PESTICIDES MONITORING JOURNAL

JUNE 1979

VOLUME 13 NUMBER 1

PEMJAA (13) 1–46 (1979)

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

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

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

The *Pesticides Monitoring Journal* is published by the Technical Services Division, Office of Pesticide Programs, U.S. Environmental Protection Agency.

Pesticide monitoring activities of the Federal Government, particularly in those agencies represented on the Monitoring Panel which participate in operation of the national pesticides monitoring network, are expected to be the principal sources of data and articles. However, pertinent data in summarized form, together with discussions, are invited from both Federal and non-Federal sources, including those associated with State and community monitoring programs, universities, hospitals, and nongovernmental research institutions, both domestic and foreign. Results of studies in which monitoring data play a major or minor role or serve as support for research investigation also are welcome; however, the Journal is not intended as a primary medium for the publication of basic research. Publication of scientific data, general information, trade names, and commercial sources in the *Pesticides Monitoring Journal* does not represent endorsement by any Federal agency.

Manuscripts received for publication are reviewed by an Editorial Advisory Board established by the Monitoring Panel. Authors are given the benefit of review comments prior to publication. For further information on Journal scope and manuscript preparation, see Information for Contributors at the back of this issue.

Address correspondence to:

Paul Fuschini (TS-793)
Editorial Manager
Pesticides Monitoring Journal
U. S. Environmental Protection Agency
Washington, D.C. 20460

Editor
Martha Finan

CONTENTS

Volume 13 June 1979 Number 1

FISH, WILDLIFE, AND ESTUARIES

Polychlorinated Biphenyls and Other Organic Chemical Residues in Fish from Major Watersheds of the United States, 1976

Gilman D. Veith, Douglas W. Kuehl, Edward N. Leonard, Frank A. Puglisi, and Armond E. Lemke [1]

ABSTRACT

Composite samples of fish were collected from major United States watersheds in 1976 and analyzed for PCBs and related organic chemicals. PCBs were found in 93 percent of the fish samples; 53 percent of the samples contained more than 5 ppm PCBs, whole fish basis, which is the current tolerance level set by the Food and Drug Administration, U.S. Department of Health, Education and Welfare. Only 14 percent of the samples contained less than the proposed action level of 2 ppm PCBs. PCB concentrations ranged from less than 0.3 ppm to 140 ppm in the composite samples. ΣDDT concentrations ranged from less than 0.05 ppm to 4.53 ppm. Hexachlorobenzene was identified in 19 percent of the samples, and chlordane components were identified in 36 percent of the samples. Chemicals identified by gas chromatography/mass spectrometry but not quantified include chlorinated benzenes, styrenes, anisoles, phenols, anilines, propanes, and butadienes, as well as mixtures of petroleum hydrocarbons.

Introduction

The intent of this study was to identify by gas chromatography/mass spectrometry (GC/MS) major PCB components in fish from as many watersheds as possible. Particular attention was given to the occurrence of the lesser chlorinated PCBs having 2, 3, and 4 chlorine atoms. In response to the September-November 1976 litigation on the proposed toxic pollutant effluent standards for PCBs, requests for the collection of composite fish samples from major United States watersheds were sent to each regional office of the U.S. Environmental Protection Agency in spring 1976 (*6*).

Each region was initially requested to send 10-lb composite samples of fish from the lower reaches of waters that, in the opinion of the regional staff, were major drainages. Such samples are not adequate for monitoring programs aimed at establishing relative concentrations of residues or trends in residues from year to year. However, residue-forming chemicals accumulate in any aquatic organism even though the extent of accumulation may vary with the species. Consequently, primary emphasis was placed on the identification of accumulating chemicals; the quantities of these chemicals were of secondary importance.

Methods and Procedures

PREPARATION OF SAMPLES

Fish samples were collected by state and federal field crews and shipped frozen to the Environmental Research Laboratory, Duluth, Minnesota. Fish samples were homogenized as a composite and given laboratory numbers consecutively from 1 to 58. Subsamples weighing 20 g and 30 g were exhaustively extracted on a Soxhlet extractor with a 1:1 mixture of hexane and methylene chloride. In addition, 10 samples showing comparatively large quantities or numbers of chemicals were selected for more detailed GC/MS analyses in which the extract of a 100-g subsample was used.

The 20-g sample extract was concentrated and placed on a 20-g Florisil column. PCBs and related chemicals were eluted with 250 ml hexane, and the extract was concentrated to 100 ml for initial electron-capture analysis. Recovery of PCBs and DDE from spiked samples was 85 ± 4 percent, and has been presented in detail previously (*7*).

The 30-g and 100-g samples were concentrated on a Kuderna-Danish concentrator and a 3-ball Snyder column to a lipid concentration of 100 μg ml in methylene chloride for cleanup by gel permeation chromatography (*5*). The extract was cleaned by sequential elution of 5-ml aliquots on a 60-cm · 2-cm bed of SX-2 Bio-Beads (Bio-Rad Laboratories); methylene chloride was used as a solvent. The combined 160–225-ml fraction containing the PCBs from each extract was passed through a

[1]U.S. Environmental Protection Agency, Environmental Research Laboratory, 6201 Congdon Boulevard, Duluth, Minn. 55804.

column containing 15 g Celite 545 impregnated with 9 ml of a 1:1 mixture of H_2SO_4 and fuming H_2SO_4 (30 percent SO_3). The extract was concentrated to 1–3 ml for screening on a flame ionization detector before GC/MS analysis. Recoveries of PCBs and related nonpolar chemicals are greater than 90 percent by this procedure (*5*).

ELECTRON-CAPTURE ANALYSIS

Analyses of 20-g sample extracts for PCBs were performed on a Hewlett-Packard Model 5700A gas chromatograph equipped with a Model 3352B Laboratory Data System, an automatic sampler, and linearized argon-methane detector. Instrument parameters and operating conditions follow:

Column:	glass, 6 ft × ¼ inch ID, packed with 80–100-mesh Gas-Chrom Q coated with a mixture of 4 percent SE-30 and 6 percent OV-210.
Column temperature:	programmed from 160° to 220°C at 2 /minute, followed by an 8-minute hold at 220 C.
Carrier gas:	a mixture of 90 percent argon and 10 percent methane flowing at 30 ml/minute.

The chromatograms were interpreted by a computer program in which 16 reference PCB peaks were monitored. Eight reference peaks corresponded to PCBs found in Aroclor 1016 (or Aroclor 1242), and eight reference peaks corresponded to PCBs found in Aroclor 1254. The program estimated the quantity of the Aroclor 1016/1242 or Aroclor 1254 by comparing them with the individual peak areas obtained for standard Aroclor mixtures. The means and standard deviations of the respective mixtures, based on all reference peaks found, were computed, and peaks with areas more than twice the standard deviation were considered to be contaminated by an interfering chemical and were eliminated from the PCB estimate of the mixture. At least four of the eight reference peaks were required to be present before a PCB mixture could be identified.

GC/MS ANALYSIS

Extracts of the 30-g and 100-g tissue samples were screened by using a flame ionization detector (FID) and then were subjected to analysis by GC/MS.

The GC/MS analyses for both 30-g and 100-g samples were performed on a Varian Mat Ch-5 mass spectrometer interfaced with a Varian Model 620i modified data system (*2*). Instrument parameters and operating conditions were as follows:

Column:	glass, 6 ft × ¼ inch ID, packed with 80–100-mesh Gas-Chrom Q coated with 3 percent OV-101
Column temperature:	programmed from 100° to 225 C at 4°/minute, followed by a 5-minute hold at 100°C.

Spectra were acquired repetitively every 7 seconds at 3.5 seconds/mass decade. Resolution was 1000 during the gas chromatographic elution period. After mass conversion on the 620i computer, spectra were transmitted to Varian Model 620L computer for data formatting and analysis. The GC/MS data were screened by selecting ions in the mass spectra of chemicals of interest and searching all of the spectra for the GC peaks where the ions occurred most intensely (*4*).

Results and Discussion

A summary of sampling areas, sample composition, and estimates of PCB concentrations are given in Table 1. Of the 58 samples analyzed, 93 percent contained measurable quantities of PCBs. The total PCB concentrations, whole fish basis, ranged from less than 0.3 ppm to a maximum of 140 ppm in the composite sample from Lake Hartwell, South Carolina (Region IV). Approximately 86 percent of the samples contained more than 2 ppm PCBs, 53 percent contained more than 5 ppm PCBs, and 21 percent contained more than 10 ppm PCBs. The high concentrations of PCBs in fish from the Acushnet, Hoosic, and Merrimack Rivers in Massachusetts, Choccoloco Creek in Alabama, Coosa and Altamaha Rivers in Georgia, Lake Hartwell in South Carolina, Fort Loudoun Reservoir in Tennessee, Saginaw River in Michigan, Lake Michigan in Wisconsin, and the Huron River in Ohio suggest that these watersheds are receiving comparatively high concentrations of PCBs.

Composition of the PCB mixtures in fish residues is especially noteworthy because of the frequency of PCB components resembling Aroclor 1016 and Aroclor 1242 formulations. Although PCB components similar to those in Aroclor 1254 accounted for over 80 percent of the total PCB residue in the majority of the samples (Table 1), PCB residues similar to Aroclors 1016 and 1242 were found in 71 percent of the samples. Moreover, Aroclor 1016 and 1242 residues were equal to or greater than the Aroclor 1254 residues in 16 percent of the samples. The highest Aroclor 1016 and 1242 residues were found in the Acushnet River and Lake Hartwell where concentrations were 25.2 ppm and 42.5 ppm, respectively. These data refute contentions that Aroclors 1016 and 1242 do not persist in the environment.

Hexachlorobenzene (HCB) was confirmed by GC/MS in 19 percent of the watershed samples (Table 2). Even though acceptable spectra which unequivocally identify HCB could not be obtained for more than 19 percent of the samples, the electron-capture gas chromatograms suggested that HCB was present at comparatively low concentration in an additional 33 percent of the samples. HCB concentrations ranged from less than 0.005 ppm in 48 percent of the samples to a maximum of 11.6 ppm in a composite sample of eels from the Altamaha River at Darien, Georgia. Approximately 15 percent of the 58 samples contained more than 0.1 ppm HCB. The rivers that were most contaminated with HCB were the

TABLE 1. *Concentration of PCBs in 58 composite whole fish samples from major United States watersheds, 1976*

Sampling Area	Sample Composition	Lab. Ident.	PCB Residues, ppm 1016-1242	1254	Total
EPA—REGION I					
Kennebec River, southwest area of Merry Meeting Bay, Sagadahoc County, Me.	6 white sucker 3 white perch	76072	2.55	4.90	7.45
Connecticut River, ¼ mile north of Vernon Dam near Hinsdale, N H.	9 white sucker	76079	0.56	2.10	2.66
Penobscot River near East Eddington, Me.	10 white sucker	76112	0.19	5.80	5.99
Acushnet River Reservoir near New Bedford, Mass.	32 sea perch	76116	25.2	22.0	47.2
Hoosic River near North Adams, Mass.	5 longnose sucker 20 white sucker	76118	7.45	4.74	12.2
Merrimack River, ½ mile upstream from Lowell, Mass.	2 sucker 30 sucker 2 catfish 1 carp 1 goldfish 3 bass	76121	0.58	11.1	11.68
EPA—REGION IV					
Choccolocco Creek, 1 mile above Highway 71 bridge in Talladega County near Anniston, Ala.	2 goldfish 4 channel catfish 4 gizzard shad 1 redear sunfish 4 largemouth bass	76064	10.5	78.8	89.3
Coosa River above Weiss Reservoir, Cherokee County, Ga., and Alabama state line	2 goldfish 1 carp 4 largemouth bass 4 gizzard shad 2 bullhead catfish	76065	5.00	60.0	65.0
Savannah River, Ga.	1 black crappie 5 channel catfish 1 bullhead catfish 2 redhorse sucker 1 summer flounder 1 largemouth bass 1 white catfish 1 striped bass	76066	<0.10	3.07	3.07
Lake Hartwell, S.C.	3 carp sucker 3 white catfish 1 channel catfish 1 carp	76068	42.5	97.5	140
Coosa River at Rome, Ga.	2 channel catfish 1 largemouth bass 1 black crappie 1 white bass 1 gizzard shad 1 smallmouth buffalo 1 spotted sucker 1 carp	76069	5.29	69.7	75.0
Duck River below Columbia, Murfreesboro, Tenn.	2 channel catfish 6 carp sucker 2 redhorse sucker	76070	5.29	3.78	9.07
Dennison Slough at Wilson Reservoir, Ala.	3 gar 6 gizzard shad 3 largemouth bass 3 redear sunfish	76071	0.26	74.00	77.26
Chattahoochee River, Albany, Ga.	3 largemouth bass 1 black crappie 1 white catfish	76073	2.54	4.92	7.46
Lake Jackson, Ga., immediately above dam	8 largemouth bass 5 bluegill 2 redbreast sunfish 8 bullhead 1 warmouth	76074	<0.10	<0.20	<0.3
Altamaha River, Darien, Ga.	7 American eel	76075	<0.10	24.5	24.5
Chattahoochee River below W. F. George Reservoir at Albany, Ga.	1 carp 1 largemouth bass 1 black crappie 1 white catfish 1 bluegill	76082	4.15	4.28	8.43
Chattahoochee River at Route 166 bridge, Atlanta, Ga.	6 carp 1 spotted bass	76083	5.29	3.78	9.07
Nickajack Tailwater from the Tennessee Wildlife Resource Agency at Cookeville, Tenn.	4 catfish	76089	0.76	5.87	6.63
St. John's River at Cross Creek, Crescent City, Fla.	4 channel catfish	76090	<0.10	2.62	2.62
Cumberland River at Navigation Mile 93.5 Barkley Reservoir in Nashville, Tenn.	1 blue catfish 2 carp 2 channel catfish 2 drum	76105 76106	0.16 0.11	3.20 1.04	3.36 1.15
Duck River mouth at Tennessee Navigation Mile 111, Tenn.	1 blue catfish 2 carp				

