.							
Fall 1972	Star drum	—	—	—	—	—	—
Fall 1972	Weakfish	—	—	11	—	—	—
Spring 1973	Star drum	—	—	15	—	—	429
Spring 1973	Weakfish	—	—	—	—	—	286
Fall 1973	Star drum	—	—	13	—	—	<20
Fall 1973	Weakfish	—	—	—	—	—	—
Spring 1974	Star drum	—	—	—	—	—	<20
Spring 1974	Weakfish	—	—	—	—	—	—
Port Royal Sound, S.C.							
Fall 1972	Silver perch	—	—	—	—	—	—
Fall 1972	Star drum	—	—	—	—	182[1]	—
Spring 1973	Silver perch	—	—	15	—	—	629
Spring 1973	Star drum	—	33	—	—	—	143
Fall 1973	Silver perch	—	—	—	—	—	48
Fall 1973	Star drum	—	—	—	—	—	—
Spring 1974	Silver perch	—	—	18	10	—	—
Spring 1974	Star drum	—	—	—	—	—	<20

(Continued next page)

TABLE 2 (cont'd). *Chlorinated hydrocarbon and mercury concentrations in young-of-the-year ichthyofauna, South Carolina and Georgia—1972-74*

Date	Common Name	Whole-body wet weight, µg/kg					
		Dieldrin	DDT	DDE	TDE	PCB's	Mercury
Savannah River, Ga.							
Fall 1972	Spot	—	—	40	10	—	—
Fall 1972	Sea catfish	—	—	—	10	—	—
Spring 1973	Blackcheek tonguefish	—	—	—	—	—	194
Spring 1973	Atlantic croaker	22	—	11	—	—	19
Fall 1973	Southern kingfish	—	—	—	—	—	—
Fall 1973	Blackcheek tonguefish	—	—	—	—	—	—
Spring 1974	Star drum	—	—	—	—	137[1]	—
Spring 1974	Atlantic croaker	—	—	—	—	—	—
St. Catherines Sound, Ga.							
Fall 1972	Weakfish	—	13	13	—	—	—
Fall 1972	Sea catfish	—	—	—	—	—	—
Spring 1973	Spot	—	—	—	—	—	48
Spring 1973	Fringed flounder	—	—	—	—	—	65
Fall 1973	Southern kingfish	—	—	—	—	—	—
Spring 1974	Bay anchovy	—	—	—	—	—	—
Spring 1974	Weakfish	—	—	—	—	—	—
Altamaha Sound, Ga.							
Fall 1972	Sea catfish	—	—	—	—	—	—
Fall 1972	Star drum	—	—	—	—	—	—
Spring 1973	Atlantic croaker	—	—	—	—	—	136
Spring 1973	Star drum	—	—	—	—	—	227
Fall 1973	Blackcheek tonguefish	—	—	—	—	—	—
Fall 1973	Southern kingfish	—	—	—	—	—	—
Spring 1974	Atlantic menhaden	—	—	18	14	—	—
Spring 1974	Atlantic croaker	—	—	—	—	—	—
St. Simons Sound, Ga.							
Fall 1972		sample not available					
Fall 1972		sample not available					
Spring 1973		sample not available					
Spring 1973		sample not available					
Fall 1973	Star drum	—	—	—	—	—	130
Fall 1973	Silver perch	—	—	—	—	—	—
Spring 1974	Bay anchovy	—	—	—	—	—	—
Spring 1974	Striped cusk-eel	—	—	—	—	—	—
St. Andrews Sound, Ga.							
Fall 1972	Star drum	98	22	—	43	508[1]	—
Fall 1972	Blackcheek tonguefish	—	—	—	—	—	—
Spring 1973	Star drum	—	—	—	—	—	210
Spring 1973	Atlantic menhaden	—	—	16	—	—	161
Fall 1973	Star drum	—	—	—	—	—	70
Fall 1973	Fringed flounder	—	—	—	—	—	—
Spring 1974	Harvestfish	—	—	—	—	—	—
Spring 1974	Bay anchovy	—	—	—	—	—	—

NOTE: — = not detectable.
[1] Compound equivalent to Aroclor 1254.

Nationwide Residues of Organochlorines in Wings of Adult Mallards and Black Ducks, 1972-73

Donald H. White [1] and Robert G. Heath [2]

ABSTRACT

Organochlorine residues in wings of adult mallards and black ducks were monitored during the 1972-73 hunting season. DDE, DDT, DDD, dieldrin, and polychlorinated biphenyls (PCB's) were present in all samples. Mallard wings from Alabama contained the highest mean levels of DDE, DDT, DDD, dieldrin, and PCB's. Mallards and black ducks from the Atlantic Flyway and mallards from the Pacific Flyway contained significantly lower DDE residues than in 1969-70. Black ducks from the Atlantic Flyway contained significantly less dieldrin than in 1969-70, and mallards in the Central and Pacific Flyways contained significantly lower levels of PCB's. As in 1969-70, DDE residues were lowest in the Central Flyway and highest in the Atlantic Flyway. The average PCB level remained unchanged in the Atlantic Flyway but was higher in the Mississippi Flyway than in 1969-70, probably because of the unusually high levels in Alabama samples. All organochlorine residues in black ducks from the Atlantic Flyway significantly correlated. DDE concentrations in mallards from the Atlantic Flyway significantly correlated with those of DDT, DDD, and PCB's.

Introduction

Use of technical DDT as a control agent for insect pests in the United States began in the 1940's. Domestic use exceeded 55 million pounds in 1950 and reached a maximum of more than 75 million pounds in 1959. Usage gradually declined to a low of 13 million pounds in 1971, but increased in 1972 to 23.5 million pounds (*1,2*). In the environment, DDT breaks down to many different metabolites. DDE is by far the most persistent of these and occurs most frequently in nature (*3*). It is conceivable, then, that a decline in usage of technical DDT would be reflected in a decline of residues of DDT and its metabolites in waterfowl tissues. Longcore and Mulhern (*4*) found lowered levels of DDE in black ducks eggs between 1964 and 1971.

The Fish and Wildlife Service, U.S. Department of Interior, began nationwide monitoring of organochlorine pesticides in waterfowl wings in 1965-66 as part of the National Pesticides Monitoring Program. Samples were taken again in 1966-67 and were scheduled for every third year thereafter to detect trends in residue levels. Wings of adult mallards (*Anas platyrhynchos*) and black ducks (*Anas rubripes*) are sampled because their combined range covers the continental United States. Overall objectives and procedures have been discussed in earlier papers (*5-8*).

This paper presents results for the 1972-73 hunting season. Authors have included mean residue levels for each State, a comparison of State residues in the four sampling periods since 1965, a comparison of flyway residues in 1969-70 and 1972-73, and correlations of residues in mallards and black ducks in the Atlantic Flyway.

Collection Methods

Cooperating hunters mailed wings of approximately 5,400 adult mallards and black ducks to a collection station within each flyway where wings were classified according to age and sex, and grouped according to State. Wings from each State were then sorted systematically into pools of 25 wings. Pools from each State were selected randomly for chemical analysis; the number taken was roughly proportional to each State's harvest. Pools were given a code number, placed in individually tagged plastic bags, and shipped in dry ice to WARF Institute, Inc., Madison, Wis. Wings were kept frozen in storage until chemical analyses were performed. A total of 237 pools were analyzed for organochlorine residues.

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Analytical Procedures

Prior to analysis, feathers were trimmed and the wings from each pool were ground together by hand in a meat grinder. A 40-g aliquot was weighed into a 260-ml beaker and placed in a 40°C oven for 190 hours. After drying, the sample was reweighed and the dry weight was recorded. The sample was ground with approximately 30 g Na_2SO_4, placed in a 43-by-123-mm Whatman extraction thimble, and extracted for 8 hours in a Soxhlet with 105 ml ethyl ether and 255 ml petroleum ether. The solvent was evaporated to 5-10 ml on a steam bath and diluted to 50 ml with petroleum ether.

A 10-ml aliquot of the sample was placed on a previously standardized florisil column and eluted with 260 ml of 20 percent ethyl ether in petroleum ether. This solution was evaporated to 5-10 ml, placed on florisil, and eluted with 150 ml of 3 percent ethyl ether in petroleum ether, followed by 260 ml of 15 percent ethyl ether in petroleum ether. After florisil cleanup the resulting eluates were evaporated separately on a steam bath to 5-10 ml and each was diluted to 25 ml with hexane.

The first elution from the florisil was injected into the gas chromatograph to identify BHC, HCB, and lindane, and to approximate the amount of polychlorinated biphenyl (PCB) intereference present. An aliquot of this solution containing up to 5 μg DDE and 20 μg PCB's was run through a silicic acid/celite column according to the method of Armour and Burke for separating PCB's from DDT and its analogs (*9*). Each resulting solution was chromatographed and residues were quantified.

Identifications were made by injecting up to 10 μl of the sample solutions into a Barber-Coleman model 5360 pesticide analyzer. The column was glass, 1219 mm by 4 mm, and packed with 5 percent DC-200 80/100 mesh Gas-Chrom Q. Temperatures were: column, 205°C; injector, 225°C; and detector, 245°C. The carrier gas was nitrogen at a flow rate of 80 ml/min. Residues in 5 percent of the samples were confirmed by mass spectrometry.

All residues are expressed as ppm wet weight. They may be converted to approximate dry or lipid weight by dividing by 0.60 or 0.13, the mean proportions of dry and lipid material in the samples, respectively. Limits of sensitivity were 0.005 ppm for organochlorine pesticides and 0.01 ppm for PCB's. Recovery percentages from spiked samples were: DDE, 80; DDT, 94; DDD, 88; dieldrin, 82; and PCB's, 78. Analytical results have not been corrected for recovery.

Results and Discussion

Table 1 lists the means, standard errors, and ranges of organochlorine residues in wing pools from the 1972-73 and 1969-70 hunting seasons, and the combined residues for the 1965-66 and 1966-67 hunting seasons. Data are arranged by State and major flyway. Waterfowl are highly mobile species and may cover a wide range of habitats in many States. Therefore, interpretations should not be made on strictly statewide bases. Residue levels are not indicative of year-round levels because collections were made only in the fall and winter months. DDT and DDD residues were not reported for the 1965 and 1966 seasons because of possible PCB interference.

DDE, DDT, and PCB's were present in all wing pools at levels equal to or exceeding limits of analytical sensitivity. DDD and dieldrin were present in at least trace amounts in all samples. DDE residues in individual pools of mallard wings ranged from a low of 0.04 ppm in eastern Wyoming to a high of 4.12 ppm in Alabama; DDE residues in pools of black duck wings ranged from a low of 0.07 ppm in New Hampshire to a high of 1.60 ppm in New Jersey. The State with the lowest mean value for DDE was Wyoming (0.06 ppm); Alabama had the highest (1.85 ppm). Levels of PCB's ranged from 0.02 ppm in a pool from Texas to 7.73 ppm in a pool from Alabama. The lowest mean value for PCB's was 0.04 ppm in Nebraska and western Wyoming; the highest was 6.34 ppm in Alabama. Residues of DDD and dieldrin seldom exceeded 0.05 ppm in individual pools. State means for these two compounds averaged 0.01-0.02 ppm.

Heptachlor epoxide, HCB, and BHC were present in all samples in at least trace amounts. Because residues of these three chemicals rarely exceeded 0.02 ppm, they were excluded from the tables. Lindane was present in trace amounts in approximately 75 percent of the samples. A few samples contained traces of alpha- and gamma-chlordane.