(Continued next page)

TABLE 1 (cont'd.). *Concentration of PCBs in 58 composite whole fish samples from major United States watersheds, 1976*

Sampling Area	Sample Composition	Lab. Ident.	PCB Residues, ppm 1016-1242	1254	Total
EPA—REGION IV (cont'd)					
Pee Dee River, 15 miles above Georgetown, S.C.	7 bullhead 1 perch 2 sunfish	76111	0.12	0.56	0.68
Fort Loudoun Reservoir between Alcoa Highway bridge and Knoxville's Third Creek Sewage Treatment Plant, Morristown, Tenn.	2 catfish 1 smallmouth buffalo	76113	2.48	22.2	24.7
Roanoke River, Raleigh, N.C.	8 white catfish 1 brown bullhead 1 channel catfish	76124	0.22	2.70	2.92
Cape Fear River upstream from Black River at confluence of Hood Creek, N.C.	3 yellow bullhead 2 white catfish 2 brown bullhead 1 channel catfish 1 carp	76127	<0.10	1.99	1.99
EPA—REGION V					
Grand River, Station No. 3, Mich.	3 channel catfish 1 redhorse	76067	<0.10	0.75	0.75
Wabash River, Station No. 1, Evansville, Ind.	3 drum	76076	<0.10	7.88	7.88
Saginaw River below Tittabawassee River, Mich.	1 perch 1 drum 1 sucker	76077	6.08	5.85	11.9
Ohio River, Gallipolis, Oh.	9 channel catfish	76078	1.04	1.87	2.91
St. Joseph River, Station No. 3, Mich.	1 dogfish 1 sucker 3 catfish 1 rock bass	76081	0.94	4.40	5.34
Saginaw River mouth above power plant, Mich.	13 catfish 1 drum	76085	4.90	3.65	8.55
Saginaw River below Cheyboyganing Creek, Mich.	3 perch 1 catfish 1 drum	76086	3.24	5.68	8.92
Detroit River off end of Grosse Ile, Mich.	2 carp	76087	2.38	4.90	7.28
Grand River, Station No. 2, Mich.	3 sucker 2 rock bass	76093	0.44	1.83	2.27
Rocky River mouth, Oh.	1 carp 3 bullhead 5 drum 1 goldfish	76095	<0.10	3.44	3.44
Wabash River, Station No. 2, Evansville, Ind.	1 bowtin	76096	<0.10	5.90	5.90
Wabash River, Station No. 3, Evansville, Ind.	6 catfish 9 drum	76097	1.01	2.20	3.21
Green Bay area south of Long Tail Point, Wis.	5 carp	76123	13.1	6.3	19.4
Illinois River, Peoria Lake, Ill.	3 drum 3 carp	76125	2.66	4.34	7.00
St. Louis River, Mich.	1 walleye 1 northern	76103	<0.10	2.25	2.25
St. Joseph River, Station No. 1, Mich.	4 bullhead 1 rock bass	76109	0.18	3.86	4.04
Maumee River, Oh.	2 carp 1 catfish	76110	0.31	5.05	5.36
Huron River mouth, Oh.	3 goldfish 2 carp 1 bullhead 2 channel catfish 4 white bass 6 drum	76119	9.22	2.65	11.9
Ashtabula River, Oh.	3 alewives 9 gizzard shad 3 white bass 1 yellow perch	76120	4.46	2.74	7.2
Red River, North Halstad, Minn.	3 bullhead 6 carp 1 channel catfish 1 redhorse 1 goldeye	76122	0.28	3.55	3.83
Morgan's Point in Houston ship channel, Tex.	24 gizzard shad 12 sabre fish 30 croaker 4 cutlassfish	76080	0.14	1.98	2.12
Lower White River, Ark.	5 freshwater drum 1 carp	76084	<0.10	<0.20	<0.3
Arkansas River, Site 22B, Ark.	1 catfish 2 channel catfish 1 freshwater drum	76088	<0.10	<0.20	<0.3
Lower Arkansas River, Ark.	3 catfish 2 freshwater drum	76094	0.28	2.60	2.88
Arkansas River, Site 22A, Ark.	4 carp	76104	<0.10	<0.20	<0.3

(Continued next page)

TABLE 1 (cont'd.). *Concentration of PCBs in 58 composite whole fish samples from major United States watersheds, 1976*

Sampling Area	Sample Composition	Lab. Ident.	PCB Residues, ppm 1016-1242	1254	Total
EPA—REGION V (cont'd)					
Coody Creek mouth, Muskogee, Okla.	2 carp 2 smallmouth buffalo 1 bigmouth buffalo	76107	<0.10	6.94	6.94
Nueces Bay, Corpus Christi, Tex.	1 alligator gar 1 striped mullet 1 gulf menhaden 3 spotted seatrout	76108	0.11	3.19	3.30
Adams Bayou at F.M. 1006 in Orange, Tex	1 alligator gar 1 European carp	76114	<0.10	2.99	2.99
Adams Bayou at F.M. 1006 in Orange, Tex.	1 alligator gar 1 European carp	76115	<0.10	5.30	5.30
FISH AND WILDLIFE SERVICE ALBUQUERQUE, N.M.					
Morgan Lake, N.M.	5 carp 5 channel catfish 2 bluegill 1 green sunfish	76092	<0.10	4.47	4.47
Colorado River, Blythe, Calif.	3 channel catfish 1 bluegill 4 treadfin shad	76126	0.22	3.33	3.55
Rio Grande River, Elephant Butte, N.M.	1 bluegill 1 crappie 1 walleye 3 white bass 1 softshell turtle 1 carp sucker 2 buffalo 1 carp 1 catfish 1 black bullhead 1 channel catfish 2 northern 1 shad 1 largemouth	76117	0.15	3.94	4.09

Altamaha River; the Wabash River, Evansville, Indiana; the Ashtabula River, Ohio; and the Saginaw River, Michigan.

ΣDDT concentrations in fish collected in this study were much smaller than expected (Table 2). DDT concentration was below the determinable limit of 0.05 ppm in approximately 9 percent of the samples, and 59 percent of the samples contained less than 1 ppm ΣDDT. The maximum DDT concentration of 4.53 ppm was found in composite samples from the Coosa River, Georgia. Residues of DDT probably have decreased significantly since its use was banned from the United States in 1972. In contrast to earlier work where DDT was a predominant contaminant in fish in many watersheds, measuring DDT residues is now a much greater analytical problem because of their small concentrations compared to other chemical contaminants.

Chlordane and nonachlor isomers were identified in 36 percent of the samples (Table 2). Residues could not be quantified, however, because of inadequate separation of these chemicals from interferences in the samples.

Ten samples gave atypical chromatograms and were subjected to more detailed GC/MS analyses to identify the major chemical residues. Table 3 presents a summary of the chemicals found in these samples. Authors followed specific techniques developed for measuring chemical residues found most commonly in fish from the Great Lakes. The list of chemicals in Table 3 excludes the numerous PCB homologs and the hydrocarbons which were identified. The Saginaw, Detroit, Ohio, Arkansas, and Ashtabula Rivers contained numerous chlorinated benzenes. The chlorinated styrenes and, in particular, octachlorostyrene previously reported by Kuehl et al. (*3*), were present in the Saginaw, Detroit, and Ashtabula Rivers. These residues are of interest because the authors have been unable to identify any industry in the United States which produces these chemicals. In the present study, the Ashtabula River contained the greatest variety of organochlorines in addition to a series of polychlorinated butadienes, chlorinated propane and propene, and chlorinated norbornenes.

Although only semiquantitative, the amounts of the chemicals in a sample relative to the other samples from this study and other ongoing research can be estimated from the ion intensities in the reconstructed mass chromatograms used in the GC/MS analyses. From

TABLE 2. *Concentrations of ΣDDT and HCB and occurrence of chlordane and nonachlor in 58 composite whole fish samples from major United States watersheds, 1976*

Sampling Area	Lab. Ident.	ΣDDT, ppm	HCB (C_6Cl_6), ppb	Chlordane		Nonachlor	
				cis	trans	cis	trans
EPA—REGION I							
Kennebec River in the southwest area of Merry Meeting Bay, Sagadahoc County, Me.	76072	0.59	20	—	—	—	—
Connecticut River, ¼ mile north of Vernon Dam near Hinsdale, N.H.	76079	<0.05	<5	—	—	—	—
Penobscot River near East Eddington, Me.	76112	0.11	<5	—	—	—	—
Acushnet River Reservoir near New Bedford, Me.	76116	1.68	<5	—	—	—	—
Hoosic River near North Adams, Mass.	76118	1.95	81	—	—	—	—
Merrimack River, ½ mile upstream from Lowell, Mass.	76121	0.33	39	X*	X*	X	X
EPA—REGION IV							
Choccolocco Creek 1 mile above Highway 71 bridge in Talladega County near Anniston, Ala.	76064	<0.05	<5	—	—	—	—
Coosa River above Weiss Reservoir, Cherokee County, Ga. and Alabama state line	76065	4.53	<5	—	—	—	—
Savannah River, Ga.	76066	0.21	<5	—	—	—	—
Lake Hartwell, S.C.	76068	<0.05	<5	—	—	—	—
Coosa River at Rome, Ga.	76069	4.06	<5	—	—	—	—
Duck River below Columbia, Murfreesboro, Tenn.	76070	0.71	<5	—	—	—	—
Dennison Slough at Wilson Reservoir, Ala.	76071	3.60	5	—	—	—	—
Chattahoochee River, Albany, Ga.	76073	2.52	<5	X	X	X	X
Lake Jackson, Ga., immediately above dam	76074	0.91	7	X	X	X	X
Altamaha River, Darien, Ga.	76075		11,600	—	—	—	—
Chattahoochee River below W. F. George Reservoir at Albany, Ga.	76082	1.24	<5	X	X	X	X
Chattahoochee River at Route 166 bridge, Atlanta, Ga.	76083	<0.05	<5	X	X	X	X
Nickajack Tailwater from the Tennessee Wildlife Resource Agency at Cookeville, Tenn.	76089	3.20	53	X	X	X	X
St. John's River at Cross Creek, Crescent City, Fla.	76090	0.62	<5	—	—	—	—
Cumberland River at Navigation Mile 93.5 Barkley Reservoir, Nashville, Tenn.	76105	0.62	6	—	—	—	—
Duck River mouth at Tennessee Navigation Mile 111, Tenn.	76106	0.34	<5	—	—	—	—
Pee Dee River 15 miles above Georgetown, S.C.	76111	0.09	128	—	—	—	—
Fort Loudoun Reservoir between Alcoa Highway bridge and Knoxville's Third Creek Sewage Treatment Plant, Morristown, Tenn.	76113	3.86	70	X	X	—	X
Roanoke River, Raleigh, N.C.	76124	1.16	<5	—	—	—	—
Cape Fear River upstream from Black River at confluence of Hood Creek, N.C.	76127	0.16	45	—	—	—	—
EPA—REGION V							
Grand River, Station No. 3, Mich.	76067	2.26	19	X	X	X	X
Wabash River, Station No. 1, Evansville, Ind.	76076	1.66	1,310	X	X	X	X
Saginaw River below Tittabawassee River, Mich.	76077	1.88	490	—	—	—	—
Ohio River, Gallipolis, Oh.	76078	0.28	137	X	X	X	X
St. Joseph River, Station No. 3, Mich.	76081	4.05	16	X	X	X	X
Saginaw River mouth above power plant, Mich.	76085	0.23	131	—	—	—	—
Saginaw River below Cheyboyganing Creek, Mich.	76086	1.08	237	—	—	—	—
Detroit River off end of Grosse Ile, Mich.	76087	1.14	167	—	—	—	—
Grand River, Station No. 2, Mich.	76093	1.93	<5	X	X	X	X
Rocky River mouth, Oh.	76095	0.28	14	X	X	X	X
Wabash River, Station No. 2, Evansville, Ind.	76096	0.27	21	X	X	X	X
Wabash River, Station No. 3, Evansville, Ind.	76097	0.26	34	X	X	X	X
Green Bay area south of Long Tail Point, Wis.	76123	1.14	14	—	—	—	—
Illinois River, Peoria Lake, Ill.	76125	0.65	<5	X	X	X	X
St. Louis River, Minn.	76103	0.12	5	—	—	—	—
St. Joseph River, Station No. 1, Mich.	76109	0.45	<5	—	—	—	—
Maumee River, Oh.	76110	0.13	<5	—	—	—	—
Huron River mouth, Oh.	76119	0.61	74	X	X	X	X
Ashtabula River, Oh.	76120	0.13	3,140	—	—	—	—
Red River, North Halstad, Minn.	76122	0.19	<5	—	—	—	—
EPA—REGION VI							
Morgan's Point in Houston ship channel, Tex.	76080	0.05	53	—	—	—	—
Lower White River, Ark.	76084	2.83	68	—	—	—	—
Arkansas River, Site 22B, Ark.	76088	1.03	<5	—	—	—	—
Lower Arkansas River, Ark.	76094	3.59	<5	—	—	—	—
Arkansas River, Site 22A, Ark.	76104	1.22	7	X	X	X	X
Coody Creek mouth, Muskogee, Okla.	76107	1.08	<5	X	X	X	X
Nueces Bay, Corpus Christi, Tex.	76108	0.33	83	X	X	X	X
Adams Bayou at F.M. 1006, Orange, Tex.	76114	0.31	<5	—	—	—	—
Adams Bayou at F.M. 1006, Orange, Tex.	76115	0.44	<5	X	X	X	X
FISH AND WILDLIFE SERVICE ALBUQUERQUE, N.M.							
Morgan Lake, N.M.	76092	<0.05	<5	—	—	—	—
Colorado River, Blythe, Calif.	76126	0.37	<5	—	—	—	—
Rio Grande River, Elephant Butte, N.M.	76117	0.11	<5	—	—	—	—