Table 2 lists the mean residues and standard errors of samples of mallards and black ducks from the major flyways (Atlantic, Mississippi, Central, and Pacific) in the 1972 and 1969 hunting seasons. Statistical comparisons were made to detect residue trends. Residues of DDE declined in both mallards and black ducks. The changes were highly significant statistically: $p < 0.01$ or $p < 0.001$. Residues of DDE declined by 57 percent in mallards and 73 percent in black ducks in the Atlantic Flyway, and by 52 percent in mallards in the Pacific Flyway (Table 2). DDE residues in mallards from the Mississippi Flyway remained relatively unchanged during the sampling period. Residues appeared to be lower in the Central Flyway, but not significantly so. Flyway means for DDT and DDD showed no change over the 3-year period. The only exception was in the Pacific Flyway where DDT residues decreased by 73 percent, a significant change ($p < 0.01$). Dieldrin residues declined in black ducks in the Atlantic Flyway by 86 percent, a significant change ($p < 0.01$), but remained unchanged in mallards from all flyways.

TABLE 1. *Residues of organochlorines in 25 wing pools of adult mallards and black ducks, 1965-66, 1969 and 1972*

State, Year	No. Pools [1]	Residues, ppm wet weight														
		DDE			DDT			DDD			Dieldrin			PCB's		
		Mean	Range	Standard Error	Mean	Range	Standard Error	Mean	Range	Standard Error	Mean	Range	Standard Error	Mean	Range	Standard Error
Black Ducks, Atlantic Flyway																
Maine																
1972	4	0.16	0.09-0.29	0.045	0.05	0.03-0.11	0.020	0.01	0.009-0.02	0.002	(0.01)	t-0.009	(0.001)	0.72	0.56-0.82	0.059
1969	3	0.60	0.33-0.85	0.122	0.05	0.03-0.07	0.009	(0.01)	all t	(0.007)	0.44	t-1.72	0.426	0.79	0.20-1.64	0.332
1965-66	4+4	0.48	0.32-0.82	0.064							(0.02)		(0.006)			
Vt.																
1972	2	0.24	0.10-0.38	0.140	0.04	0.03-0.05	0.010	0.02	0.01-0.04	0.015	(0.01)	0.005-0.007	(0.001)	1.85	0.37-3.33	1.48
1969	2	0.66	0.60-0.71	0.055	0.03	—	0	(0.01)	all t	(0.010)	(0.01)	all t	(0.010)	0.83	0.33-1.33	0.500
1965-66	3+3	0.75	0.18-2.10	0.279							(0.02)		(0.008)			
N.H.																
1972	3	0.20	0.07-0.28	0.064	0.03	0.02-0.04	0.007	(0.01)	t-0.01	(0.002)	0.01	0.006-0.02	0.004	0.97	0.60-1.47	0.259
1969	2	0.87	0.80-0.93	0.065	0.04	t-0.06	0.025	(0.01)	all t	(0.010)	0.02	—	0	1.50	1.33-1.67	0.170
1965-66	3+3	0.88	0.48-2.17	0.262							0.10	ND-0.55	0.092			
Mass.																
1972	4	0.40	0.29-0.62	0.076	0.08	0.06-0.09	0.006	0.03	0.03-0.04	0.002	0.08	0.05-0.14	0.021	2.44	1.83-3.00	0.249
1969	4	1.90	1.11-2.34	0.286	0.09	t-0.19	0.038	0.04	0.02-0.05	0.007	0.18	0.05-0.49	0.105	2.12	1.64-3.00	0.303
1965-66	4+4	1.69	1.28-2.67	0.166							0.10	ND-0.38	0.045			
Conn.																
1972	3	0.25	0.20-0.28	0.027	0.07	0.05-0.09	0.012	0.02	0.01-0.02	0.003	0.02	0.02-0.03	0.003	2.04	1.92-2.14	0.065
1969	3	1.06	0.98-1.22	0.078	0.13	0.09-0.16	0.022	0.02	0.02-0.03	0.003	0.16	0.08-0.22	0.042	3.88	2.67-5.00	0.674
1965-66	3+3	1.51	0.77-2.62	0.311							0.06	ND-0.18	0.029			
R.I.																
1972	3	0.34	0.22-0.48	0.076	0.08	0.07-0.09	0.006	0.03	0.02-0.04	0.006	0.06	0.02-0.08	0.018	2.41	2.21-2.61	0.115
1969	3	1.36	1.27-1.45	0.052	0.18	0.15-0.24	0.029	0.03	0.02-0.03	0.003	0.26	0.23-0.29	0.018	1.58	1.00-1.96	0.295
1965-66	3+3	0.94	0.56-1.50	0.156							0.21	ND-0.43	0.061			
N.Y.																
1972	4	0.57	0.14-1.03	0.195	0.14	0.06-0.29	0.052	0.06	0.02-0.14	0.028	0.02	0.01-0.02	0.002	2.41	1.27-4.71	0.786
1969	4	1.19	0.90-1.69	0.174	0.13	0.02-0.23	0.043	0.02	0.02-0.03	0.003	0.03	0.02-0.04	0.004	1.64	0.25-3.00	0.578
1965-66	4+4	1.24	0.78-1.58	0.092							0.05	ND-0.15	0.021			
Pa.																
1972	3	0.33	0.23-0.38	0.048	0.04	0.03-0.05	0.007	0.03	0.008-0.06	0.016	0.02	—	0	1.09	0.77-1.62	0.266
1969	3	0.78	0.70-0.91	0.067	0.06	0.04-0.07	0.009	(0.01)	all t	(0.007)	0.16	0.03-0.30	0.078	1.00	0.50-1.67	0.348
1965-66	3+3	1.14	0.33-3.60	0.511							(0.03)	ND-0.10	(0.016)			
N.J.																
1972	5	0.77	0.37-1.60	0.227	0.14	0.13-0.20	0.022	0.04	0.02-0.06	0.008	0.02	0.01-0.02	0.002	1.35	0.42-2.69	0.381
1969	5	3.42	2.31-5.27	0.520	0.27	0.18-0.35	0.036	0.09	0.06-0.12	0.010	0.06	0.02-0.12	0.018	0.92	0.13-1.66	0.295
1965-66	5+5	2.10	1.32-3.45	0.228							(0.03)	ND-0.08	(0.010)			
Del.																
1972	3	0.49	0.34-0.69	0.103	0.09	0.07-0.11	0.012	0.02	0.01-0.03	0.006	0.02	0.02-0.03	0.003	0.97	0.76-1.12	0.109
1969	2	1.54	1.52-1.55	0.015	0.12	0.11-0.12	0.005	0.04	0.03-0.04	0.005	0.03	—	0	1.06	0.62-1.50	0.440
1965-66	3+3	0.88	0.50-1.50	0.171							0.05	ND-0.19	0.032			
Md.																
1972	3	0.15	0.09-0.19	0.030	0.06	0.05-0.07	0.007	0.01	0.01-0.02	0.003	0.02	0.01-0.04	0.010	0.38	0.35-0.40	0.015
1969	3	0.55	0.47-0.63	0.046	0.06	0.05-0.08	0.009	(0.01)	all t	(0.007)	0.03	0.02-0.03	0.003	0.39	0.10-0.83	0.223
1965-66	3+3	0.33	0.13-0.51	0.056							(0.03)	ND-0.06	(0.010)			

(Continued next page)

TABLE 1 (cont'd). *Residues of organochlorines in 25 wing pools of adult mallards and black ducks, 1965-66, 1969, and 1972*

State, Year	No. Pools [1]	Residues, ppm wet weight														
		DDE			DDT			DDD			Dieldrin			PCB's		
		Mean	Range	Standard Error	Mean	Range	Standard Error	Mean	Range	Standard Error	Mean	Range	Standard Error	Mean	Range	Standard Error
Black Ducks, Atlantic Flyway—Continued																
Va.																
1972	3	0.12	0.12-0.13	0.003	0.06	0.05-0.07	0.006	0.01	0.009-0.02	0.004	0.01	0.008-0.02	0.004	0.53	0.29-0.81	0.152
1969	3	0.89	0.64-1.18	0.157	0.14	0.04-0.30	0.081	0.02	t-0.03	0.006	0.13	t-0.32	0.096	1.17	0.50-2.00	0.441
1965-66	3+3	0.40	0.20-0.72	0.077							0.11	ND-0.43	0.071			
N.C.																
1972	2	0.17	0.11-0.23	0.060	0.08	0.05-0.11	0.030	0.02	—	0	0.01	—	0	0.46	0.42-0.50	0.040
1969	2	0.80	0.74-0.86	0.060	0.08	0.06-0.09	0.015	0.02	0.02-0.03	0.005	0.30	0.03-0.57	0.270	0.66	0.49-0.83	0.170
1965-66	1+2	0.48	0.31-0.66	0.101							(0.02)	—	(0.017)			
S.C.																
1972	2	0.20	0.18-0.23	0.025	0.08	0.07-0.10	0.015	0.02	0.01-0.02	0.005	0.02	0.006-0.03	0.012	0.30	0.27-0.32	0.025
1969	2	1.03	0.76-1.30	0.270	0.06	0.05-0.07	0.010	0.03	0.02-0.04	0.010	0.10	0.06-0.15	0.045	1.25	0.50-2.00	0.750
1965-66	2+2	0.30	0.18-0.53	0.081							(0.03)	ND-0.07	(0.017)			
Mallards, Atlantic Flyway																
N.Y.																
1972	3	0.85	0.47-1.41	0.286	0.12	0.11-0.15	0.018	0.34	0.02-0.97	0.315	0.01	0.01-0.02	0.003	2.65	1.13-4.82	1.11
1969	3	0.99	0.86-1.11	0.072	0.10	0.07-0.14	0.020	0.02	0.02-0.03	0.003	0.02	t-0.03	0.007	1.33	0.33-2.00	0.511
1965-66	3+3	1.24	0.52-2.15	0.237							T	ND-0.11	—			
Pa.																
1972	3	0.37	0.29-0.44	0.044	0.05	0.02-0.08	0.018	0.01	0.008-0.02	0 004	0.03	0.02-0.04	0.007	1.81	1.47-2.34	0.268
1969	3	1.48	0.92-2.61	0.563	0.05	0.04-0.07	0.010	(0.01)	all t	(0.007)	0.14	0.03-0.35	0.105	1.00	0.33-1.67	0.387
1965-66	3+3	0.78	0.37-1.50	0.189							0.05	ND-0.16	0.027			
N.J.																
1972	3	0.61	0.28-0.87	0.173	0.14	0.04-0.24	0.058	0.02	0.01-0.03	0.007	0.01	0.01-0.02	0.003	1.62	0.55-2.45	0.561
1969	3	2.62	2.38-2.86	0.240	0.22	0.17-0.26	0.045	0.05	—	0	0.07	0.05-0.09	0.020	5.94	0.18-11.7	5.76
1965-66	3+3	1.08	0.40-2.60	0.383							T	ND-0.06	—			
Md.																
1972	3	0.25	0.24-0.25	0.003	0.04	—	0	0.01	0.01-0.02	0.003	0.02	0.01-0.03	0.007	0.84	0.56-1.22	0.196
1969	2	0.55	0.38-0.77	0.116	0.03	t-0.05	0.012	(0.01)	all t	(0.010)	(0.01)	t-0.02	(0.007)	0.62	0.20-1.33	0.357
1965-66	3+2	0.44	0.20-0.84	0.118							0.05	ND-0.17	0.034			
Va.																
1972	3	0.31	0.18-0.47	0.086	0.05	0.02-0.09	0.021	(0.01)	ND-0.02	(0.007)	0.01	0.009-0.01	0.003	0.71	0.31-1.18	0.254
1969	2	0.45	0.41-0.48	0.035	0.22	0.05-0.40	0.175	0.03	0.02-0.03	0.005	0.04	t-0.07	0.030	0.56	0.13-1.00	0.435
1965-66	3+3	0.30	0.19-0.59	0.061							0.06	ND-0.11	0.018			
S.C.																
1972	3	0.18	0.15-0.23	0.025	0.06	0.05-0.08	0.009	(0.01)	0.009-0.01	(0.003)	0.02	0.02-0.03	0.003	0.56	0.31-0.74	0.128
1969	3	0.65	0.44-0.94	0.151	0.14	0.09-0.22	0.040	0.02	—	0	0.02	0.02-0.03	0.003	0.52	0.17-0.99	0.244
1965-66	3+3	0.37	0.13-1.00	0.133							0.05	ND-0.16	0.026			
Ga. & Fla.																
1972	3	0.54	0.18-0.97	0.230	0.07	0.04-0.11	0.021	0.02	0.009-0.03	0.006	0.03	0.006-0.07	0.021	0.48	0.37-0.62	0.074
1969	2	0.82	0.49-1.32	0.255	0.06	0.05-0.06	0.003	(0.01)	t-0.02	(0.010)	0.02	t-0.02	0.003	0.97	0.25-1.67	0.410
1965-66	2+2	0.53	0.35-0.70	0.079							ND	—	—			

(Continued next page)

TABLE 1 (cont'd). *Residues of organochlorines in 25 wing pools of adult mallards and black ducks, 1965-66, 1969, and 1972*

State, Year	No. Pools [1]	Residues, ppm wet weight														
		DDE			DDT			DDD			Dieldrin			PCB's		
		Mean	Range	Standard Error	Mean	Range	Standard Error	Mean	Range	Standard Error	Mean	Range	Standard Error	Mean	Range	Standard Error
Mallards, Mississippi Flyway																
Minn.																
1972	5	0.27	0.12-0.39	0.050	0.03	0.02-0.04	0.004	(0.01)	t-0.01	(0.002)	(0.01)	t-0.01	(0.001)	0.16	0.11-0.23	0.027
1969	5	0.30	0.20-0.42	0.040	0.04	0.02-0.08	0.010	T	all t	—	(0.01)	all t	(0.004)	0.70	0.16-1.33	0.214
1965-66	7+6	0.24	0.08-0.52	0.039							ND	—	—			
Wis.																
1972	5	0.33	0.11-0.64	0.091	0.04	0.02-0.07	0.009	(0.01)	t-0.01	(0.002)	0.01	0.006-0.03	0.004	0.46	0.23-0.86	0.107
1969	5	0.34	0.19-0.48	0.055	0.03	0.02-0.05	0.005	T	all t	—	(0.01)	all t	(0.004)	0.58	0.17-1.00	0.179
1965-66	3+5	0.28	0.08-0.81	0.096							T	ND-0.05	—			
Mich.																
1972	3	0.22	0.20-0.23	0.009	0.04	0.03-0.05	0.007	(0.01)	all t	(0.001)	(0.01)	t-0.02	(0.005)	0.65	0.36-0.97	0.177
1969	3	0.45	0.33-0.53	0.061	0.05	0.02-0.08	0.018	T	t-0.02	—	0.03	0.02-0.05	0.010	0.62	t-1.00	0.302
1965-66	2+3	0.22	0.10-0.48	0.067							ND	—	—			
Iowa																
1972	5	0.27	0.05-0.78	0.131	0.02	0.02-0.03	0.002	T	t-0.006	—	0.01	t-0.02	0.004	0.14	0.08-0.29	0.039
1969	4	0.33	0.16-0.54	0.094	0.05	t-0.09	0.019	T	all t	—	0.03	0.02-0.05	0.006	0.13	0.07-0.25	0.041
1965-66	5+5	0.22	0.06-0.92	0.080							ND	—	—			
Ill.																
1972	6	0.19	0.13-0.29	0.025	0.01	0.009-0.02	0.002	T	t-0.005	—	0.02	0.01-0.02	0.002	0.20	0.07-0.50	0.062
1969	6	0.73	0.18-2.69	0.395	0.12	0.02-0.54	0.085	0.05	t-0.26	0.043	0.04	0.02-0.07	0.008	0.36	0.13-1.00	0.131
1965-66	7+6	0.09	ND-0.27	0.020							T	ND-0.06	—			
Ind.																
1972	3	0.18	0.13-0.22	0.027	0.11	0.02-0.27	0.080	(0.01)	t-0.02	(0.005)	0.05	0.04-0.06	0.006	0.26	0.12-0.34	0.072
1969	1	0.19	—	—	0.02	—	—	T	—	—	0.03	—	—	1.00	—	—
1965-66	4+3	0.17	0.06-0.29	0.034							T	ND <0.05	—			
Ohio																
1972	3	0.17	0.13-0.20	0.020	0.03	0.02-0.03	0.003	0.02	0.005-0.06	0.018	0.01	—	0	0.60	0.50-1.00	0.206
1969	3	0.38	0.24-0.54	0.087	0.18	0.05-0.30	0.073	T	t-0.02	—	0.09	0.04-0.15	0.033	0.66	0.03-1.66	0.504
1965-66	3+3	0.24	0.15-0.31	0.028							ND	—	—			
Mo.																
1972	5	0.23	0.10-0.27	0.032	0.07	0.02-0.15	0.022	(0.01)	t-0.01	(0.002)	0.01	0.007-0.02	0.003	0.06	0.04-0.11	0.014
1969	5	0.20	0.13-0.30	0.029	0.02	t-0.04	0.007	T	all t	—	0.05	0.04-0.06	0.004	0.21	0.10-0.33	0.052
1965-66	6+5	0.13	ND-0.72	0.065							ND	—	—			
Ky.																
1972	3	0.12	0.11-0.15	0.013	0.03	0.03-0.04	0.003	(0.01)	0.006-0.009	(0.001)	0.03	0.03-0.04	0.003	0.54	0.20-0.97	0.227
1969	1	0.33	—	—	0.04	—	—	T	—	—	0.03	—	—	0.33	—	—
1965-66	3+3	0.30	0.13-0.62	0.080							ND	—	—			
Ark.																
1972	6	0.27	0.11-0.50	0.054	0.19	0.14-0.33	0.029	0.04	0.02-0.07	0.007	0.03	0.02-0.04	0.003	0.06	0.03-0.08	0.008
1969	6	0.25	0.21-0.28	0.013	0.12	0.04-0.16	0.019	0.03	t-0.04	0.004	0.06	0.02-0.11	0.013	0.16	t-0.67	0.103
1965-66	7+6	0.20	0.08-0.31	0.021							0.08	ND-0.34	0.028			
Tenn.																
1972	4	0.34	0.12-0.89	0.185	0.29	0.02-1.05	0.254	0.06	t-0.24	0.058	0.02	0.02-0.03	0.002	0.42	0.16-0.59	0.092
1969	4	0.26	0.20-0.34	0.029	0.06	0.02-0.11	0.023	T	all t	—	0.04	0.02-0.04	0.005	0.71	0.25-1.66	0.333
1965-66	5+4	0.33	0.11-1.10	0.099							0.06	ND-0.39	0.043			

(Continued next page)

TABLE 1 (cont'd). *Residues of organochlorines in 25 wing pools of adult mallards and black ducks, 1965-66, 1969, and 1972*

State, Year	No. Pools [1]	Residues, ppm wet weight															
		DDE			DDT			DDD			Dieldrin			PCB's			
		Mean	Range	Standard Error	Mean	Range	Standard Error	Mean	Range	Standard Error	Mean	Range	Standard Error	Mean	Range	Standard Error	
Mallards, Mississippi Flyway—Continued																	
La.																	
1972	5	0.27	0.10-0.59	0.085	0.15	0.05-0.23	0.034	0.02	0.008-0.03	0.004	0.04	0.02-0.05	0.006	0.11	0.04-0.24	0.036	
1969	5	0.44	0.27-0.74	0.081	0.11	0.07-0.19	0.026	0.02	t-0.03	0.003	0.05	0.04-0.07	0.007	0.23	0.07-0.50	0.074	
1965-66	5+6	0.18	0.05-0.26	0.018							T	ND-0.05	—				
Miss.																	
1972	3	0.68	0.15-1.28	0.328	0.69	0.04-1.56	0.452	0.17	0.007-0.43	0.130	0.03	0.02-0.04	0.007	0.20	0.06-0.47	0.137	
1969	2	0.52	0.36-0.68	0.160	0.14	0.05-0.22	0.009	0.04	0.04-0.05	0.005	0.04	0.04-0.05	0.005	0.10	t-0.17	0.075	
1965-66	3+3	0.51	0.21-0.96	0.137							T	ND-0.05	—				
Ala.																	
1972	4	1.85	0.79-4.12	0.767	1.03	0.23-2.98	0.653	0.44	0.09-1.23	0.267	0.03	0.01-0.05	0.008	6.34	0.21-7.73	3.93	
1969	1	1.75	—	—	0.09	—	—	2.07	—	—	0.09	—	—	0.42	—	—	
1965-66	2+3	2.17	0.54-5.31	0.922							0.05	ND-0.14	0.035				
Mallards, Central Flyway																	
Mont. (east)																	
1972	4	0.07	0.05-0.09	0.009	0.01	0.007-0.01	0.001	T	all t	—	(0.01)	0.006-0.01	(0.001)	0.06	0.04-0.07	0.008	
1969	4	0.11	0.08-0.17	0.020	0.03	t-0.08	0.017	0.02	t-0.03	0.008	0.04	t-0.05	0.010	0.18	0.13-0.25	0.025	
1965-66	8+4	0.09	0.05-0.16	0.010							T	ND-0.16	—				
N.Dak.																	
1972	6	0.19	0.08-0.33	0.037	0.03	0.006-0.08	0.011	(0.01)	0.005-0.02	(0.002)	(0.01)	t-0.01	(0.001)	0.12	0.08-0.25	0.027	
1969	6	0.25	0.14-0.44	0.050	0.03	t-0.06	0.008	T	all t	—	(0.01)	all t	(0.003)	0.13	t-0.50	0.076	
1965-66	8+8	0.12	0.05-0.43	0.022							ND	—	—				
S.Dak.																	
1972	6	0.17	0.08-0.18	0.031	0.02	0.01-0.04	0.005	T	all t	—	(0.01)	t-0.02	(0.003)	0.12	0.08-0.19	0.016	
1969	6	0.09	0.07-0.14	0.011	(0.01)	t-0.02	(0.003)	T	ND-t	—	(0.01)	all t	(0.003)	0.13	t-0.25	0.034	
1965-66	7+8	0.11	ND-0.20	0.014							ND	—	—				
Wyo. (east)																	
1972	3	0.06	0.04-0.08	0.012	(0.01)	0.007-0.009	(0.001)	T	all t	—	0.01	0.007-0.02	0.004	0.10	0.08-0.12	0.012	
1969	3	0.13	0.08-0.19	0.032	0.02	t-0.03	0.009	T	all t	—	0.02	t-0.02	0.003	0.30	0.25-0.33	0.027	
1965-66	1+3	0.16	0.05-0.45	0.097							ND	—	—				
Nebr.																	
1972	8	0.10	0.06-0.16	0.012	0.01	0.007-0.02	0.002	T	all t	—	T	t-0.008	0.001	0.04	0.03-0.06	0.004	
1969	7	0.13	0.06-0.19	0.017	(0.01)	t-0.02	(0.003)	T	all t	—	(0.01)	t-0.02	(0.004)	0.06	t-0.13	0.015	
1965-66	6+7	0.10	0.05-0.17	0.009							ND	—	—				
Colo. (east)																	
1972	6	0.16	0.10-0.26	0.026	0.02	0.01-0.02	0.002	T	t-0.006	—	0.02	0.008-0.08	0.012	0.25	0.15-0.34	0.034	
1969	4	0.46	0.13-1.25	0.266	0.06	0.02-0.09	0.015	T	t-0.02	—	0.02	t-0.03	0.006	0.43	0.07-1.33	0.301	
1965-66	10+4	0.30	0.17-0.85	0.048							ND	—	—				
Kans.																	
1972	6	0.18	0.11-0.24	0.021	0.03	0.02-0.05	0.005	T	t-0.007	—	0.01	0.008-0.02	0.002	0.07	0.06-0.11	0.008	
1969	6	0.11	0.08-0.15	0.011	0.02	t-0.06	0.008	T	t-0.02	—	0.02	t-0.03	0.005	0.15	0.03-0.50	0.072	
1965-66	7+6	0.08	ND-0.12	0.009							ND	—	—				