NOTE: X = positive; — = negative; * = GC/MS confirmation of this chemical in sample.

TABLE 3. *Organochlorines except PCBs identified by GC/MS analysis of selected composite whole fish samples from major United States watersheds, 1976*

Compounds Identified	Saginaw R. 77104	Detroit R. 77103	Ark. R. 77102	Ohio R. 77101	Ashtabula R. 77098	Wabash R 77099	Lower White R. Ark. 77159	Morgans Pt. 77139	Ill. R. 77106	Green Bay Lake Mich.
Dichlorobenzene I*	X			X						X
Dichlorobenzene II	X									
Trichlorobenzene I	X		X							
Trichlorobenzene II	X									
Tetrachlorobenzene I	X		X		X					
Tetrachlorobenzene II	X		X							
Pentachlorobenzene	X		X		X	X				
Hexachlorobenzene	X	X	X	X	X	X				
Hexachlorostyrene I					X					
Hexachlorostyrene II					X					
Heptachlorostyrene I	X				X					
Heptachlorostyrene II					X					
Octachlorostyrene	X	X			X					
Trichloroanisole			X							
Pentachloroanisole		X								
cis-Chlordane		X	X	X	X				X	X
trans-Chlordane				X					X	X
cis-Nonachlor									X	
trans-Nonachlor		X	X	X	X				X	X
Dichloronaphthalene			X							
DDE	X		X		X	X		X	X	
TDE			X			X				
DDT			X			X				
Pentachlorobenzyl alcohol						X				
Pentachlorophenol						X				
Tetrachlorobutadiene I					X					
Tetrachlorobutadiene II					X					
Pentachlorobutadiene I					X					
Pentachlorobutadiene II					X					
Hexachlorobutadiene					X	X				
Tetrachloropropene					X					
Pentachloropropane					X					
Pentachloronorbornene					X					
Heptachloronorbornene						X				
Heptachloronorbornadiene						X				
Chlordene isomer						X				
Heptachlor isomer						X				
Dihydroheptachloro isomer						X				
Heptachlor epoxide						X				
Hexachlorocyclopentane							X			

NOTE: Roman numerals indicate different isomers found. Other compounds tested for and not found were pentachloroaniline, pentachlorotoluene, mirex, photomirex, α-hexachlorocyclohexane, γ-hexachlorocyclohexane, oxychlordane, toxaphene ($C_{10}H_8Cl_7$), toxaphene ($C_{10}H_7Cl_8$), pentachlorohydroxy biphenyl, hexachlorohydroxy biphenyl, heptachlorohydroxy biphenyl, hexachlorostyrene III, heptachlorostyrene III, tetrachloroanthracene, and DDMU.

these analyses, the following determinations were made: Arkansas River fish contained high concentrations of trichloroanisole, which was not identified in any other watershed. Wabash River fish contained high concentrations of pentachlorophenol, pentachlorobenzyl alcohol, heptachloronorbornene, and hexachlorobornadiene. Detroit River fish contained high concentrations of pentachloroanisole. Lower White River fish contained high concentrations of hexachlorocyclopentane.

Large amounts of hydrocarbons were also present in many of the samples, and considerable effort was made to identify the components. With a few exceptions, however, the majority of the hydrocarbons exist as complex mixtures of unresolved peaks that cannot presently be explicitly characterized. Although the hydrocarbons are generally not observed in monitoring studies involving electron-capture gas chromatography, they are readily observed when a flame ionization detector is used.

The majority of the hydrocarbon mixtures consist of saturated and unsaturated hydrocarbons similar to those found in petroleum products. Although the mixtures vary greatly among the samples, there are apparently two major distributions of hydrocarbons of approximately 18 and 26 carbon atoms (Fig. 1).

Heptadecane, a 17-carbon straight-chain hydrocarbon, can be seen in many chromatograms as a peak eluting at approximately 18 minutes. Hydrocarbons with 18, 19, 20, or more carbons can be seen as peaks eluting at regular intervals in the chromatograms at retention times longer than heptadecane. Unfortunately, chromatograms of hydrocarbons appear more complex because of the peaks from the branched-chain and alkylaromatic hydrocarbons among the straight-chain, or normal, hydrocarbons in the mixture. Authors of the present study concluded that the clusters of hydrocarbons eluting near heptadecane are similar to those observed in fuel oil mixtures, and those eluting at higher temperatures are similar to heavier oils such as crankcase oil. Because heptadecane is present at concentrations greater than 50 ppm, authors further conclude that many of the fish analyzed in the present study contain concentrations of hydrocarbons many times greater than concentrations of other contaminants and, in some cases, in quantities sufficient to simply weight the total residue. For example, Figure 2 presents the FID chromatogram of the Connecticut River, New Hampshire, fish extract in which the late-eluting hydrocarbons predominate the chromatogram.

From this preliminary work, authors do not conclude that all hydrocarbons found in fish are derived from contamination of the watersheds by petroleum. Indeed, heptadecane is thought to occur naturally, originating in benthic algae. The same is likely true of higher-molecular-weight *n*-paraffins such as those observed in Figure 3. Despite the high concentrations of PCBs in the Coosa River sample, the PCBs do not contribute significantly to the FID chromatogram, and the chromatogram resembles those obtained from fish caught in open waters of the Gulf of Mexico (*1*). It is characterized by a large heptadecane component and a series of other paraffins. If these are indicative of natural residues of hydrocarbons, the large clusters of hydrocarbons in Figures 1 and 2 which completely obscure the natural paraffins suggest contamination of the watershed by petroleum.

The characterization of these mixtures remains a major research problem in the exploration of contaminants in fish.

Acknowledgments

We thank all personnel of the regional offices of the U. S. Environmental Protection Agency and the Fish and Wildlife Service, U. S. Department of the Interior, who helped coordinate the collection of fish analyzed in this study.

LITERATURE CITED

(*1*) *Giam, C.-S., H. S. Chan, and G. S. Neff. 1976.* Distribution of *n*-paraffins in selected marine benthic organisms. Bull. Environ. Contam. Toxicol. 16(1):37–43.

(*2*) *Kuehl, D. W., G. E. Glass, and F. A. Puglisi. 1974.* Automatic high temperature vent system for a gas chromatograph/mass spectrometer interface. Anal. Chem. 46(6):804–805.

(*3*) *Kuehl, D. W., H. L. Lopperman, G. D. Veith, and G. E. Glass. 1976.* Isolation and identification of polychlorinated styrenes in Great Lakes fish. Bull. Environ. Contam. Toxicol. 16(2):127–132.

(*4*) *Kuehl, D. W. 1977.* Identification of trace contaminants in environmental samples by selected ion summation analysis of gas chromatographic-mass spectral data. Anal. Chem. 49(3):521–522.

(*5*) *Kuehl, D. W., and E. N. Leonard. 1978.* Isolation of xenobiotic chemicals from tissue samples by gel permeation chromatography. Anal. Chem. 50(1):182–185.

(*6*) *U.S. Environmental Protection Agency. 1976.* Hearings on Federal Water Pollution Control Act Section 307(a) before the U.S. Environmental Protection Agency. Transcript on PCBs (Veith testimony 20 pp).

(*7*) *Veith, G. D. 1975.* Baseline concentrations of polychlorinated biphenyls and DDT in Lake Michigan fish, 1971. Pestic. Monit. J. 9(1):21–29.

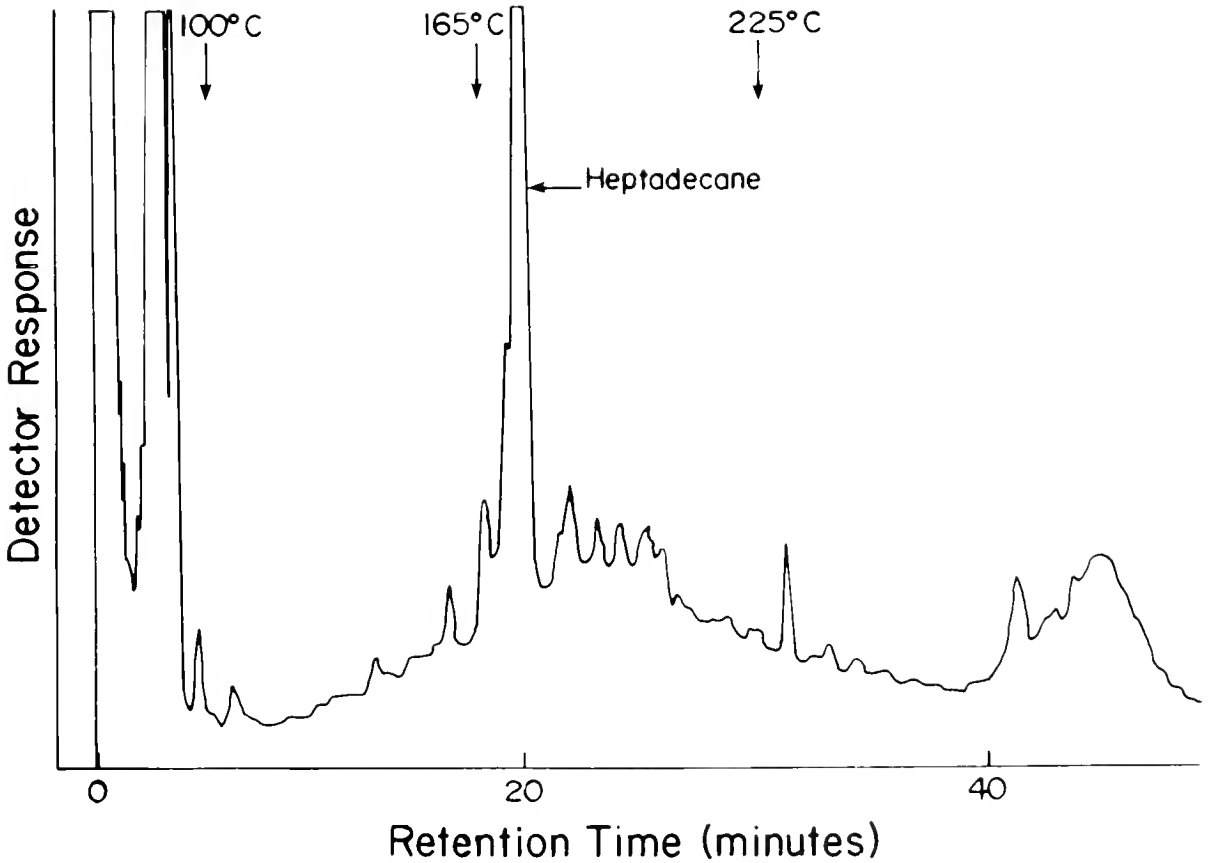


FIGURE 1. *Flame ionization detector chromatogram of whole fish extract from the Chattahoochee River, Georgia, 1976*

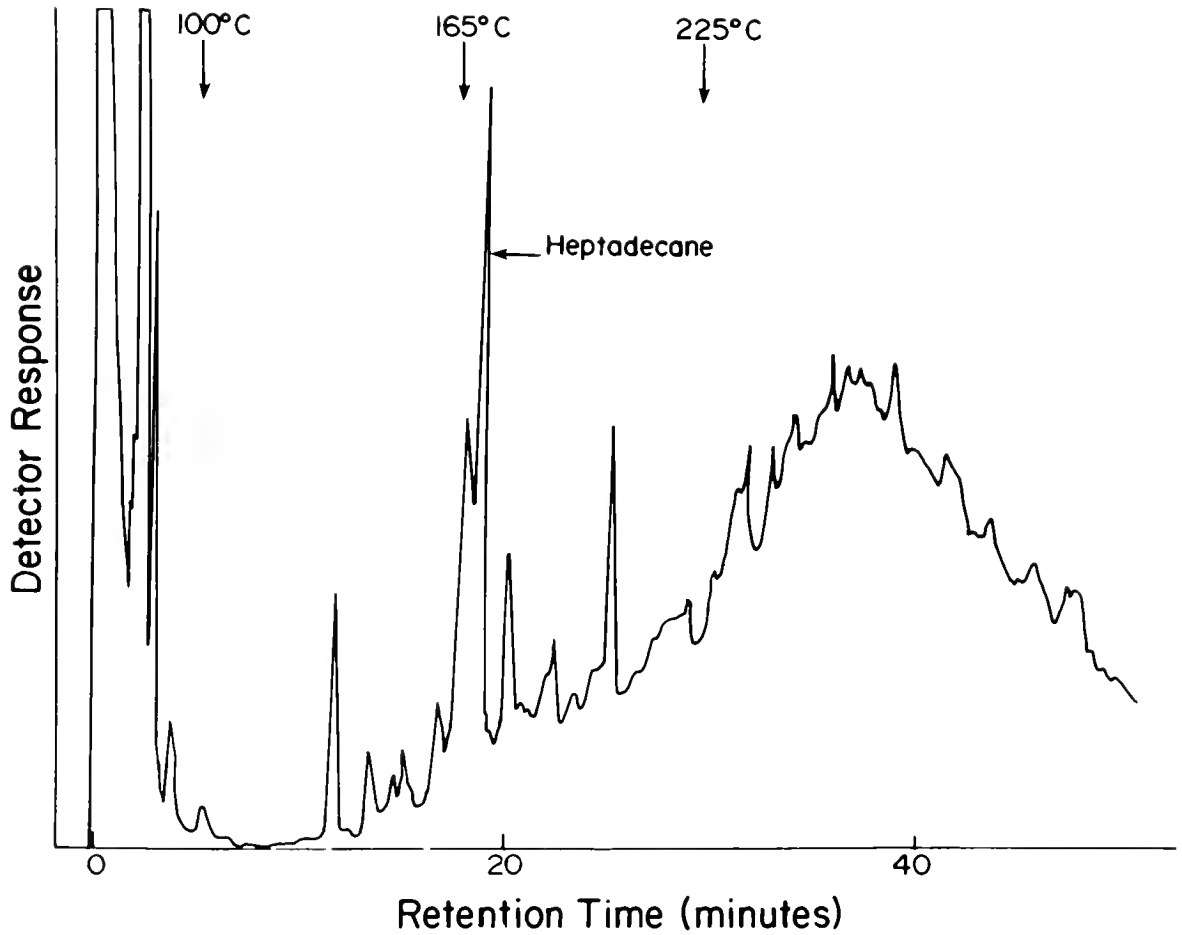


FIGURE 2. *Flame ionization detector chromatogram of whole fish extract from the Connecticut River, New Hampshire, 1976*

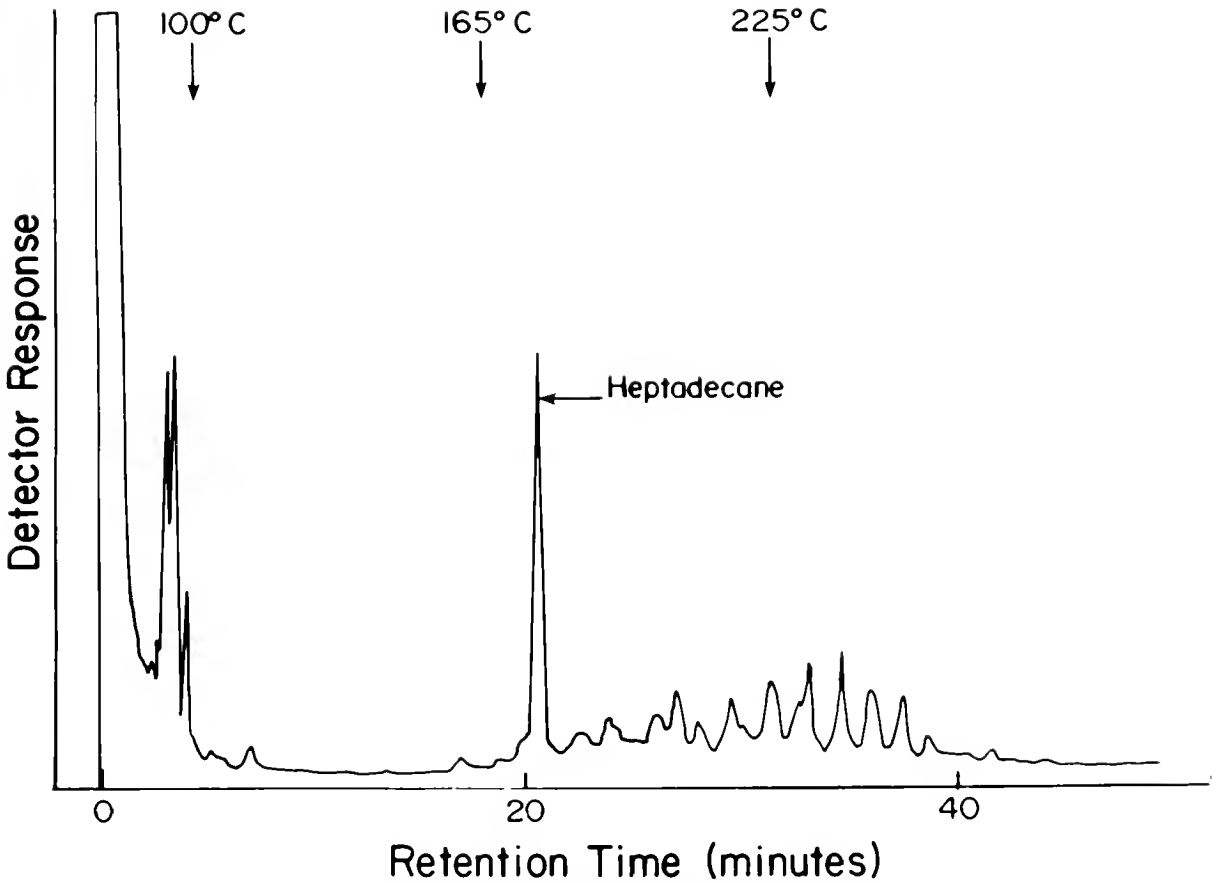


FIGURE 3. *Flame ionization detector chromatogram of whole fish extract from the Coosa River, Georgia, 1976*

Nationwide Residues of Organochlorine Compounds in Wings of Adult Mallards and Black Ducks, 1976–77

Donald H. White [1]

ABSTRACT

Organochlorine residues in wings of adult mallards and black ducks were monitored nationwide during the 1976–77 hunting season. DDE was found in all samples. Levels were unchanged since the 1972–73 collections in all migratory routes except the Pacific Flyway, in which residue levels declined significantly. Dieldrin levels had not changed in any flyway and residues remained low. PCB levels declined significantly in the Atlantic Flyway but remained stable in other flyways. Heptachlor epoxide, mirex, endrin, hexachlorobenzene, and chlordane isomers were detected in low amounts in some samples.

Introduction

The Fish and Wildlife Service, U.S. Department of the Interior, began nationwide monitoring of organochlorine pesticides in waterfowl wings during 1965–66 as part of the National Pesticide Monitoring Program. Samples were taken again in 1966–67 and subsequent collections were scheduled every third year to detect trends in residue levels. Wings of adult mallards (*Anas platyrhynchos*) and black ducks (*Anas rubripes*) are sampled because the combined ranges of these waterfowl cover the contiguous 48 states. Overall objectives and procedures have been discussed in earlier papers (*1–3*). The present paper gives the results of the 1976-77 duck wing collections, including mean residue levels for each state, a comparison of mean residues by major flyway for 1972–73 and 1976–77, and the percentage of pools containing each compound by major flyway. Major flyways are corridors comprised of states or parts of states through which large numbers of waterfowl migrate each spring and fall. The states that make up each of the four major flyways are listed in Table 1.

Collection Methods

Duck wings from the contiguous 48 states are available for monitoring purposes as a byproduct of a nationwide survey of waterfowl productivity. Cooperating hunters mailed wings of approximately 5,600 adult mallards and black ducks taken during the 1976–77 hunting season 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 sorted systematically into pools of 25 wings. Pools from each state were selected randomly for chemical analysis; the number used was roughy proportional to each state's harvest. Pools were given a code number, placed in individually tagged plastic bags, and shipped in Dry Ice to Raltech Scientific Services, Inc., Madison, Wisconsin, for chemical analysis. Wings were stored frozen until analysis. A total of 227 pools were analyzed for organochlorine residues.

Analytical Procedures

Before being analyzed, the wings were plucked of most of the primary feathers and the distal joint (manus) was removed. The remaining portions were homogenized in a Hobart food grinder. A 40-g sample was weighed into a 250-ml beaker and mixed with 100 g anhydrous sodium sulfate. The sample was allowed to air dry overnight in a hood and was then transferred to a 43-mm × 123-mm prewashed Whatman extraction thimble plugged with glass wool. The thimble was placed in a desiccator overnight, and the sample was extracted on a Soxhlet extractor for 8 hours with a mixture of 150 ml ethyl ether and 150 ml petroleum ether. The extract was concentrated to near dryness on a steam bath and the remaining solvent was removed with nitrogen at room temperature. The residue was transferred to a 50-ml volumetric flask and diluted to volume with a 3:1 solution of toluene–ethyl acetate.

A 5-ml portion of the extract was placed on an Auto-Prep 1001 gel permeation chromatograph, standardized for organochlorine insecticides and PCBs. Instrument parameters and operating conditions follow:

Packing:	80 g of Bio-Beads (SX-3), 200–400-mesh
Column:	600 mm × 25 mm ID
Solvent:	3:1 toluene–ethyl acetate solution
Flow rate:	5.5 ml/minute
Dump time:	30 minutes
Collect time:	14 minutes
Wash time:	4 minutes

The resulting solution was concentrated on a flash

[1] Fish and Wildlife Service, U.S. Department of the Interior, Patuxent Wildlife Research Center, Gulf Coast Field Station, P.O. Box 2506, Victoria, Tex. 77901.

evaporator to approximately 5 ml in the presence of 5 ml isooctane and was diluted to 25 ml with petroleum ether.

A 10-ml portion of the extract from the gel permeation chromatograph was placed on a 15-g standardized Silicar CC-4 column which had been washed to remove interfering compounds. Typical elutions follow:

Fraction I:	60 ml petroleum ether, contains HCB and mirex
Fraction II:	350 ml petroleum ether, contains PCBs and some DDE
Fraction III:	150-ml mixture of 1 percent acetonitrile, 19 percent hexane, and 80 percent methylene chloride, contains the remaining organochlorine compounds

Fractions I and II were concentrated on a steam bath to 1–2 ml and diluted to 10 ml with petroleum ether. Fraction III was concentrated on a flash evaporator to 1–2 ml and diluted to 10 ml with petroleum ether. Aliquots of 4 μl of each solution were injected into a gas chromatograph equipped with an electron-capture detector.