(Continued next page)

TABLE 1 (cont'd). *Residues of organochlorines in 25 wing pools of adult mallards and black ducks, 1965-66, 1969, and 1972*

State, Year	No. Pools [1]	Residues, ppm wet weight														
		DDE			DDT			DDD			Dieldrin			PCB's		
		Mean	Range	Standard Error	Mean	Range	Standard Error	Mean	Range	Standard Error	Mean	Range	Standard Error	Mean	Range	Standard Error
Mallards, Central Flyway—Continued																
N.Mex. (east)																
1972	4	0.18	0.09-0.26	0.040	0.02	—	0	(0.01)	t-0.009	(0.001)	0.01	0.007-0.03	0.005	0.25	0.07-0.62	0.126
1969	3	0.37	0.26-0.57	0.099	0.03	0.02-0.05	0.009	T	all t	—	0.02	t-0.02	0.003	0.18	0.13-0.25	0.037
1965-66	3+3	0.74	0.22-2.44	0.349							T	ND-0.06	—			
Okla.																
1972	4	0.22	0.08-0.49	0.097	0.02	0.02-0.04	0.005	T	t-0.01	—	0.01	0.007-0.03	0.005	0.08	0.04-0.12	0.017
1969	4	0.15	0.13-0.18	0.012	0.02	—	0	T	t-0.02	—	0.03	t-0.08	0.019	0.12	t-0.23	0.058
1965-66	5+4	0.11	0.07-0.20	0.016							ND	—	—			
Tex.																
1972	9	0.17	0.05-0.43	0.040	0.03	0.01-0.06	0.006	(0.01)	t-0.01	(0.001)	0.07	0.008-0.30	0.033	0.05	0.02-0.08	0.007
1969	6	0.98	0.13-4.38	0.683	0.09	t-0.38	0.059	T	t-0.02	—	0.07	t-0.26	0.039	0.20	t-0.67	0.100
1965-66	6+9	0.35	0.12-1.14	0.072							0.08	ND-0.53	0.037			
Mallards, Pacific Flyway																
Wash.																
1972	8	0.19	0.09-0.32	0.031	0.02	0.005-0.05	0.005	T	t-0.009	—	(0.01)	t-0.02	(0.002)	0.09	0.07-0.12	0.009
1969	8	0.36	0.19-0.48	0.037	0.04	0.03-0.05	0.003	T	t-0.02	—	(0.01)	t-0.02	(0.004)	0.14	t-0.33	0.039
1965-66	13+11	0.47	0.06-2.75	0.125							T	ND-0.10	—			
Oreg.																
1972	7	0.32	0.14-0.58	0.066	0.05	0.02-0.13	0.014	(0.01)	t-0.02	(0.003)	0.03	0.009-0.07	0.010	0.09	0.05-0.14	0.011
1969	7	0.48	0.21-1.03	0.122	0.09	0.03-0.29	0.037	T	t-0.03	—	0.03	t-0.12	0.017	0.10	t-0.20	0.020
1965-66	7+7	0.36	0.12-0.59	0.038							T	ND-0.09	—			
Idaho																
1972	8	0.44	0.22-0.84	0.064	0.60	0.04-0.10	0.009	(0.01)	0.006-0.02	(0.002)	0.02	0.008-0.03	0.003	0.09	0.05-0.19	0.010
1969	8	0.48	0.23-0.79	0.069	0.08	0.05-0.22	0.021	T	t-0.02	—	0.02	t-0.05	0.006	0.14	0.10-0.32	0.028
1965-66	9+9	0.51	0.06-2.77	0.140							T	ND-0.09	—			
Mont. (west)																
1972	4	0.08	0.06-0.12	0.015	(0.01)	0.006-0.02	(0.003)	T	all t	—	0.01	0.006-0.03	0.006	0.06	0.04-0.08	0.009
1969	4	0.14	0.07-0.21	0.029	0.03	t-0.05	0.009	T	all t	—	(0.01)	all t	(0.005)	0.15	0.03-0.27	0.050
1965-66	4+4	0.17	0.08-0.34	0.031							T	ND-0.06	—			
Wyo. (west)																
1972	2	0.06	0.05-0.07	0.010	(0.01)	0.007-0.009	(0.001)	T	all t	—	T	all t	—	0.04	0.04-0.05	0.005
1969	2	0.12	0.09-0.14	0.025	0.02	t-0.03	0.010	T	all t	—	0.02	t-0.03	0.010	0.12	0.10-0.13	0.015
1965-66	2+3	0.07	ND-0.10	0.015							ND	—	—			
Calif.																
1972	10	0.60	0.30-2.30	0.192	0.04	0.02-0.07	0.005	(0.01)	t-0.02	(0.001)	0.01	0.007-0.02	0.002	0.12	0.06-0.28	0.020
1969	8	1.52	0.99-2.70	0.190	0.19	0.09-0.37	0.035	0.04	t-0.22	0.026	0.02	t-0.10	0.012	0.04	t-0.10	0.013
1965-66	11+11	1.45	0.02-3.50	0.174							T	ND-0.08	—			
Nev.																
1972	3	0.14	0.10-0.16	0.019	(0.01)	0.008-0.01	(0.001)	T	t-0.008	—	(0.01)	ND-0.02	(0.005)	0.10	0.06-0.13	0.02
1969	3	0.24	0.20-0.33	0.043	0.05	0.02-0.08	0.018	T	all t	—	0.02	t-0.05	0.014	0.73	t-1.66	0.487
1965-66	2+3	0.23	0.08-0.37	0.047							ND	—	—			

(Continued next page)

TABLE 1 (cont'd). *Residues of organochlorines in 25 wing pools of adult mallards and black ducks, 1965-66, 1969, and 1972*

State, Year	No. Pools [1]	Residues, ppm wet weight														
		DDE			DDT			DDD			Dieldrin			PCB's		
		Mean	Range	Standard Error	Mean	Range	Standard Error	Mean	Range	Standard Error	Mean	Range	Standard Error	Mean	Range	Standard Error
Mallards, Pacific Flyway—Continued																
Utah																
1972	7	0.44	0.25-0.65	0.053	0.02	0.01-0.02	0.003	0.01	0.005-0.02	0.002	(0.01)	0.006-0.02	(0.002)	0.22	0.16-0.44	0.037
1969	5	1.29	0.49-2.09	0.294	0.28	0.04-0.44	0.075	0.03	0.02-0.03	0.002	0.08	0.03-0.23	0.037	0.26	0.07-0.50	0.069
1965-66	6+5	0.93	0.39-1.41	0.102							0.05	ND-0.16	0.019			
Colo. (west)																
1972	3	0.20	0.07-0.30	0.069	0.04	0.02-0.12	0.014	0.005	t-0.007	0.001	(0.01)	0.006-0.01	(0.001)	0.14	0.09-0.22	0.040
1969	3	0.36	0.19-0.63	0.137	0.05	0.02-0.08	0.018	T	all t	—	0.05	t-0.11	0.032	0.22	0.17-0.25	0.024
1965-66	3+3	0.69	0.11-3.20	0.504							ND	—	—			
Ariz. & N.Mex. (west)																
1972	3	0.38	0.14-0.60	0.135	0.02	0.01-0.02	0.003	(0.01)	0.006-0.007	(0.003)	0.02	t-0.02	0.005	0.14	0.09-0.16	0.023
1969	3	0.68	0.25-1.52	0.418	0.02	t-0.03	0.006	T	t-0.02	—	(0.01)	all t	(0.007)	0.12	t-0.17	0.050
1965-66	1+3	0.31	ND-0.73	0.146							0.05	ND-0.12	0.030			

NOTE: Residues may be converted to approximate ppm dry weight or ppm lipid weight by dividing wet-weight value by 0.60 or 0.13, the mean proportions of dry and lipid material in the samples. Parenthesized values are approximations involving trace residues. Means assume trace values as half the limit of quantification. Standard errors have been maximized.
t = trace residue below limit of quantification
ND = not detected
T = mean residue below limit of quantification
— = not applicable

[1] Plus sign divides the number of 1965 and 1966 wing pools.

TABLE 2. *Mean residues of organochlorines in wing pools by major flyway, 1969 and 1972*

Species	Flyway	Year	No. Pools	Residues, ppm wet weight									
				DDE		DDT		DDD		Dieldrin		PCB's	
				Mean	Standard Error	Mean	Standard Error	Mean	Standard Error	Mean	Standard Error	Mean	Standard Error
Black Duck	Atlantic	1972	44	0.35[1]	0.043	0.07	0.009	0.02	0.003	0.02[2]	0.004	1.36	0.149
		1969	42	1.32	0.149	0.12	0.011	0.03	0.019	0.14	0.057	1.37	0.161
Mallard	Atlantic	1972	21	0.44[2]	0.069	0.08	0.011	0.06	0.050	0.02	0.003	1.24	0.230
		1969	19	1.03	0.173	0.09	0.014	0.02	0.002	0.05	0.025	1.29	0.457
Mallard	Mississippi	1972	61	0.37	0.072	0.18	0.057	(0.06)	—	0.02	0.001	0.66	0.303
		1969	51	0.40	0.058	0.08	0.012	(0.05)	—	0.04	0.003	0.44	0.061
Mallard	Central	1972	56	0.15	0.012	0.02	0.001	T	—	(0.02)	—	0.10[3]	0.013
		1969	49	0.30	0.098	0.03	0.009	T	—	0.02	0.006	0.20	0.039
Mallard	Pacific	1972	55	0.34[1]	0.043	0.03[1]	0.003	(0.01)	—	(0.01)	—	0.11[3]	0.009
		1969	51	0.71	0.054	0.11	0.012	T	—	0.02	0.005	0.20	0.014

NOTE: T = mean residue below limit of quantification
t = trace residue below limit of quantification
— = not applicable
Parenthesized values are approximations involving trace residues.
[1] Flyway means for the 2 years significantly different: $p < 0.001$.
[2] Flyway means for the 2 years significantly different: $p < 0.01$.
[3] Flyway means for the 2 years significantly different: $p < 0.05$.