Analyses were performed on a Hewlett-Packard Model 5710A gas chromatograph equipped with a linear Ni^{63} detector and automatic injector, attached to a Hewlett-Packard Model 3352C data acquisition system. Instrument parameters and operating conditions for determining organochlorine pesticides and PCBs were:

Column:	1219 mm × 4 mm ID, glass, packed with a mixture of 1.95 percent OV–17 and 1.5 percent QF–1 on 80–100-mesh Supelcoport	
Temperatures, C:	column	200
	injector	250
	detector	300
Carrier gas:	a mixture of 95 percent argon and 5 percent methane flowing at 33 ml/minute	

Instrument parameters and operating conditions for determining chlordane isomers were:

Column:	1219 mm × 4 mm ID, glass, packed with 3 percent OV–1 on 80–100-mesh Gas-Chrom Q	
Temperatures, C:	column	190
	injector	250
	detector	300
Carrier gas:	a mixture of 95 percent argon and 5 percent methane flowing at 32 ml/minute	

TABLE 1. *Organochlorine residues in pools of wings of adult mallards and black ducks, 1976–77*

State	No. of Pools	Residues, ppm Wet Weight									
		DDE		DDT		TDE		Dieldrin		PCBs [1]	
		$\bar{X} \pm$ SE	Range	$\bar{X} \pm$ SE	Range	$\bar{X} \pm$ SE	Range	$\bar{X} \pm$ SE	Range	$\bar{X} \pm$ SE	Range
BLACK DUCKS, ATLANTIC FLYWAY											
Maine	4 [2]	0.35±0.14 (4)	0.20–0.77	0.09±0.00 (1)	ND–0.09	0.03±0.01 (2)	ND–0.04	0.01±0.00 (3)	ND–0.02	0.38±0.05 (4)	0.29–0.49
Vermont	1 [2]	0.15±0.00 (1)	—	ND	—	ND	—	ND	—	0.12±0.00 (1)	—
New Hampshire	1 [2]	0.55±0.00 (1)	—	0.06±0.00 (1)	—	ND	—	0.01±0.00 (1)	—	0.64±0.00 (1)	—
Massachusetts	4 [2]	0.39±0.13 (4)	0.04–0.67	0.08±0.02 (4)	0.06–0.14	0.02±0.01 (4)	0.01–0.04	0.08±0.05 (4)	0.02–0.22	0.96±0.13 (4)	0.70–1.31
Connecticut	2	0.36±0.00 (2)	0.35–0.36	0.05±0.01 (2)	0.03–0.06	0.02±0.00 (2)	0.01–0.02	0.03±0.00 (2)	—	1.11±0.28 (2)	0.83–1.38
Rhode Island	1	0.12±0.00 (1)	—	0.11±0.00 (1)	—	0.03±0.00 (1)	—	0.15±0.00 (1)	—	0.49±0.00 (1)	—
New York	4	0.48±0.08 (4)	0.32–0.69	0.06±0.04 (3)	ND–0.13	0.02±0.00 (4)	0.01–0.03	0.03±0.00 (4)	0.02–0.04	0.81±0.23 (4)	0.45–1.48
Pennsylvania	2 [2]	0.25±0.09 (2)	0.16–0.34	0.02±0.00 (1)	ND–0.02	0.01±0.00 (1)	ND–0.01	ND	—	0.38±0.02 (2)	0.35–0.40
New Jersey	5	0.45±0.07 (5)	0.27–0.63	0.06±0.04 (3)	ND–0.13	0.04±0.01 (2)	ND–0.05	0.03±0.00 (5)	0.02–0.04	0.50±0.06 (5)	0.33–0.68
Delaware	1	1.13±0.00 (1)	—	0.07±0.00 (1)	—	0.05±0.00 (1)	—	0.07±0.00 (1)	—	0.37±0.00 (1)	—
Maryland	3	0.18±0.02 (3)	0.15–0.21	0.05±0.04 (2)	ND–0.09	0.03±0.02 (2)	ND–0.05	0.02±0.00 (3)	—	0.22±0.06 (3)	0.12–0.34
Virginia	3	0.36±0.10 (3)	0.16–0.50	0.04±0.02 (2)	ND–0.06	0.02±0.00 (1)	ND–0.02	0.03±0.00 (2)	ND–0.03	0.46±0.13 (3)	0.21–0.65
North Carolina	1	0.32±0.00 (1)	—	0.04±0.00 (1)	—	0.04±0.00 (1)	—	0.03±0.00 (1)	—	0.31±0.00 (1)	—
MALLARDS, ATLANTIC FLYWAY											
New York	3	0.53±0.19 (3)	0.25–0.89	0.08±0.05 (2)	ND–0.13	0.02±0.01 (2)	ND–0.03	0.03±0.00 (2)	ND–0.03	0.23±0.05 (3)	0.15–0.32
Pennsylvania	3	0.42±0.07 (3)	0.34–0.55	0.08±0.01 (3)	0.06–0.11	0.02±0.00 (2)	ND–0.02	0.03±0.01 (3)	0.02–0.04	1.01±0.21 (3)	0.62–1.33
New Jersey	3	0.59±0.06 (3)	0.48–0.66	0.05±0.01 (3)	0.03–0.07	0.01±0.00 (3)	—	0.02±0.00 (3)	0.02–0.03	0.52±0.09 (3)	0.39–0.70
Maryland	2	0.13±0.00 (2)	—	ND	—	ND	—	0.03±0.00 (2)	0.02–0.03	0.14±0.02 (2)	0.12–0.16
Virginia	3	0.17±0.02 (3)	0.13–0.19	0.05±0.01 (2)	ND–0.06	0.04±0.00 (1)	ND–0.04	0.23±0.00 (1)	ND–0.23	0.22±0.07 (3)	0.08–0.33
South Carolina	3 [2]	0.18±0.04 (3)	0.11–0.23	0.08±0.00 (1)	ND–0.08	0.04±0.00 (1)	ND–0.04	0.01±0.00 (3)	0.01–0.02	0.16±0.02 (3)	0.13–0.19
Georgia and Florida	3	0.22±0.02 (3)	0.20–0.25	0.05±0.00 (1)	ND–0.05	0.01±0.00 (1)	ND–0.01	0.04±0.03 (3)	0.01–0.09	1.35±0.71 (3)	0.51–2.75

(*continued next page*)

TABLE 1 (cont'd.). *Organochlorine residues in pools of wings of adult mallards and black ducks, 1976–77*

State	No. of Pools	Residues, ppm Wet Weight									
		DDE		DDT		TDE		Dieldrin		PCBs [1]	
		$\bar{X} \pm$ SE	Range	$\bar{X} \pm$ SE	Range	$\bar{X} \pm$ SE	Range	$\bar{X} \pm$ SE	Range	$\bar{X} \pm$ SE	Range
MALLARDS, MISSISSIPPI FLYWAY											
Minnesota	5	0.18±0.03 (5)	0.11–0.25	0.07±0.01 (4)	ND–0.09	0.02±0.00 (1)	ND–0.02	ND	—	0.13±0.02 (3)	ND–0.17
Wisconsin	5	0.17±0.03 (5)	0.11–0.26	0.05±0.01 (4)	ND–0.08	0.02±0.00 (1)	ND–0.02	0.02±0.00 (4)	ND–0.02	0.22±0.02 (4)	ND–0.27
Michigan	5	0.28±0.04 (5)	0.17–0.39	0.05±0.01 (4)	ND–0.07	0.01±0.00 (1)	ND–0.01	0.04±0.01 (5)	0.01–0.09	0.37±0.11 (5)	0.14–0.81
Iowa	5	0.19±0.04 (5)	0.11–0.32	0.05±0.01 (5)	0.02–0.08	0.05±0.02 (3)	ND–0.09	0.03±0.00 (3)	ND–0.03	0.46±0.34 (2)	ND–0.80
Illinois	6	0.16±0.04 (6)	0.07–0.34	0.05±0.01 (4)	ND–0.07	0.02±0.00 (1)	ND–0.02	0.02±0.01 (4)	ND–0.03	0.14±0.01 (4)	ND–0.17
Indiana	4	0.15±0.03 (4)	0.09–0.24	0.03±0.01 (3)	ND–0.05	0.02±0.00 (1)	ND–0.02	0.02±0.01 (4)	0.01–0.04	0.13±0.03 (4)	0.10–0.21
Ohio	4	0.22±0.03 (4)	0.15–0.29	0.06±0.01 (4)	0.05–0.08	0.02±0.01 (3)	ND–0.03	0.03±0.00 (4)	0.02–0.03	0.30±0.06 (4)	0.18–0.46
Missouri	5	0.12±0.03 (5)	0.07–0.23	0.06±0.01 (5)	0.04–0.10	0.03±0.01 (2)	ND–0.04	0.01±0.00 (3)	ND–0.02	ND	—
Kentucky	3	0.29±0.11 (3)	0.15–0.51	0.06±0.02 (3)	0.03–0.08	0.02±0.00 (1)	ND–0.02	0.03±0.01 (3)	0.02–0.04	0.17±0.02 (2)	ND–0.19
Arkansas	6	0.25±0.05 (6)	0.14–0.40	0.05±0.01 (6)	0.02–0.07	0.03±0.00 (1)	ND–0.03	0.12±0.08 (5)	ND–0.45	0.12±0.00 (1)	ND–0.12
Tennessee	4	0.20±0.07 (4)	0.03–0.36	0.05±0.01 (3)	ND–0.07	0.01±0.00 (1)	ND–0.01	0.02±0.00 (3)	ND–0.03	0.21±0.06 (3)	ND–0.32
Louisiana	5	0.18±0.02 (5)	0.11–0.22	0.07±0.01 (4)	ND–0.09	0.04±0.00 (2)	ND–0.04	0.18±0.15 (5)	0.02–0.77	0.15±0.00 (1)	ND–0.15
Mississippi	6	0.46±0.08 (6)	0.18–0.66	0.15±0.03 (6)	0.05–0.28	0.02±0.00 (3)	ND–0.03	0.06±0.01 (6)	0.03–0.11	0.21±0.08 (3)	ND–0.36
Alabama	6	0.69±0.34 (6)	0.17–2.39	0.19±0.06 (5)	ND–0.41	0.38±0.33 (5)	ND–1.72	0.07±0.02 (5)	ND–0.13	0.36±0.08 (6)	0.11–0.60
MALLARDS, CENTRAL FLYWAY											
Montana (eastern)	4	0.08±0.02 (4)	0.05–0.13	0.04±0.01 (4)	0.02–0.07	0.03±0.01 (2)	ND–0.04	0.04±0.02 (3)	ND–0.06	ND	—
North Dakota	6	0.17±0.03 (6)	0.09–0.28	0.04–0.01 (5)	ND–0.06	0.02±0.00 (3)	ND–0.03	0.09±0.07 (3)	ND–0.23	ND	—
South Dakota	4	0.15±0.03 (4)	0.08–0.20	0.07±0.01 (3)	ND–0.08	0.07±0.03 (2)	ND–0.10	0.03±0.00 (1)	ND–0.03	0.14±0.00 (1)	ND–0.14
Wyoming (eastern)	4	0.07±0.01 (4)	0.05–0.08	0.06±0.01 (2)	ND–0.07	0.05±0.00 (1)	ND–0.05	0.02±0.00 (3)	ND–0.02	0.12±0.00 (1)	ND–0.12
Nebraska	8	0.07±0.01 (8)	0.03–0.16	0.05±0.01 (4)	ND–0.06	0.02±0.01 (4)	ND–0.04	0.01±0.00 (5)	ND–0.02	0.18±0.00 (1)	ND–0.18
Colorado (eastern)	6	0.12±0.02 (6)	0.07–0.19	0.06±0.01 (5)	ND–0.11	0.02±0.00 (4)	ND–0.02	0.01±0.00 (3)	ND–0.02	0.16±0.04 (2)	ND–0.20
Kansas	6	0.07±0.01 (6)	0.02–0.11	0.03±0.01 (5)	ND–0.05	0.03±0.00 (1)	ND–0.03	0.02±0.00 (2)	ND–0.02	ND	—
New Mexico (eastern)	3	1.81±0.72 (3)	0.42–2.82	0.08±0.02 (3)	0.05–0.10	0.08±0.02 (2)	ND–0.10	0.01±0.00 (2)	ND–0.01	ND	—
Oklahoma	6	0.13±0.02 (6)	0.07–0.20	0.04±0.01 (6)	0.01–0.09	0.02±0.01 (4)	ND–0.04	0.03±0.01 (6)	0.01–0.07	ND	—
Texas	9	0.17±0.01 (9)	0.09–0.24	0.04±0.01 (7)	ND–0.07	0.02±0.00 (2)	ND–0.02	0.03±0.00 (8)	ND–0.04	0.13±0.03 (2)	ND–0.16
MALLARDS, PACIFIC FLYWAY											
Washington State	8	0.20±0.02 (8)	0.14–0.27	0.07±0.01 (6)	ND–0.10	0.05±0.02 (3)	ND–0.08	0.02±0.00 (7)	ND–0.04	0.11±0.00 (1)	ND–0.11
Oregon	6	0.25±0.06 (6)	0.13–0.52	0.70±0.02 (6)	0.03–0.14	0.04±0.02 (2)	ND–0.06	0.02±0.00 (4)	ND–0.03	ND	—
Idaho	9	0.24±0.04 (9)	0.12–0.51	0.04±0.01 (9)	0.01–0.07	0.03±0.01 (6)	ND–0.06	0.02±0.00 (6)	ND–0.03	ND	—
Montana (western)	5	0.08±0.01 (5)	0.05–0.12	0.05±0.02 (4)	ND–0.09	0.02±0.01 (4)	ND–0.03	ND	—	ND	—
Wyoming (western)	2	0.08±0.01 (2)	0.06–0.09	0.08±0.02 (2)	0.05–0.10	ND	—	0.02±0.00 (2)	0.01–0.02	ND	—
California	10	0.44±0.12 (10)	0.15–1.18	0.06±0.01 (9)	ND–0.11	0.02±0.00 (7)	ND–0.04	0.05±0.01 (7)	ND–0.09	ND	—
Nevada	2	0.14±0.04 (2)	0.10–0.18	0.07±0.01 (2)	0.06–0.08	0.05±0.00 (1)	ND–0.05	ND	—	ND	—
Utah	2	0.33±0.03 (2)	0.30–0.36	0.04±0.03 (2)	0.01–0.07	0.01±0.00 (2)	—	0.02±0.00 (2)	—	0.27±0.13 (2)	0.13–0.40
Colorado (western)	3	0.13±0.02 (3)	0.10–0.15	0.09±0.02 (3)	0.06–0.12	0.04±0.01 (2)	ND–0.05	0.01±0.00 (1)	ND–0.01	0.12±0.02 (2)	ND–0.14
Arizona and New Mexico (western)	3	0.33±0.14 (3)	0.11–0.59	0.06±0.02 (3)	0.04–0.10	0.02±0.01 (2)	ND–0.03	0.02±0.00 (2)	ND–0.02	0.15±0.04 (2)	ND–0.19

NOTE: Pools contained 25 wings each. ND = not detected; — = not applicable. Values in parentheses are actual number of pools containing residues; means were calculated using these values.