As reported in the 1969 survey (*8*), PCB residues showed pronounced geographical differences: levels were highest in the Atlantic Flyway and diminished westward. PCB levels in mallards declined by 50 percent in the Central Flyway and by 45 percent in the Pacific Flyway ($p < 0.01$) but not in the Atlantic or Mississippi Flyways. In fact, PCB levels in the Mississippi Flyway increased somewhat, but the increase was insignificant, probably because of the high variability in 1972 results. Correlation of organochlorine residues among wild bird tissues, already well documented (*10,11*), is further illustrated by data in the present study. Regression analyses indicate highly significant correlations ($p < 0.01$) among all residues in Atlantic Flyway black ducks (Table 3). In Atlantic Flyway mallards, however, DDE correlated significantly with residues of all pesticides except dieldrin. None of the other residues significantly correlated (Table 3).

TABLE 3. *Correlation among residues in Atlantic Flyway black ducks and mallards, 1972-73*[1]

	Product-Moment Correlation Coefficients				
	DDE	DDT	DDD	Dieldrin	PCB's
Black Ducks					
DDE	1	0.7710[2]	0.6890[2]	0.4140[2]	0.5094[2]
DDT		1	0.8019[2]	0.2895[2]	0.4295[2]
DDD			1	0.3803[2]	0.6352[2]
Dieldrin				1	0.5103[2]
PCB's					1
Mallards					
DDE	1	0.6502[2]	0.7129[2]	0.0265	0.5274[2]
DDT		1	0.3558	0.1273	0.3236
DDD			1	0.3752	0.3064
Dieldrin				1	0.1778
PCB's					1

[1] Residues were power transformed by the equation $y = ax^b$ before regression analysis.
[2] $p < 0.01$

Conclusions

Residues of DDE, DDT, dieldrin, and PCB's in mallards and black ducks have declined since 1969 in certain flyways, showing that duck wings can serve as indicators of environmental levels of organochlorines and thus provide information on residue trends over time. Geographical differences in levels of contamination also were detected.

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GENERAL

Seasonal Concentrations of Dieldrin in Water, Channel Catfish, and Catfish-Food Organisms, Des Moines River, Iowa—1971-73 [1]

R. L. Kellogg [2] and R. V. Bulkley [2]

ABSTRACT

Concentrations of dieldrin in aquatic insects, crayfish, minnows, and small carpsuckers, and muscle tissue of channel catfish (Ictalurus punctatus) *were compared with the dieldrin content of Des Moines River water in 1971-73. Monthly mean concentrations of dieldrin in river water and most aquatic organisms were highest in June and July, soon after aldrin had been applied to corn land in the watershed. Several groups of aquatic organisms also exhibited high dieldrin levels in the fall when the dieldrin content of river water was seasonally low. The influence of temperature on metabolic rate and enzyme activity and the differences in body fat content were suggested as probable causes of variations observed in the dieldrin content of aquatic organisms.*

Introduction

Chlorinated hydrocarbon insecticides have been used on midwestern farmland for many years. Most uses of these substances including DDT and clordane were discontinued in the late 1960's but aldrin was used widely against soil insects as late as 1974. Between 1961 and 1965, aldrin was applied in Iowa at the rate of 5-6.5 million pounds/year for control of western corn rootworm. As rootworms became more resistant to aldrin, usage against rootworms and other soil insects decreased to 2 million pounds annually between 1968 and 1973 (Harold Stockdale, 1973, Extension Entomologist, Department of Entomology, Iowa State University, Ames, Iowa: personal communication).

Use of aldrin and other pesticides has contributed significantly to the production of record corn crops. Morris and Ebert (*1*), however, reported that aldrin applied to row crops in Iowa was appearing in the form of high concentrations of dieldrin, the initial oxidation product of aldrin, in edible tissue of channel catfish (*Ictalurus punctatus*) in rivers draining cropland. Morris and Johnson (*2*) found that dieldrin concentrations in some large catfish collected from several Iowa rivers exceeded 300 ppb, the level in human food permitted by the Food and Drug Administration, U.S. Department of Health, Education, and Welfare. Concentrations were as high as 1,600 ppb in muscle tissue: this represents more than five times the allowable level. Inasmuch as the channel catfish is an important game fish in Iowa, contamination of this species with dieldrin could seriously affect the sport and commercial fisheries of the State.

From 1971 to 1973, authors attempted to obtain more information on dieldrin concentrations in channel catfish. The portion of the study reported here covers seasonal variations of dieldrin levels in river water, catfish muscle tissue, and organisms important in the catfish diet.

The Des Moines River above Boone, Iowa, was selected as the study site because of its importance as a catfish angling stream, its similarity to many other Iowa rivers, and the extensive row-crop farmland in its watershed. The Des Moines, the largest river flowing through Iowa, arises in a glacial moraine in southwestern Minnesota and flows southeasterly across Iowa to the Mississippi River. The collection site in Boone County is about 426 km upstream from the mouth of the river. At this point the river drains about 1.4 million ha. or 38 percent of the total drainage area of the basin (*3*). Nearly 80 percent of the Des Moines River watershed is cropland, 10-15 percent is permanent pasture, and 5 percent is urban (*4*).

The river basin has a temperate climate. The average yearly temperature of the Iowa portion of the basin

[1] Journal Paper No. J-8215, Project No. 1928, Iowa Agriculture and Home Economics Experiment Station, Ames, Iowa. Financed by grant from Office of Water Resources Research, U.S. Department of Interior (Agreements 14-31-0001-3515, -3815, -4015) under Public Law 88-379. Made available through Iowa State Water Resources Research Institute to the Iowa Cooperative Fishery Research Unit, which is sponsored by the Iowa State Conservation Commission, Iowa State University of Science and Technology, and the Fish and Wildlife Service, U.S. Department of Interior.

[2] Iowa Cooperative Fishery Research Unit, Iowa State University, Ames, Iowa 50011.

ranges from about 8° to 10°C from north to south (*3*). Annual precipitation over the dainage area averages about 70 cm, ranging from 63 cm in the north to 79 cm in the south. Precipitation is usually heaviest in May and June, a period when the river reaches its high levels each year. Frequently an early spring flood follows thawing and fast runoff. Cloudbursts and heavy rains occasionally cause temporary flooding in summer and even in early fall.

The river bottom is composed chiefly of sand and gravel but includes sand-silt, rubble, and boulders in limited areas. During times of low water levels many sand bars appear. Deep holes are present below the bars and at bends. The river has few connecting sloughs and backwaters except during high water.

Methods

SAMPLE COLLECTION AND ANALYSIS

Authors collected 1-liter water samples monthly from May through October in 1971 and duplicate 1-liter water samples weekly from April 24 through June and twice monthly from July to October 15, 1972. A clean glass container was submerged about 300 mm below the surface of the water in a rapidly flowing section of the river to obtain the sample. The containers were then sealed with screw caps lined with Teflon or aluminum foil. Samples were shaken thoroughly and 750 ml was decanted off for single extraction with 60 ml of 15 percent ethyl ether : hexane in 1971. A second extraction with 60 ml hexane was performed on water samples in 1972 (*5*). Extracts were concentrated to 1 ml for quantitation.

In 1973, triplicate 2-liter samples were collected twice weekly from April 21 through July and usually weekly from August 1 to November 16. Samples were filtered through pre-extracted No. 40 Whatman filter paper to separate dissolved fractions from suspended fractions. The dissolved fraction was extracted twice with 120 ml of 15 percent ethyl ether and hexane, followed by a third extraction with 150 ml hexane. Collection vessels were rinsed with a portion of the initial extraction solvent to remove pesticides adhering to the container walls. Extracts were combined and concentrated to 1 ml for quantitation. Florisil cleanup (*5*) was employed when necessary.

The suspended fraction retained on the filter paper was extracted with 300 ml acetonitrile in a Soxhlet extraction assembly for 18 hours. The pesticide residues were partitioned into petroleum ether by adding 200 ml distilled water to the acetonitrile and extracting three 60-ml portions of petroleum ether. The final extraction was followed by the addition of 1,200 ml distilled water. Petroleum ether extracts were combined and washed with distilled water to remove the remaining acetonitrile. Further cleanup on florisil columns was necessary. Samples were concentrated to 1 ml for quantitation. Results were expressed as parts per trillion (pptr) for both dissolved and suspended fractions.

Bottom sediment samples were collected monthly from July to November 1973. The top 15 mm of sediment was scooped from shallow, silty areas of the river bottom in an attempt to collect newly deposited material. Samples were passed through a No. 230 standard sieve with 63-μ openings and allowed to dry thoroughly at room temperature. Three 100-g aliquots were Soxhlet-extracted with 300 ml chloroform for 18 hours. Extracts were concentrated to 2-3 ml and introduced onto a 6-by-90 mm Fisher coconut charcoal column with 15 ml of 25 percent acetone and ethyl ether to remove polychlorinated biphenyl (PCB) interferences (*6*). Pesticide residues were eluted from the charcoal column with 90 ml of 25 percent acetone and ethyl ether leaving the PCB's absorbed on the charcoal. This eluate was concentrated to 2-3 ml, introduced onto a florisil column, and eluted with 200 ml of 20 percent ethyl ether and petroleum ether. Samples were concentrated to 10 ml for quantitation.

In 1972 authors collected mayfly naiads (*Potamanthus* sp.) from April 23 to July 10, and crayfish (*Orconectes rusticus*) from April 23 to October 15, by moving rocks in riffle areas and capturing the dislodged organisms with a dip net. *Potamanthus* collections were pooled into three subsamples for each collection date. Individual analyses were run on *O. rusticus*.

In 1973, aquatic insects, crayfish, minnows, and small carpsuckers (*Carpiodes* sp.) were collected from June to November. Early spring collections could not be taken because the river was flooded. Aquatic insects were collected in basket substrate samplers suspended from floats and by dislodging rocks in riffle areas. Insects collected and grouped by taxon for pesticide analysis were: *Acroneuria, Pteronarcys, Potamanthus, Isonychia, Ephoron, Corydalus, Heptageniidae, Chironomidae,* and *Tricoptera*. Because the faunal assemblage varied throughout the sampling period, it was not possible to collect representatives from more than four of the groups at any one time in sufficient numbers for pesticide analysis. *Orconectes rusticus, O. virilis,* spotfin shiners (*Notropis spilopterus*), sand shiners (*N. stramineus*), bluntnose minnows (*Pimephales notatus*), and young-of-the-year and yearling carpsuckers were collected regularly throughout the sampling period by seining. Collections were pooled by taxonomic groups, blotted dry, and weighed. Sample size of most aquatic insects ranged from 0.3 to 8.0 g. Samples ranged from 4 to 50 g for *Corydalus* and *Orconectes*, and from 12 to 82 g for minnows. Replicate samples were run when sample size was adequate. Tissue samples were analyzed according to the procedures in the *Pesticide Analytical Manual* of the U.S. Department of Health, Education, and Welfare (*7*). The extraction procedure was slightly

modified when a double petroleum ether extraction was made during the partitioning phase.

Extracts were concentrated and eluted in the same manner as the sediment extracts. Samples were concentrated to 1-10 ml for quantitation.

In 1971, authors collected channel catfish monthly from April through October in hoop nets and by electroshocking. Total length was measured at capture. Fish were then wrapped in aluminum foil and frozen until analysis. Dorsal muscle tissue of catfish 300-399 mm long and of all catfish taken in June was analyzed individually (7). Catfish 200-299 mm long, which were collected during months other than June, were pooled on each collection date for a single analysis.

In 1973, channel catfish were collected monthly from June to September. Spring and fall flooding prevented further sampling. Specimens were grouped for pesticide analysis in four lengths: 150-199 mm, 200-299 mm, 300-399 mm, and 450-550 mm. Muscle tissue from 4 to 15 catfish in each length group was pooled into three subsamples for each collection day. Small numbers of 450-550-mm catfish occasionally were analyzed individually. Samples were extracted and cleaned on charcoal and florisil columns as previously described for crayfish and small fish.