[1] PCBs were quantified on the basis of Aroclor 1254.

[2] One or more pools in this group contained fewer than 25 wings.

Residues in 5 percent of the samples were confirmed by mass spectrometry. Recoveries from spiked samples ranged from 75 to 134 percent; analytical results were not corrected.

All residues are expressed as ppm wet weight. They may be converted to dry or lipid weight by dividing a given wet weight value by 0.62 or 0.13, the mean proportions of dry or lipid material, respectively, in the samples. The quantification limit was 0.01 ppm for organochlorine pesticides and PCBs. Trace residues were not reported.

Results and Discussion

Residues of DDE, DDT, TDE, dieldrin, and PCBs in duck wings for 1976 are shown in Table 1; data are arranged by state within major flyways. Because waterfowl are highly mobile species and may cover a wide range of habitats in many states, findings should not be interpreted strictly on a statewide basis. However, samples from some localities consistently contain higher residues of certain chemicals than do those from other localities (*4*), suggesting that samples are reflecting local environmental contamination. Residue levels do not indicate year-round averages because collections were made only during fall and winter.

DDE residues occurred in all wing pools, ranging from 0.02 to 2.82 ppm (Table 2); the lowest was in a pool from Kansas and the highest level was in a pool from eastern New Mexico (Table 1). PCBs were detected in all pools from the Atlantic Flyway (Table 2), ranging up to 2.75 ppm in a mallard pool from Georgia and Florida; the percentage of PCBs in samples from each flyway diminished westward. Dieldrin occurred in 62–85 percent of the samples from each flyway (Table 2), but levels seldom exceeded 0.05 ppm in individual pools. The highest level of dieldrin, 0.77 ppm, was detected in a wing pool from Louisiana.

In addition to the organochlorine compounds listed in Table 1, heptachlor epoxide, mirex, endrin, hexachlorobenzene (HCB), and chlordane isomers were found in duck wings less frequently. Since residues seldom exceeded 0.1 ppm, these chemicals were omitted from Table 1, but the percentage occurrence and ranges are listed in Table 2 by flyway.

Means of DDE, DDT, TDE, and dieldrin for the 1972 and 1976 collections, by flyway, were statistically compared to detect residue trends over time (Table 3). DDE levels remained unchanged during the 4-year period in all areas except the Pacific Flyway, where residues declined ($P < 0.01$) 36 percent. DDT levels declined ($P < 0.05$) 62 percent in the Mississippi Flyway but remained unchanged in the other flyways. Dieldrin levels did not change significantly ($P > 0.05$) in any flyway and mean residues remained quite low. Different quantification methods were used for PCBs between years; therefore, results were not compared statistically because of possible bias in the analysis.

Conclusions

Residues of DDE and DDT in mallards and black ducks have declined since 1972 in certain flyways. Geographical differences in contamination levels were detected.

Acknowledgments

Special thanks are extended to the following for their help with duck wing collections: Samuel Carney, James Elder, Robert Hillen, David Lenhart, and James Spann,

TABLE 2. *Percent occurrence and range of organochlorine residues detected in duck wings by flyway, 1976–77*

Species	Residues, ppm Wet Weight									
	DDE	DDT	TDE	Dieldrin	PCBs	Heptachlor Epoxide	Mirex	Endrin	HCB	Chlordane Isomers
ATLANTIC FLYWAY										
Black duck	100[1]	69	66	84	100	34	19	3	16	59
	0.04–1.13	0.01–0.14	0.01–0.05	0.01–0.22	0.12–1.48	0.01–0.04	0.02–0.04	0.01	0.01	0.01–0.05
Mallard	100	60	50	85	100	50	50	5	10	55
	0.11–0.89	0.02–0.13	0.01–0.04	0.01–0.23	0.08–2.75	0.02–0.17	0.01–0.14	0.02	0.01–0.03	0.01–0.06
MISSISSIPPI FLYWAY										
Mallard	100	87	38	78	61	45	29	4	7	22
	0.03–2.39	0.01–0.41	0.01–1.72	0.01–0.77	0.10–0.81	0.01–0.11	0.01–0.03	0.02	0.01–0.12	0.01–0.02
CENTRAL FLYWAY										
Mallard	100	79	45	64	13	48	14	2	9	14
	0.02–2.82	0.01–0.11	0.01–0.10	0.01–0.23	0.10–0.20	0.01–0.30	0.01–0.06	0.02	0.01–0.03	0.01–0.02
PACIFIC FLYWAY										
Mallard	100	92	58	62	14	32	4	0	24	14
	0.05–1.18	0.01–0.14	0.01–0.08	0.01–0.09	0.10–0.40	0.01–0.09	0.02–0.03	—	0.01–0.50	0.01–0.02

[1]Percent occurrence. Total number of pools per flyway: Atlantic (black ducks), 32; Atlantic (mallards), 20; Mississippi, 69; Central, 56; Pacific, 50.

TABLE 3. *Means and standard errors of organochlorine residues in waterfowl wing pools by major flyway, 1972 and 1976*

Species	Flyway	Year	No. of Pools	Residues, ppm Wet Weight				
				DDE	DDT	TDE	Dieldrin	PCBs
Black duck	Atlantic	1972	44	0.35±0.04 (44)	0.07±0.01 (44)	0.02±0.00 (44)	0.02±0.00 (44)	1.36±0.15 (44)
		1976	32	0.39±0.07 (32)	0.06±0.01 (22)	0.03±0.00 (21)	0.04±0.01 (27)	0.52±0.08 (32)
Mallard	Atlantic	1972	21	0.44±0.07 (21)	0.08±0.01 (21)	0.06±0.05 (21)	0.02±0.00 (21)	1.24±0.23 (21)
		1976	20	0.32±0.07 (20)	0.07±0.01 (12)	0.02±0.01 (10)	0.06±0.03 (17)	0.52±0.18 (20)
Mallard	Mississippi	1972	61	0.37±0.07 (61)	0.18±0.06 (61)	0.06±0.00 (61)	0.02±0.00 (61)	0.66±0.30 (61)
		1976	69	0.25±0.04 (69)	0.07±0.01[1] (60)	0.05±0.03 (26)	0.05±0.01 (54)	0.23±0.03 (42)
Mallard	Central	1972	56	0.15±0.01 (56)	0.02±0.00 (56)	0.01±0.00 (56)	0.02±0.00 (56)	0.10±0.01 (56)
		1976	56	0.28±0.17 (56)	0.05±0.01 (44)	0.04±0.01 (25)	0.03±0.01 (36)	0.15±0.01 (7)
Mallard	Pacific	1972	55	0.34±0.04 (55)	0.03±0.00 (55)	0.01±0.00 (55)	0.01±0.00 (55)	0.11±0.01 (55)
		1976	50	0.22±0.04[2] (50)	0.06±0.01 (46)	0.03±0.00 (29)	0.02±0.00 (31)	0.16±0.04 (7)

NOTE: Values in parentheses are actual number of pools containing residues; means were calculated using these values.
[1] Flyway means for the 2 years were significantly different: $P < 0.05$, analysis of variance.
[2] Flyway means for the 2 years were significantly different: $P < 0.01$, analysis of variance.

Fish and Wildlife Service. Christine Mitchell compiled the tables and performed many of the statistical computations.

LITERATURE CITED

(*1*) *Heath, R. G. 1969.* Nationwide residues of organochlorine pesticides in wings of mallards and black ducks. Pestic. Monit. J. 3(2):115–123.

(*2*) *Heath, R. G., and S. A. Hill. 1974.* Nationwide organochlorine and mercury residues in wings of adult mallards and black ducks during the 1969–70 hunting season. Pestic. Monit. J. 7(3/4):153–164.

(*3*) *Heath, R. G., and R. M. Prouty. 1967.* Trial monitoring of pesticides in wings of mallards and black ducks. Bull. Environ. Contam. Toxicol. 2(2):101–110.

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

SOILS

Pesticide Residue Concentrations in Soils of Five United States Cities, 1971 —Urban Soils Monitoring Program

Ann E. Carey,[1] Pamela Douglas,[2] Han Tai,[3] William G. Mitchell,[3] and G. Bruce Wiersma[4]

ABSTRACT

Soil samples from five metropolitan areas including Baltimore, Maryland; Gadsden, Alabama; Hartford, Connecticut; Macon, Georgia; and Newport News, Virginia were analyzed for elemental arsenic, organochlorine pesticides, and polychlorinated biphenyls (PCBs). A representative number of samples were analyzed for organophosphorus pesticides, but none was detected. All areas exhibited heavy soil concentrations of organochlorine pesticides including ΣDDT, aldrin, dieldrin, photodieldrin, chlordane, heptachlor, heptachlor epoxide, endrin, endrin ketone, and endosulfan sulfate. PCBs were detected in three of the five metropolitan areas. Within the metropolitan areas, samples from the urban, or core city, locations generally had higher pesticide concentrations than did samples from suburban locations. Finally, pesticide residue concentrations were generally higher in soils of metropolitan areas than in nearby agricultural soils.

Introduction

The concept of pest control as the decrease or elimination of unwanted or menacing organisms has probably existed since the dawn of civilization. Only within the past 30 years, however, has technology advanced sufficiently to provide the degree of control now possible with chemical pesticides. Although large-scale use of pesticides is often considered an agricultural phenomenon, surveys indicate that significant amounts of the compounds are being applied in urban areas (*6*). A survey of 196 urban households in Charleston, South Carolina, showed that 89 percent used pesticides (*4*).

The published data on urban soil residues reveal that there are significant pesticide loads, comprised primarily of ΣDDT, present in United States cities. In 1963, Fahey et al. found that 89 percent of turf grass and soil samples taken in Battle Creek, Michigan, contained organochlorine pesticide residues (*2*). In that study, DDT concentrations in soil ranged from 0.07 to 79.98 ppm. Wiersma et al. confirmed the presence of pesticide loads in urban soils and noted significant variations among individual cities (*7*). In addition, overall examination of the distribution of ΣDDT within the eight urban areas sampled showed that compound concentrations were significantly higher in lawn or garden areas than in unkept or waste areas. Carey et al. found that ΣDDT concentration differed significantly between lawn and waste areas in seven of thirteen cities examined (*1*).

The present study was initiated to confirm and extend previous data by examining pesticide residues in Baltimore, Maryland; Gadsden, Alabama; Hartford, Connecticut; Macon, Georgia; and Newport News, Virginia.

Sampling Procedures

Five Standard Metropolitan Statistical Areas (SMSAs), as defined by the United States Bureau of the Census (*5*), were randomly selected from a list of all SMSAs stratified by population. Group 1 contained SMSAs with populations greater than one million, group 2 SMSAs had populations between one million and 100,000, and group 3 SMSAs had populations of less than 100,000. One metropolitan area was randomly selected from group 1, three were selected from group 2, and one was selected from group 3.

A Standard Metropolitan Statistical Area generally includes a city and all contiguous counties. In each SMSA, sampling sites were randomly allocated within the political boundaries of the city to yield a density of one site per 2.59 km^2 or one square mile. These were designated

[1]Ecological Monitoring Branch, Benefits and Field Studies Division, Office of Pesticide Programs, U.S. Environmental Protection Agency, TS-768, Washington, D.C. 20460.
[2]Medical College of Virginia, Richmond, Va.
[3]Ecological Monitoring Branch, Benefits and Field Studies Division, Office of Pesticide Programs, U.S. Environmental Protection Agency, Pesticides Monitoring Laboratory, Bay St. Louis, Miss.
[4]Chief, Pollutant Pathways Branch, Environmental Monitoring and Support Laboratory, U.S. Environmental Protection Agency, Las Vegas, Nev.

as urban sites. Within the adjacent counties, sites were allocated at a density of one site per 51.8 km² or 20 square miles. These were designated as suburban sites.