QUANTITATION

A Beckman GC-5 gas chromatograph equipped with a discharge electron-capture detector was employed for the quantitation of all samples. Quantitation was accomplished on a 5 percent OV-210 column at 180°C and a 1.5 percent OV-17/QF-1 column at 200°C. Helium flow was about 100 mm/min and attenuation was $2\times10^{+3}$. A 4 percent SE-3/6/QF-1 column with a gas flow rate of 120 mm/min, a temperature of 200°C, and an attenuation of $2\times10^{+3}$ was used as a qualitative check. Confirmation was made by comparing retention time of the samples to that of a dieldrin standard filtered through two chromatographic columns of different polarity.

Background levels of 8.4 ng (standard deviation: 0.8 ng) of what seemed to be dieldrin were measured from a series of blanks in 1973. This contamination was usually less than 1 percent for crayfish and fish samples weighing more than 10 g. Background dieldrin levels for aquatic insect samples, however, varied from 2 to 27 percent because very little tissue was available for analysis. The reported dieldrin concentrations in aquatic insects were corrected for this contamination. Pesticides in all organisms were expressed on a wet-weight basis.

RECOVERY

Channel catfish were exposed to 10 ppb ^{14}C-dieldrin in 360 liters of water for 6 hours. A 519 ppb (standard deviation: 31 ppb) stock mesh and a 53.6 ppb (standard deviation: 2.8 ppb) stock mesh were prepared by homogenizing muscle tissue of the exposed catfish with portions of cold tissue in a Waring blendor. Stock mesh dieldrin levels were determined by directly counting tissue samples. Three replicates of four dieldrin levels (5190.0, 1072.0, 107.0, and 53.6 ng) were prepared by varying sample sizes from the two stock meshes in order to cover the range of dieldrin levels encountered in the survey. These samples were extracted and cleaned according to the method of analysis employed throughout the investigation. Aliquots of these extracts were removed to scintillation vials with 15 ml BBOT scintillation cocktail for counting on a Packard Tri-Carb scintillation counter. Quenching was corrected by internal standardization. Recovery of dieldrin from catfish muscle tissue averaged 86 percent and ranged from 78 to 99 percent. Results were not corrected for percent recovery.

Results

Dieldrin concentrations in Des Moines River water and suspended sediment ranged from 10 to 50 pptr in 1971, from less than 10 to 40 pptr in 1972, and from 1 to 31 pptr in 1973. Variation within and among years was significant (Fig. 1). Average dieldrin concentrations from May to September decreased from 32 pptr in 1971 to less than 15 pptr in 1972 and to 8 pptr in 1973 (Table 1). Wide variations in stream flow and suspended sediment load also occurred during the 3-year period. Flow during the study period was about normal in 1971, higher in 1972, and at record highs in 1973. Because concentrations might vary directly or inversely with flow, authors calculated the actual amount of dieldrin being transported past the study site. Comparisons of dieldrin concentrations were most reliable on an annual basis for 1971 and 1973 and for June and July of all 3 years. The average amount of dieldrin transported downstream per day was 174 g in 1971 but only 89 g in 1973. Concentrations and amounts of dieldrin transported downstream decreased in June and July each year.

Seasonal trends in dieldrin concentrations were also consistent from year to year: the dieldrin content was low in early spring, increased rapidly thereafter, and decreased in late summer (Fig. 1). Average concentrations were highest in June and July. When mean monthly concentrations for the 3 years combined were plotted to reveal general trends more clearly, the relatively high concentrations during June and July were very evident (Fig. 2).

This seasonal trend in dieldrin levels was evaluated in light of occurrences in the watershed. Most Iowa farmland is plowed in late fall so that the land is clear of vegetation in early spring when final preparations, including the application of aldrin, are made for planting. Heavy rains during the spring sometimes deposit huge quantities of soil in the streams. For example, a storm

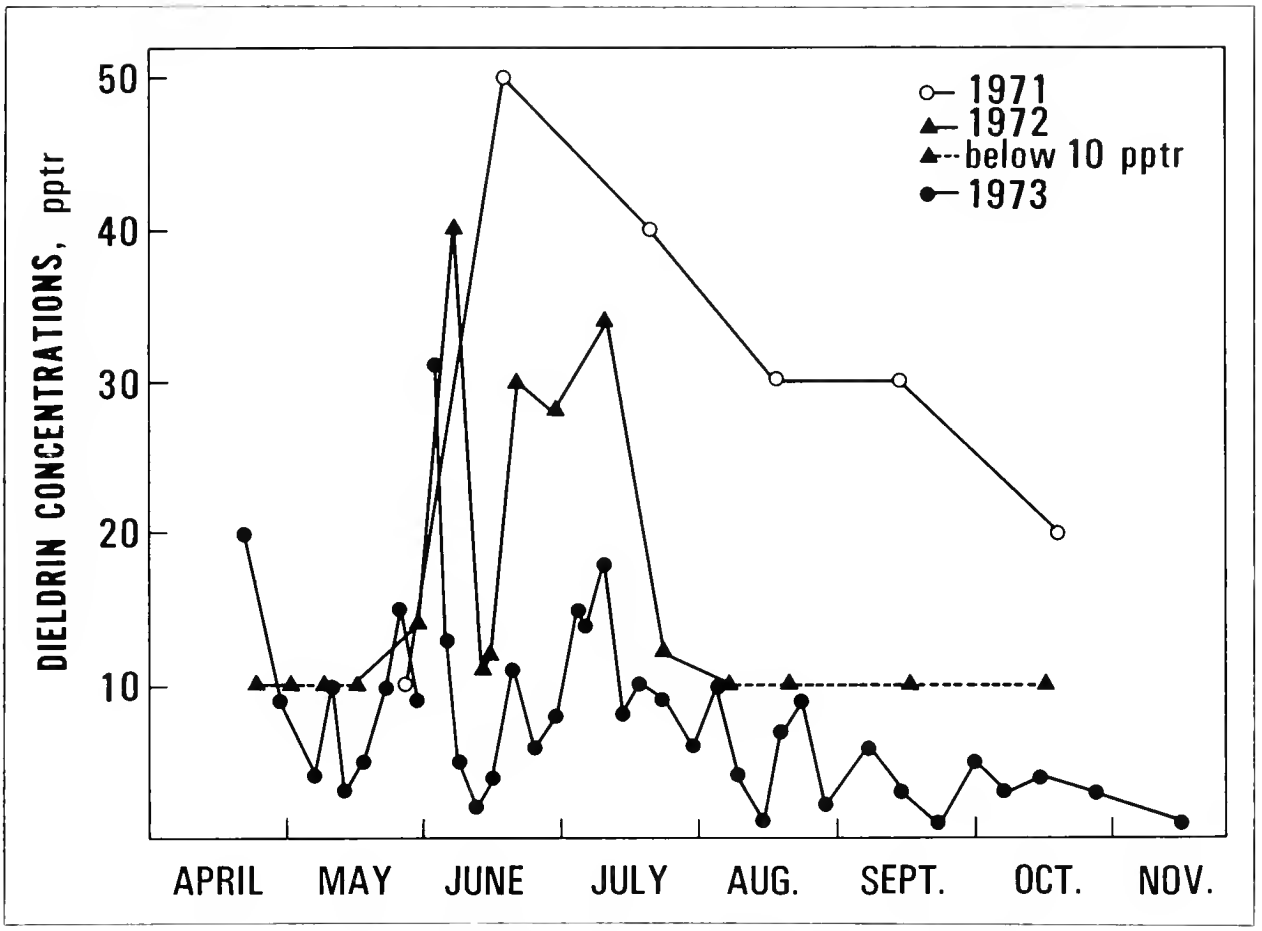

FIGURE 1. *Total dieldrin concentration, unfiltered Des Moines River water, Iowa—1971-73*

on the watershed caused increased river flow and heavy sediment discharge from May 30 to June 2, 1973. On May 31, 19,233 metric tons of suspended sediment were carried downriver past the Saylorville, Iowa, gaging station located below the study site (*8*). On June 2, when water samples were collected for analysis, stream flow was 320 m^3/sec; sediment load was 12,973 metric tons. A total of 858 g of dieldrin was transported downstream that day. This calculation was based on an average of 19 pptr (61 percent) sorbed on the suspended sediment and 12 pptr dieldrin in filtered water samples. The source of this sediment was unknown, but Glymph (*9*), who examined data on small watersheds in four Iowa counties, reported that 56-100 percent of the sediment in streams came from sheet erosion off the land. Huang and Liao (*10*) and Huang (*11,12*) illustrated the high affinity of different types of clay particles for dieldrin. Thus, the sorbed pesticide can be carried

TABLE 1. *Mean monthly concentrations of dissolved and suspended dieldrin, mean daily stream flow, and calculated dieldrin transport, Des Moines River, Iowa—May-September, 1971-73*

	No. sampling days			Mean dieldrin concentration, pptr			Mean daily stream flow, M^3/sec [1]			Calculated dieldrin transport, g/day		
Month	1971	1972	1973	1971	1972	1973	1971	1972	1973	1971	1972	1973
May	1	4	7	10	<10	8	66.1	137.9	244.6	57 [2]	<119	169
June	1	5	8	50	24	10	110.9	116.4	175.1	479	242	151
July	1	2	7	40	23	12	97.9	83.6	92.5	338	166	96
August	1	2	6	30	<10	6	14.7	114.9	26.4	38	<99	14
September	1	1	4	30	<10	4	5.7	42.3	44.2	15	<36	15
	MEAN			32	<15	8	59.1	99.0	116.6	174	<132	89

[1] See Literature Cited, references 8, 19, and 20.
[2] 10 pptr × 10^{-12} × 66.1 m^3 × 10^6 × 86,400 sec = 57 g/day.

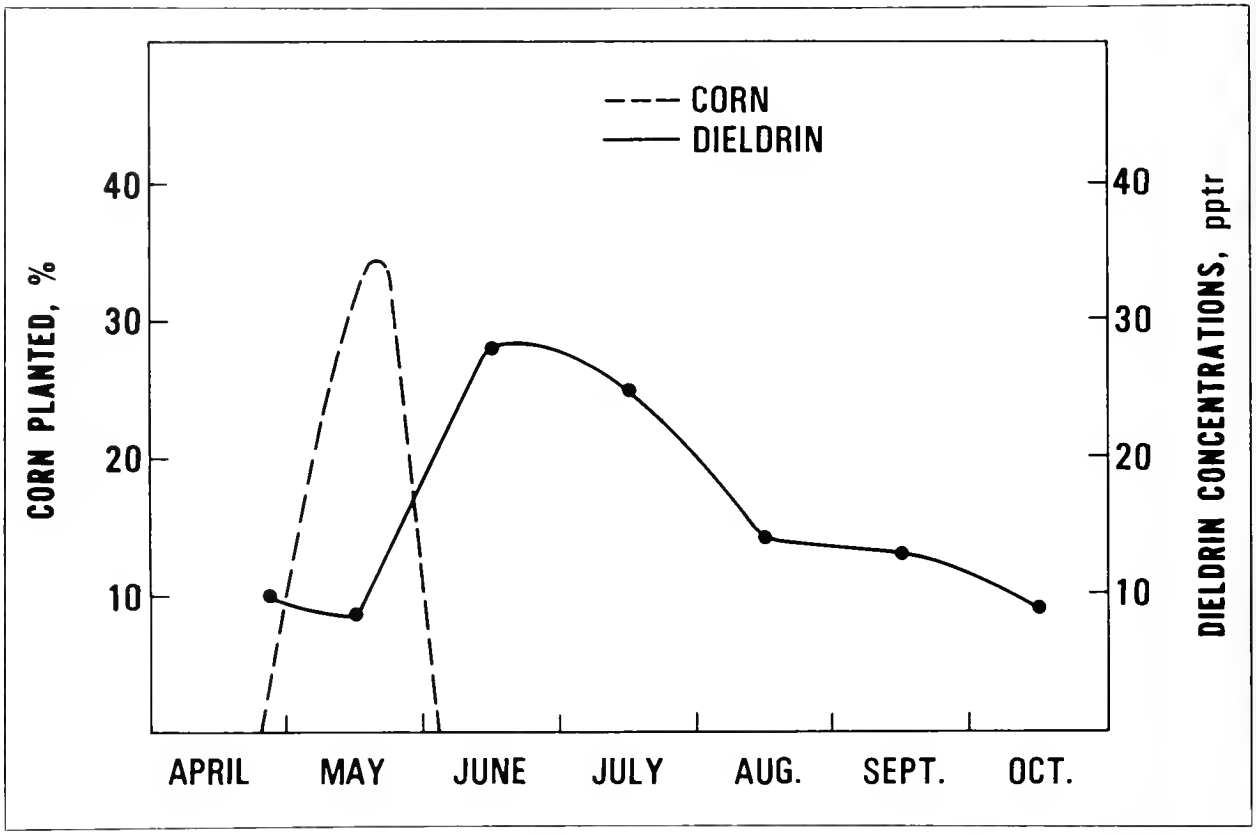

FIGURE 2. *Timing of corn planting and aldrin application in relation to monthly mean dieldrin concentrations, Des Moines River water, Iowa—1971-73*

with the soil into river systems by storm runoff. The amount of pesticide transported during any one storm depends on variables such as duration of storm runoff, antecedent soil/moisture conditions, rainfall intensity, and the source of runoff in the watershed (*13*).

Corn was planted progressively later in each of the 3 study years because of adverse weather and heavy rainfall in the spring of 1972 and 1973. About 95 percent of the corn was planted by May 24 in 1971, and by May 28 in 1972, but not until after June 4 in 1973 (*14,15*). For 3 years corn planting and aldrin application were essentially completed by the first week in June. In June and July mean dieldrin concentrations in river water were at their peak. Although authors did not determine the source of the dieldrin in river water, these relations support the premise of Johnson and Morris (*16*) that dieldrin in Iowa rivers and streams originates mainly from agricultural application of aldrin through surface runoff from cultivated areas.

Authors examined the relative amounts of dieldrin in the suspended dissolved fractions of water samples collected in 1973. Suspended dieldrin, extracted primarily from soil particles and secondarily from plankton, ranged from less than 1 pptr to 19 pptr, which was 3-67 percent of the total dieldrin measured in water samples on a given day (Fig. 3). An average of about two-thirds the total dieldrin measured was dissolved; concentrations ranged from 1 to 16 pptr. A significant correlation between amounts of suspended and dissolved dieldrin was evident ($r = 0.47$; $p = 0.01$), which indicated that both values followed the same seasonal trend. Volume of stream flow and concentration of dissolved dieldrin significantly correlated ($r = 0.55$; $p = 0.01$), but stream flow and concentration of suspended dieldrin did not correlate. Levels of suspended dieldrin were highest in late May and early June, when sediment was most likely coming from agricultural land rather than from sloughing of the stream bank.

Dieldrin concentrations in bottom-sediment samples averaged 4 ppb in July, 2.4 ppb in August, and less than 0.1 ppb in September and November. September and November samples may have been comprised largely of material scoured from the banks, resulting in the low dieldrin levels.

Dieldrin content in mayflies of the genus *Potamanthus* exhibited marked seasonal trends in 1972. Concentrations increased from 44 ppb in April and May to 115 ppb in June, and decreased to 48 ppb in July (Fig. 4). Emergence of the adult mayflies in late July prevented further sampling. This spring trend of dieldrin content

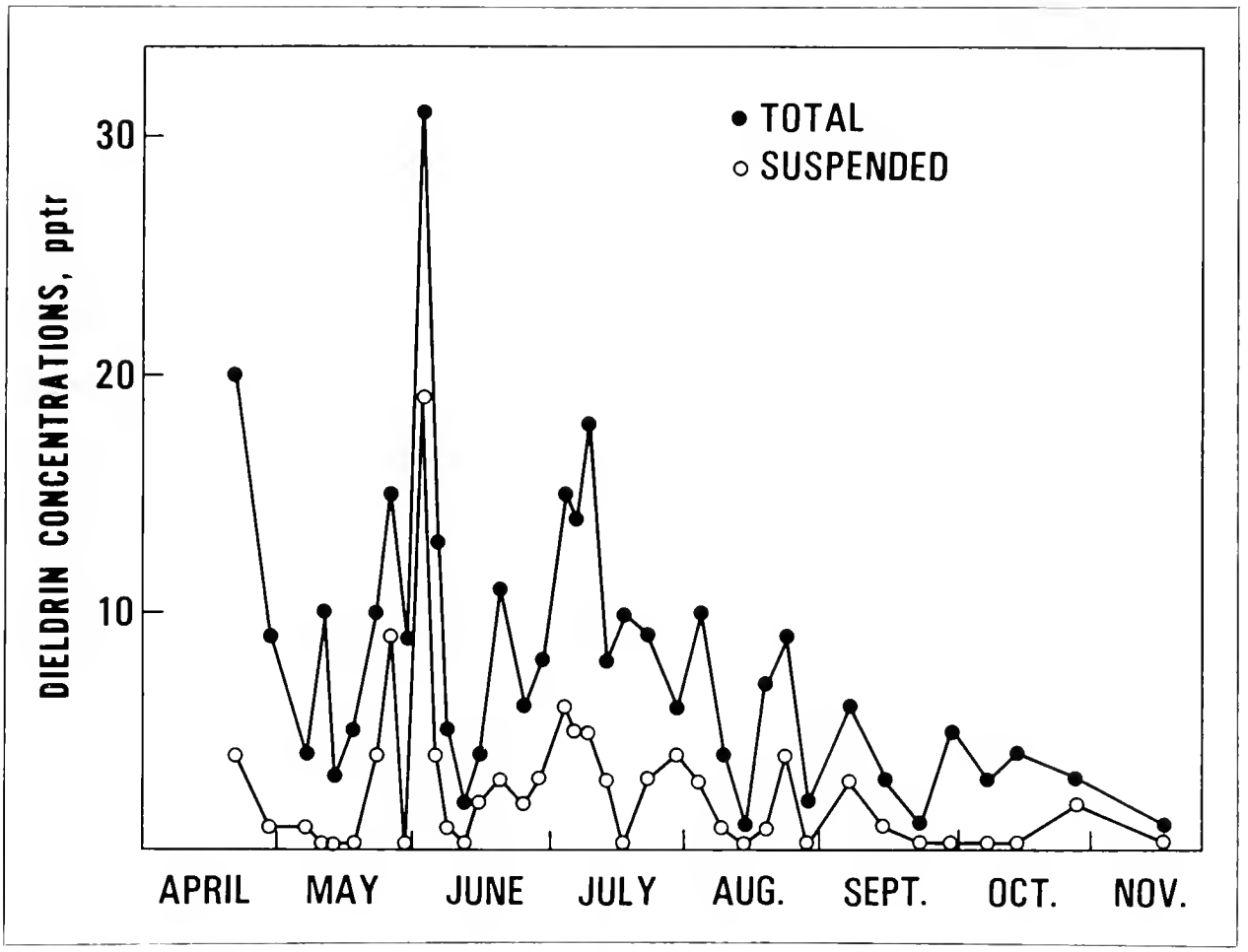

FIGURE 3. *Mean concentrations of total and suspended dieldrin, Des Moines River water, Iowa—1973*

of *Potamanthus* in 1972 was not observed in 1973 because collecting did not begin until June. Nevertheless, sharp decreases in dieldrin residues in this genus were noted from June to July in both years. A decrease in June levels from 115 ppb in 1972 and 61 ppb in 1973 also corresponded to the drop in dieldrin concentrations in June water samples between the 2 years.

In 1973, dieldrin concentrations in aquatic insects ranged from 10 to 98 ppb and were similar among the insect groups in any single month (Table 2). The mean dieldrin concentration in all insects for the 6-month period was 35 ppb. A significant seasonal trend was observed; concentrations decreased from 66 ppb in June to 15 ppb in September and then increased sharply to 63 ppb in late October.

Dieldrin content of crayfish in both 1972 and 1973 was much lower than that of aquatic insects; the mean concentration was 9 ppb in 1972 and 6 ppb in 1973 (Table 3). In 1972 no seasonal trend was evident but in 1973 there was a marked seasonal decrease from 13 ppb in June to 4 ppb in July and 2 ppb in September.

TABLE 2. *Mean dieldrin concentrations in aquatic insect groups, Des Moines River, Iowa—1973*

	Concentration, ppb					
Organism	June 17	July 8	July 25	Aug. 15	Sept. 22	Oct. 27
Acroneuria						
Small	—	25	14	11	19	—
Large	—	—	44	27	15	62
Pteronarcys	—	—	15	13	—	—
Potamanthus	61	24	—	—	—	76
Isonychia	70	38	—	—	—	—
Ephoron	—	—	14	—	—	—
Heptageniidae	44	—	—	—	—	—
Tricoptera	—	—	—	18	18	52
Corydalus						
35-55 mm	—	—	—	12	12	—
65-75 mm	—	—	—	20	14	—
Chironomidae	—	—	—	—	14	—
MEAN	66	29	22	17	15	63

NOTE: — = no sample taken

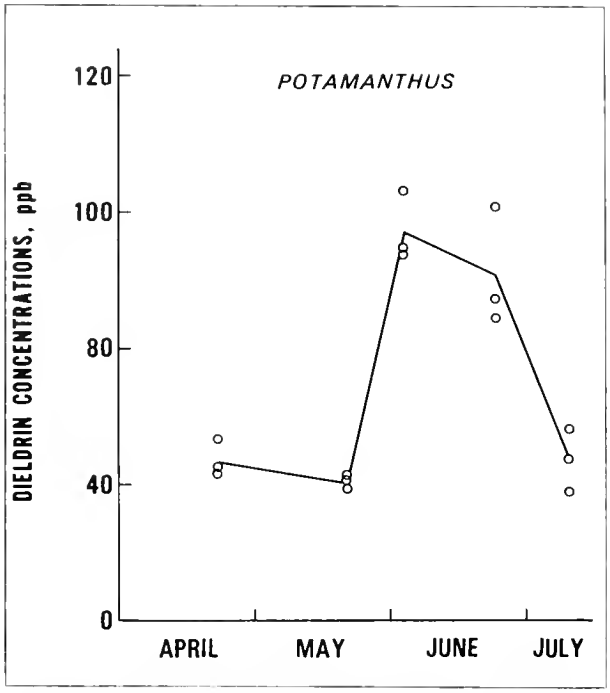

FIGURE 4. *Mean dieldrin concentrations in mayflies of genus* Potamanthus *Des Moines River, Iowa—1972*

TABLE 3. *Monthly mean dieldrin concentrations in crayfish* (Orconectes), *Des Moines River, Iowa—1972-73*

	1972		1973	
Month [1]	No. specimens	Dieldrin, ppb	No. specimens	Dieldrin, ppb
April	14	6	—	—
June	12	12	2	13
July	4	10	4	4
August	2	23	12	3
September	8	2	17	2
October	6	3	—	—
MEAN		9		6

NOTE: — = no samples taken
[1] No samples were collected in May.