All sampling sites were 231 m², usually a 15.2 m by 15.2 m plot (50 ft by 50 ft). Sixteen soil cores, each 5.1 cm in diameter by 7.6 cm deep, were taken over the site on an evenly spaced, 4 by 4 grid. The cores were composited, sieved three times through a 6.3-mm mesh screen, and thoroughly mixed. A 2-liter subsample was drawn, packed in a metal container, and shipped to the Pesticides Monitoring Laboratory, Bay St. Louis, Mississippi, for analysis.

In addition, each site was designated either lawn or waste according to the criteria used by Wiersma et al. (*7*), which indicate whether the site is likely to be cultivated and/or trimmed.

Analytical Procedures

PREPARATION OF SOIL SAMPLES

A 300-g subsample of soil was taken from the sample container, moistened with 80 ml water, and extracted with 600 ml 3:1 hexane-isopropanol by concentric rotation for 4 hours. The isopropanol was removed by three distilled water washes, and the hexane extract was dried with anhydrous sodium sulfate. The sample extract was stored at low temperature for subsequent gas-liquid chromatographic analysis.

GAS-LIQUID CHROMATOGRAPHY

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

Gas chromatographs:	Hewlett-Packard Model 402A Hewlett-Packard Model 402B Tracor Model MT-220	
Columns:	glass, 183 cm long × 6 mm OD, 4 mm ID, packed with 100–200-mesh Gas-Chrom Q coated with 9 percent QF-1 100–120 mesh Gas-Chrom Q coated with 3 percent DC-200 100–120-mesh Supelcoport coated with a mixture of 1.5 percent OV-17 and 1.95 percent QF-1	
Carrier gases:	5 percent methane-argon flowing at 80 ml/minute, prepurified nitrogen flowing at 80 ml/minute	
Temperatures, °C:	detector	200
	injection port	250
	QF-1 column	166
	DC-200 column	170–175
	mixed column	185–190

Sensitivity for organochlorines and trifluralin was 0.002–0.03 ppm except for combinations of polychlorinated biphenyls (PCBs), chlordane, toxaphene, and other chemicals which had minimum detectable levels of 0.05–0.1 ppm. Sensitivity for organophosphates was approximately 0.01–0.03 ppm. When necessary, identity of residues was confirmed by thin-layer chromatography or *p*-values.

TABLE 1. *Compounds detectable by chemical methodology of the present study, 1971—Urban Soils Monitoring Program*

ORGANOCHLORINES	
Alachlor	Endosulfan sulfate
Aldrin	Endrin
Chlordane	Heptachlor
o,p'-DDT	Heptachlor epoxide
p,p'-DDT	Isodrin
o,p'-DDE	Lindane (γ-BHC)
p,p'-DDE	Methoxychlor
o,p'-TDE	Ovex
p,p'-TDE	PCBs
Dieldrin	PCNs
Endosulfan (I)	Propachlor
Endosulfan (II)	Toxaphene
ORGANOPHOSPHATES	
DEF	Parathion, ethyl
Diazinon	Parathion, methyl
Ethion	Phorate
Malathion	Trithion
OTHER HALOGENS	
Trifluralin	

NOTE: Although trifluralin is a dinitroaniline compound, it is detected in the methodology used in the present study.

The compounds detectable by the methodology of the present study are listed in Table 1. Because trifluralin is detected by the organochlorine methodology it appears with organochlorine analyses in the tables.

ARSENIC

Arsenic was determined by atomic absorption spectrophotometry. The soil sample was extracted with 9.6*N* HCl, and arsenic was reduced to As^{+3} with stannous chloride. As^{+3} was partitioned from the acid to benzene, and then further partitioned from benzene to water for the absorption measurement. A Perkin-Elmer Model 303 spectrophotometer was used, and absorbance was measured with an arsenic cathode lamp at 1972 Å with argon as an aspirant to an air-hydrogen flame. Minimum detection limit was 0.1 ppm.

RECOVERY STUDIES

The average recovery rate for organochlorines, organophosphates, and trifluralin from soil was 90–110 percent. Recovery rate for arsenic was 70–80 percent. All residue levels in the tables are expressed as ppm dry weight and have been corrected for recovery.

Results and Discussion

Results of the chemical analyses are presented in Table 2. For each metropolitan area, the total number of sites is shown, as well as the arithmetic and estimated geometric mean concentrations for each compound, the minimum and maximum detected values, and the number and percent of sites with detectable concentrations.

TABLE 2. *Arsenic and organochlorine concentrations in soils from five United States cities, 1971 —Urban Soils Monitoring Program*

Location	Concentration, ppm Dry Weight																
	Arsenic	Aldrin	Dieldrin	Photo-dieldrin	Chlor-dane	Hepta-chlor	Hepta-chlor Epoxide	Endrin	Endrin Ketone	Endo-sulfan Sulfate	PCBs	Toxa-phene	*o,p'*-DDE	*p,p'*-DDE	*o,p'*-DDT	*p,p'*-DDT	*p,p'*-TDE	ΣDDT
Baltimore, Md., 156 samples																		
Number of positive detections	156	4	29	ND	57	ND	5	ND	ND	1	6	ND	1	81	23	71	82	95
Percent of positive detections	100.0	2.6	18.7		36.8		3.2			0.6	3.9		0.6	52.3	14.8	45.8	52.9	61.3
Detected values																		
minimum	0.6	0.01	0.01		0.01		0.17			0.17	0.09		0.15	0.01	0.01	0.01	0.01	0.01
maximum	100.6	2.04	1.40		12.35		0.09				0.74		—	7.86	0.58	5.86	6.57	17.56
Arithmetic mean	7.1	0.02	0.02		0.21		<0.01			<0.01	0.02		<0.01	0.12	0.02	0.14	0.13	0.40
Estimated geometric mean	4.7	0.001	0.003		0.016		<0.001			[1]	0.001		[1]	0.013	0.003	0.014	0.015	0.031
Gadsden, Ala., 55 samples																		
Number of positive detections	55	ND	7	ND	4	ND	1	ND	ND	ND	1	ND	ND	39	7	30	11	39
Percent of positive detections	100.0		12.7		5.1		1.8				1.8			70.9	12.7	54.5	20.0	70.9
Detected values																		
minimum	1.7		0.01		0.04		0.04				11.94			0.01	0.02	0.01	0.01	0.01
maximum	25.1		0.04		0.46									0.83	0.20	1.39	0.44	2.86
Arithmetic mean	7.8		<0.01		0.07		<0.01				0.22			0.04	0.01	0.06	0.02	0.12
Estimated geometric mean	5.9		0.001		0.002		[1]				[1]			0.015	0.003	0.018	0.004	0.033
Hartford, Conn., 48 samples																		
Number of positive detections	19[2]	4	5	ND	23	1	7	ND	ND	ND	ND	ND	2	38	15	37	25	40
Percent of positive detections	100.0	8.3	10.4		47.9	2.1	14.6						4.2	79.2	31.3	77.1	52.1	84.4
Detected values																		
minimum	1.3	0.03	0.08		0.02	0.13	0.01						0.01	0.01	0.01	0.01	0.01	0.01
maximum	50.8	0.64	1.45		140.69		1.95						0.11	1.59	0.37	2.01	1.35	4.29
Arithmetic mean	10.6	<0.01	0.06		4.00	<0.01	0.02						<0.01	0.17	0.04	0.20	0.13	0.56
Estimated geometric mean	6.4	0.003	0.004		0.067	[1]	0.004						0.001	0.046	0.010	0.058	0.019	0.123
Macon, Ga., 43 samples																		
Number of positive detections	43	ND	13	2	11	2	9	1	1	1	ND	11	4	41	33	42	11	42
Percent of positive detections	100.0		30.2	4.6	25.6	4.6	20.9	2.3	2.3	2.3		25.6	9.3	95.3	76.7	97.7	25.6	97.7
Detected values																		
minimum	0.5		0.01	0.12	0.07	0.01	0.01	0.17	0.06	0.06		0.23	0.02	0.01	0.01	0.02	0.01	0.02
maximum	5.4		6.02	0.53	0.91	0.01	0.14					4.95	0.12	1.01	0.34	1.74	0.07	3.54
Arithmetic mean	1.8		0.20	0.02	0.08	<0.01	<0.01	<0.01	<0.01	<0.01		0.24	<0.01	0.10	0.05	0.20	0.01	0.37
Estimated geometric mean	1.6		0.010	0.001	0.012	<0.001	0.004	[1]	[1]	[1]		0.019	0.002	0.049	0.027	0.097	0.004	0.175
Newport News, Va., 78 samples																		
Number of positive detections	72	ND	7	ND	10	2	3	ND	ND	ND	1	ND	ND	47	8	37	31	47
Percent of positive detections	92.3		9.0		12.8	2.6	3.8				1.3			60.3	10.3	47.4	39.8	60.3
Detected values																		
minimum	0.3		0.01		0.09	0.02	0.04				3.30			0.01	0.02	0.01	0.01	0.01
maximum	18.4		1.87		7.29	0.03	0.20							2.35	0.26	1.36	0.75	4.72
Arithmetic mean	2.4		0.04		0.16	<0.01	<0.01				0.04			0.11	<0.01	0.08	0.06	0.26
Estimated geometric mean	1.2		0.002		0.007	<0.001	0.001				[1]			0.021	0.003	0.018	0.013	0.068

NOTE: ND = not detected.

[1] Geometric mean estimate not calculated when less than two positive detections present.

[2] An additional 29 samples formed an unyielding slurry when HCl was added at the start of the extraction procedure, and could not be analyzed.

As shown in Table 2, pesticide residue data frequently contain many zero values, resulting from either the absence of pesticides or their presence at levels below the analytical sensitivity. Such data are seldom distributed normally, as shown by tests for skewness and/or kurtosis, but often approximate a log-normal distribution. After repeated tests for significant skewness and kurtosis, the log (X + 0.01) transformation was used to determine the logarithmic means. The antilogs of these figures minus 0.01 were taken to estimate the geometric mean in the untransformed dimension. The estimated geometric mean was calculated only for compounds with more than one positive detection.

ARSENIC

Elemental arsenic was detected in all five metropolitan areas and in 98 percent of all samples analyzed (Table 3). The six samples with no detectable arsenic concentrations were from Newport News sites classified as urban waste. The highest detected level of arsenic was 100.7 ppm, from an urban waste site in Baltimore.

Data for arsenic residues in Hartford were incomplete. Twenty-nine urban and suburban samples formed an unyielding slurry when HCl was added at the start of the extraction procedure, and the samples could not be analyzed. Therefore, only 19 sample results were used for the arsenic evaluation in Hartford.

Metropolitan areas were divided into two classes according to estimated geometric means of the arsenic values: high, greater than 4.7 ppm; and low, less than 1.6 ppm. Baltimore, Gadsden, and Hartford showed high levels; Macon and Newport News showed low levels. The cities sampled by Wiersma et al. showed a nearly identical division of above 5 ppm or below 2 ppm (*7*). Such overall differences among urban areas in levels of a naturally occurring element such as arsenic can probably be attributed to natural geological variation or general environmental contamination from industrial or combustion sources rather than to applications of arsenical pesticides. Neither Wiersma et al. (*7*) nor authors of the present study found significant differences in arsenic concentrations between lawn and waste areas. The difference in concentrations in urban and suburban loca-

TABLE 3. *Comparisons of detected concentrations of arsenic in soils of five United States cities, 1971 —Urban Soils Monitoring Program*

	Concentration, ppm Dry Weight					
			Urban		Suburban	
Location	Urban	Suburban	Lawn	Waste	Lawn	Waste
Baltimore, Md.						
Number of samples	74	82	44	30	10	72
Number of positive detections	74	82	44	30	10	72
Percent of positive detections	100	100	100	100	100	100
Detected values						
minimum	0.9	0.6	1.7	0.9	1.2	0.6
maximum	100.7	31.0	17.6	100.7	10.1	31.0
Arithmetic mean	8.9	5.5	6.4	12.6	5.8	5.5
Estimated geometric mean	5.6	4.1	5.2	6.3	4.8	4.0
Gadsden, Ala.						
Number of samples	30	25	15	15	7	18
Number of positive detections	30	25	15	15	7	18
Percent of positive detections	100	100	100	100	100	100
Detected values						
minimum	1.7	1.7	1.8	1.7	1.7	2.1
maximum	18.6	25.1	10.5	18.6	19.4	25.1
Arithmetic mean	6.7	9.1	6.3	7.2	6.6	10.1
Estimated geometric mean	5.6	6.2	5.4	5.7	4.4	8.6
Hartford, Conn.						
Number of samples	13	6	8	5	3	3
Number of positive detections	13	6	8	5	3	3
Percent of positive detections	100	100	100	100	100	100
Detected values						
minimum	1.9	1.3	5.0	1.9	1.8	1.3
maximum	50.8	8.3	50.8	14.7	4.3	8.3
Arithmetic mean	13.8	3.7	18.3	6.6	3.0	4.4
Estimated geometric mean	9.0	3.1	12.9	5.1	2.8	3.4
Macon, Ga.						
Number of samples	13	30	7	6	8	22
Number of positive detections	13	30	7	6	8	22
Percent of positive detections	100	100	100	100	100	100
Detected values						
minimum	0.7	0.5	0.7	1.3	0.5	0.5
maximum	4.8	5.4	2.8	4.8	2.4	5.4
Arithmetic mean	2.1	1.7	1.8	2.5	1.4	1.8
Estimated geometric mean	1.9	1.4	1.7	2.3	1.3	1.5
Newport News, Va.						
Number of samples	68	10	29	39	3	7
Number of positive detections	62	10	29	33	3	7
Percent of positive detections	91.2	100	100	84.6	100	100
Detected values						
minimum	0.3	0.5	0.3	0.3	1.5	0.5
maximum	18.4	4.6	17.8	18.4	2.3	4.6
Arithmetic mean	2.5	1.9	2.7	2.3	1.8	2.0
Estimated geometric mean	1.2	1.7	1.9	0.8	1.8	1.7

tions is probably due largely to industrial and vehicular contamination and may represent corresponding variations in air quality as demonstrated by Goodman and Robert (*3*).