Dieldrin concentration in minnows and small carpsuckers collected in 1973 averaged 48 ppb for all samples combined; the range in individual samples was 5-160 ppb. Seasonal trends were similar to trends observed in aquatic insects (Fig. 5). Dieldrin concentrations and seasonal trends differed significantly, however, among the four groups of forage fish ($F = 22.4$ and 4.9; $p = 0.01$). The spotfin shiner contained the highest dieldrin residues throughout the entire sampling period except August; mean dieldrin concentrations in this species were 156 ppb in June, 25 ppb in August, and 61 ppb in November. The sand shiner and bluntnose minnow contained somewhat lower dieldrin concentrations; averages in June were 101 ppb and 66 ppb, respectively. Seasonal trends in the two species were similar to those in the spotfin shiner. However, the decrease in concentration from June to August was much less in the bluntnose minnow than in the spotfin and sand shiners. Small carpsuckers contained the lowest dieldrin concentrations among the forage fish collected; the mean June level was 16 ppb. The seasonal trend of concentrations differed from that in the minnows: concentrations decreased slightly from June to July and then increased steadily to a high of 42 ppb in November.

In 1971, authors investigated seasonal trends in dieldrin content of muscle tissue of channel catfish collected from April to October. In June, the average dieldrin content of 32 fish 155-602 mm long was 89 ppb (range: 2-940 ppb). The mean concentration in 105 fish collected from April to October was 60 ppb. Among fish 200-299 mm long (Table 4), mean monthly concentrations were higher in July (61 ppb) than in any month except October (74 ppb). Monthly means in fish 300-399 mm long ranged from 109 ppb in July to 5 ppb in October. Differences in monthly means were statistically significant in this length group ($p = 0.05$). Concentrations in individual fish ranged from 0 to 207 ppb. Differences between monthly samples in the 200-299-mm group could not be tested statistically because fish were pooled for chemical analysis rather than analyzed individually. Mean concentrations in this length group could be compared on a monthly basis with concentrations in the 300-399-mm group. Mean monthly concentrations in the smaller fish fell within

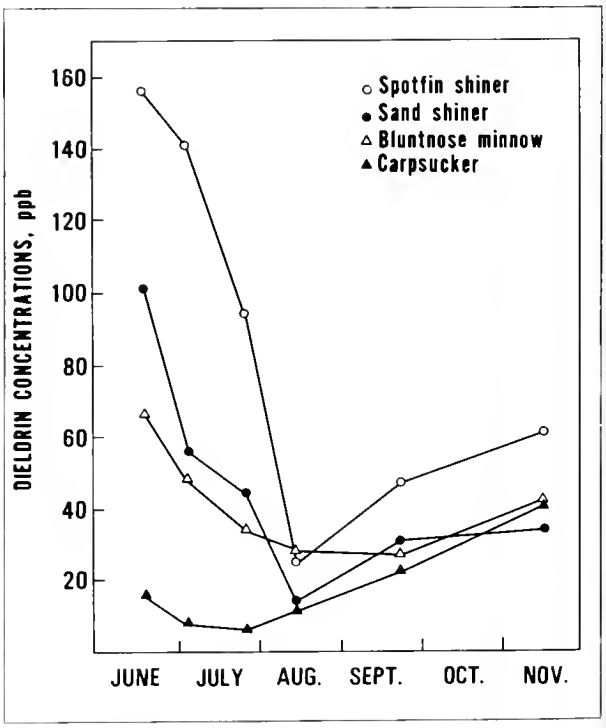

FIGURE 5. *Mean dieldrin concentrations in four groups of small fish, Des Moines River, Iowa—1973*

TABLE 4. *Dieldrin content of channel catfish, Des Moines River, Iowa—1971*

Month	No. fish	Concentration, ppb [1]
Fish Length: 200-299 mm		
April	15	29
May	7	26
June	9	33
July	6	61
August	4	35
September	3	44
October	3	74
Total/mean	47	43
Fish Length: 300-399 mm		
April	9	71 (18)
May	8	27 (9)
June	6	39 (13)
July	7	109 (19)
August	3	9 (4)
September	4	70 (24)
October	4	5 (1)
Total/mean	41	47

[1] Standard errors for fish analyzed individually are in parentheses.

the 95 percent confidence limits for the 300-399-mm group in May, June, and September and outside these limits in the other months (Table 4). Confidence limits greater than twice the monthly mean indicated the large variation in dieldrin content in muscle tissue of catfish of similar size.

In 1973, muscle of channel catfish collected from June to September contained 10-172 ppb dieldrin; the mean for all fish analyzed was 45 ppb (Table 5). Although

TABLE 5. *Monthly mean dieldrin concentration in muscle tissue of channel catfish, Des Moines River, Iowa—1973*

Length Group, mm	Dieldrin concentration, ppb				
	June	July	August	September	Mean
150-199	15(9)	14(12)	13(12)	12(15)	13
200-299	22(12)	75(12)	133(12)	113(12)	86
300-399	25(9)	72(4)	40(9)	26(12)	41
450-550	20(9)	60(4)	49(5)	36(4)	41
Mean	20(39)	54(32)	58(38)	48(43)	45

NOTE: Values in parentheses represent number of fish sampled.

dieldrin concentrations among length groups were not significantly different in the June sample, they were significantly different over the full sampling period ($F = 4.2$; $p = 0.01$) (Fig. 6). Dieldrin content was lowest in the 150-199-mm length group (mean: 13 ppb). This group had the lowest dieldrin levels from June through September. Dieldrin concentrations were highest in

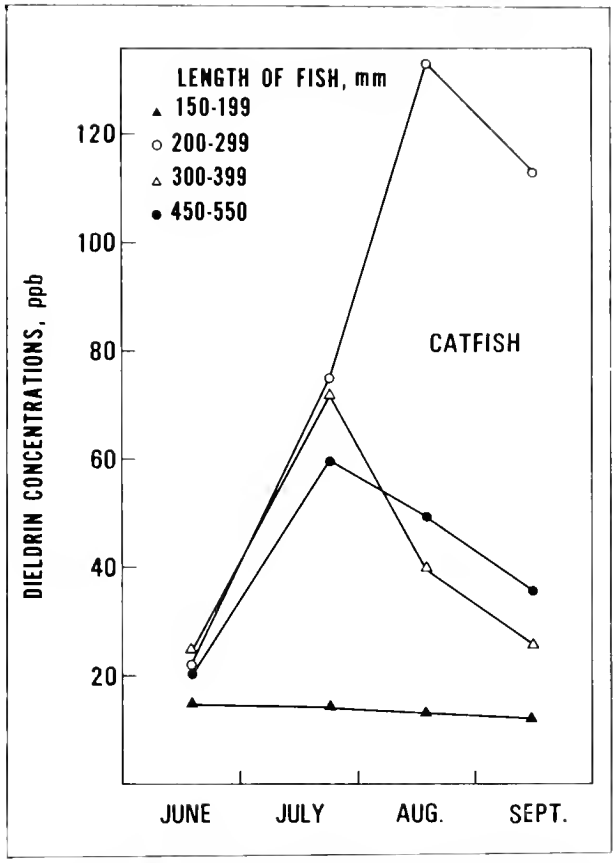

FIGURE 6. *Mean dieldrin concentrations in dorsal muscle of channel catfish, Des Moines River, Iowa—1973*

muscle of 200-299-mm fish, which contained an average of 86 ppb. Monthly mean values increased from 22 ppb in June to 133 ppb in August, and then decreased slightly in September. The 300-399-mm and 450-550-mm length groups contained maximum concentrations of 72 ppb and 60 ppb in July; concentrations then decreased in August and September.

Seasonal trends of dieldrin concentrations in muscle of 200-299-mm and 300-399-mm catfish observed in 1973 differed markedly from trends in 1971 (Tables 4, 5). Statistical evaluation of the differences in seasonal trends between the 2 years was not possible because of differences in pooling samples, but some general comparisons could be made. Mean dieldrin concentrations increased from June to July in both length groups in 1971 and 1973. Trends in dieldrin content during late summer and early fall varied considerably between the 2 years.

Mean concentrations of dieldrin in catfish muscle from June to September 1971 were not significantly different from those of all other samples during the same months in 1973 nor from concentrations in the 200-299- and 300-399-mm length groups, considered separately. Hence, even though dieldrin concentrations seemed to decrease in river water from 1971 to 1973, this de-

crease could not be detected in muscle tissue of channel catfish.

Discussion

Dieldrin concentrations varied seasonally in river water, aquatic invertebrates, minnows, and small carpsuckers, and in muscle tissue of all but one length group of channel catfish. Dieldrin content of water was highest immediately after aldrin application to the watershed. Mean dieldrin concentration in most aquatic organisms was highest in June and July, coincidental with high dieldrin levels in river water, although much variation and some exceptions were evident. In late summer and fall, increases in dieldrin content in insects, small fish, and some length groups of catfish coincided with reduced concentrations in water. This absence of a consistent correlation throughout the season between dieldrin concentrations in the water and residues in aquatic organisms is not unexpected since several environmental and physiological factors are involved in pesticide uptake and retention by animals (*17*). Authors believe that seasonal changes in fat content (*18*) and metabolic rate, caused by factors such as water temperature and reproductive activity, can alter the amount of certain pesticides stored in the body. Activity of detoxifying enzymes that degrade pesticides and thereby allow their elimination is also temperature-dependent, and thus could vary seasonally in effectiveness.

This study demonstrated clearly the absence of a consistent relation throughout the season between dieldrin concentrations in catfish of different lengths. Contrary to common expectations, concentrations were not always greater in large catfish than in small ones. Physiological differences noted above may explain this phenomenon.

Acknowledgments

Authors thank John Richard and Larry Shannon, Iowa State University, for conducting the 1971 chemical analyses on catfish tissue.

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APPENDIX

Chemical Names of Compounds Discussed in This Issue [1]

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]
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
LINDANE	*Gamma* isomer of benzene hexachloride 1,2,3,4,5,6-hexachlorocyclohexane of 99+% purity
MIREX	Dodecachlorooctahydro-1,3,4-metheno-2H-cyclobuta[cd]pentalene
PCB'S (POLYCHLORINATED BIPHENYLS	Mixtures of chlorinated biphenyl compounds having various percentages of chlorine
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

[1] Does not include chemicals listed only in tables of paper by Johnson/Manske.

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SUBJECT AND AUTHOR INDEXES

Volume 9, June 1975—March 1976

Preface

Primary headings in the subject index consist of pesticide compounds listed alphabetically by common name or trade name when there is no common name, the media in which residues are monitored, and several concept headings, as follows:

Media and Concept Headings

Air
Degradation
Factors Influencing Residues
Food and Feed
Humans
Plants (other than those used for food and feed)
Sediment
Soil
Water
Wildlife

Compound headings are used as secondary headings under the primary media and concept headings and vice versa. When a particular paper discusses five or more organochlorines, the compounds are grouped by class under the media or concept headings; in the primary headings, however, all compounds are listed individually.

In the author index, the names of both senior and junior authors appear alphabetically. Full citation is given only under the senior author, with a reference to the senior author appearing under junior authors.

SUBJECT INDEX

Z

AUTHOR INDEX

Y

Information for Contributors

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

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

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——All copy, including tables and references, should be double spaced, and all pages should be numbered. The first page of the manuscript must contain authors' full names listed under the title, with affiliations, and addresses footnoted below.

——Charts, illustrations, and tables, properly titled, should be appended at the end of the article with a notation in text to show where they should be inserted.

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