ORGANOPHOSPHATES

A representative number of samples were analyzed for organophosphorus pesticides without positive results. Residues were either absent or present at concentrations below analytical sensitivity.

ORGANOCHLORINES

Concentrations of organochlorine pesticides were detected in 292, or 77 percent, of the 379 samples analyzed. ΣDDT was detected in 263, or 69 percent, of the samples analyzed. Organochlorine pesticides other than DDT detected in all five metropolitan areas included chlordane, heptachlor epoxide, and dieldrin. Four compounds, endrin, endrin ketone, photodieldrin, and toxaphene, were detected only in Macon. Sites in Baltimore contained the highest detected levels of aldrin (0.74 ppm) and ΣDDT (17.56 ppm); sites in Hartford had the highest levels of chlordane (140.69 ppm) and heptachlor epoxide (1.95 ppm). A site in Gadsden had the highest PCB level (11.94 ppm), and a Macon site had the highest dieldrin level (6.02 ppm).

Pesticide concentrations found in Macon included four compounds not found in the other metropolitan areas. Three of the compounds, endrin, endrin ketone, and photodieldrin, were detected in low concentrations of less than 0.10 ppm, generally in urban sites. Toxaphene, however, was detected in 11 suburban sites in concentations of 0.23–4.95 ppm. Previous nearby, or on-site, agricultural applications are probably responsible for the presence and unique distribution of toxaphene.

ΣDDT was detected most frequently in Macon in 98 percent of the samples analyzed; a Baltimore site had the highest concentration (17.56 ppm). Again, the five metropolitan areas could be separated into two classes of geometric mean concentrations: high, more than 0.12 ppm; low, less than 0.05 ppm. Hartford and Macon were high; Baltimore, Gadsden, and Newport News were low.

Table 4 presents a comparison of ΣDDT concentrations in soils in the urban/suburban and lawn/waste categories.

TABLE 4. *Comparison of detected concentrations of ΣDDT in soils of five United States cities, 1971 —Urban Soils Monitoring Program*

Location	Concentration, ppm Dry Weight					
			Urban		Suburban	
	Urban	Suburban	Lawn	Waste	Lawn	Waste
Baltimore, Md.						
Number of samples	74	81	44	30	10	71
Number of positive detections	64	31	39	25	2	29
Percent of positive detections	86.5	38.3	88.6	83.3	20.0	40.8
Detected values						
minimum	0.01	0.01	0.01	0.01	0 01	0.01
maximum	17.56	1.52	5.78	17.56	1.52	0.10
Arithmetic mean	0.81	0.02	0.47	1.32	0.15	0.01
Estimated geometric mean	0.096	0.007	0.090	0.106	0.008	0.007
Gadsden, Ala.						
Number of samples	30	25	15	15	7	18
Number of positive detections	25	14	14	11	4	10
Percent of positive detections	83.3	56.0	93.3	73.3	57.1	55.6
Detected values						
minimum	0.01	0.01	0.02	0.01	0.02	0.01
maximum	2.86	0.47	2.86	0.60	0.47	0.17
Arithmetic mean	0.19	0.05	0.28	0.09	0.10	0.03
Estimated geometric mean	0.052	0.018	0.069	0.038	0.029	0.014
Hartford, Conn.						
Number of samples	16	32	11	5	11	21
Number of positive detections	13	27	9	4	8	19
Percent of positive detections	81.3	84.4	81.8	80.0	72.7	90.5
Detected values						
minimum	0.01	0.01	0.08	0.01	0.05	0.01
maximum	4.29	3.89	4.29	0.08	3.89	2.79
Arithmetic mean	0.96	0.37	1.39	0.02	0.47	0.31
Estimated geometric mean	0.156	0.109	0.379	0.016	0.094	0.182
Macon, Ga.						
Number of samples	13	30	7	6	8	22
Number of positive detections	13	29	7	6	8	21
Percent of positive detections	100	96.7	100	100	100	95.5
Detected values						
minimum	0.02	0.04	0.04	0.02	0.10	0.04
maximum	3.54	1.54	3.54	0.33	1.27	1.54
Arithmetic mean	0.55	0.30	0.90	0.13	0.38	0.27
Estimated geometric mean	0.175	0.174	0.273	0.086	0.259	0.151
Newport News, Va.						
Number of samples	68	10	29	39	3	7
Number of positive detections	43	4	17	26	2	2
Percent of positive detections	63.2	40.0	58.6	66.7	66.7	28.6
Detected values						
minimum	0.01	0.02	0.02	0.01	0.04	0.02
maximum	4.72	2.07	4.72	1.97	2.07	0.06
Arithmetic mean	0.26	0.22	0.38	0.17	0.04	0.01
Estimated geometric mean	0.049	0.017	0.055	0.044	0.024	0.005

TABLE 5. *Comparison of geometric means of arsenic, ΣDDT, and chlordane in urban and agricultural soils of five states, 1971—Urban Soils Monitoring Program* [1]

Location	Concentration, ppm Dry Weight		
	Arsenic	ΣDDT	Chlordane
Baltimore, Md.	4.73	0.096	0.016
Cropland [2]	2.65**	0.007*	<0.001*
Gadsden, Ala.	5.88	0.052	0.002
Cropland [3]	1.86**	0.106**	<0.001 NS
Hartford, Conn.	6.42	0.156	0.067
Cropland [3]	2.84 NS	0.026**	<0.001**
Macon, Ga.	1.57	0.175	0.012
Cropland	1.12*	0.172 NS	0.003 NS
Newport News, Va.	1.22	0.049	0.008
Cropland [4]	2.08 NS	0.017 NS	<0.001 NS

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

[1] Cropland data from National Soils Monitoring Program, 1971, U.S. Environmental Protection Agency, unless otherwise indicated. Data based on t-tests of the transformed variate log (X + 0.01), U.S. Environmental Protection Agency.
[2] Mid-Atlantic States: Delaware, Maryland, New Jersey.
[3] New England States: Connecticut, Maine, Massachusetts, New Hampshire, Rhode Island, and Vermont.
[4] Virginia and West Virginia.

Frequencies of detection and levels of ΣDDT were generally higher in urban portions than in suburban portions of the SMSAs, and levels were higher in lawn sites than in waste sites. The results confirm the trend first identified by Wiersma et al. (*7*) and also demonstrated by Carey et al. (*1*).

Table 5 provides a comparison between urban and agricultural soil concentrations for arsenic, ΣDDT, and chlordane. A t-test based on the transformed variate log (X + 0.01) was used to compare mean residue concentrations between the two land use categories. For arsenic and ΣDDT, significant differences in the geometric means were detected in three of five cities; for chlordane, significant differences were detected in only two of five cities. Generally, urban areas had higher levels of pesticides than did nearby agricultural areas, except in southern cities where results varied. The contradictory results in southern cities are probably due to the traditionally heavy use of pesticides in agricultural areas of the South, as suggested previously by Carey et al. (*1*).

In summary, soils of the five metropolitan areas sampled in 1971 generally exhibited heavy concentrations of organochlorine pesticides. These results coincide with similar urban soil sampling efforts (*1, 7*). In the metropolitan areas, samples from the urban, or core city, locations generally had higher pesticide levels than did samples from the suburban locations. Finally, pesticide residue levels were generally higher in soils of metropolitan areas than in nearby agricultural soils.

Acknowledgments

The authors are especially grateful to the staff of the Pesticides Monitoring Laboratory, Bay St. Louis, who received, processed, and analyzed the samples, and in particular to Jerry Gardner, Milas Blaylock, Larry Oloresisimo, and Dan Cook. Thanks are also due to the inspectors of the U.S. Department of Agriculture Animal and Plant Health Inspection Service who collected the samples.

LITERATURE CITED

(*1*) *Carey, A. E., G. B. Wiersma, and H. Tai. 1976.* Pesticide residues in urban soils from 14 United States cities, 1970. Pestic. Monit. J. 10(2):54–60.

(*2*) *Fahey, J. E., J. W. Butcher, and R. T. Murphy. 1965.* Chlorinated hydrocarbon insecticide residues in soils of urban areas, Battle Creek, Michigan. J. Econ. Entomol. 58(3):1026–1027.

(*3*) *Goodman, A. T., and T. M. Robert. 1971.* Plants and soils as indicators of metals in the air. Nature 231 (5301):287.

(*4*) *Keil, J. E., J. F. Winkler, R. L. Petsch, and R. H. Gadsden. 1969.* A pesticide use survey of urban households. Agric. Chem. 24(8):10–12.

(*5*) *U.S. Department of Commerce, Bureau of the Census. 1967.* County and City Data Book, 1967. U.S. Government Printing Office, Washington, D.C. 673 pages.

(*6*) *U.S. Environmental Protection Agency. 1972.* The use of pesticides in suburban homes and gardens and their impact on the aquatic environment. Office of Water Programs, EPA, Washington, D.C. 487 pages.

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

Monitoring Pesticides in Agricultural and Urban Soils of the United States [1]

Ann E. Carey [2]

ABSTRACT

Organochlorine pesticides were monitored annually in the major agricultural areas of the United States from 1968 to 1973. Results show that agricultural soils are widely contaminated with low levels of organochlorine residues. Residue concentrations are decreasing as applications of the compounds decrease. Annual monitoring of urban areas since 1969 has demonstrated that urban soils generally have higher pesticide residue concentrations than do agricultural soils in the same locations. High concentrations of mercury, cadmium, and lead have also been observed in urban soils.

Introduction

The use of pesticides in agricultural crop production in the United States has increased greatly in the past three decades. Presently, only a small percent of the population is engaged in farming. Yet this percentage not only feeds and clothes most of the United States population, but also exports to other nations. Increased use of pesticides, along with fertilizers, improved seed, new machinery, and intensive cultivation practices have contributed to this accomplishment.

Pesticides have been regulated in the United States since 1949 by the Federal Insecticide, Fungicide and Rodenticide Act (FIFRA), which was administered first by the U.S. Department of Agriculture and, since 1970, by the U.S. Environmental Protection Agency (EPA). This act was significantly revised and strengthened in 1972 and 1975. A recent provision requires EPA to monitor pesticides in components of the ambient environment. This new requirement gives legislative recognition to a cooperative pesticide monitoring effort by government agencies that has operated for several years.

The pesticide monitoring programs were initiated as a result of a recommendation in the 1963 Report of the President's Science Advisory Committee. The report urged that appropriate federal agencies develop a continuing network to monitor residue levels in air, water, soil, man, wildlife, and fish (*1*). In 1964, the U.S. Department of Agriculture began pesticide monitoring studies of agricultural soils and crops. In 1966, the results of the first monitoring studies were thoroughly evaluated, and a national design for monitoring agricultural soils was established (*9*). The design was tested on a pilot scale in 1967 (*10*) and was operated on a wide scale in calendar years 1968, 1969, 1971, 1972, and 1973. In 1970, the program was transferred to the newly created U.S. Environmental Protection Agency.

During 1968–1973 most major agricultural areas of the United States were monitored for pesticide residues (Fig. 1). Sampling was confined to the areas shown in Figure 1 and agricultural soil monitoring ceased after 1973 because of budget limitations.

In 1969, EPA initiated urban soil sampling which it has continued annually since that time. Results of each year's program have been published separately (*2, 3, 7, 11*). Currently 42 cities are sampled periodically in this program (Fig. 2). Approximately 5–10 of the cities are sampled annually, and cities are resampled every 6 years to determine changes in residues.

Sampling Procedures and Chemical Analyses

Agricultural soils are monitored at one 4-hectare site per 16,194 hectares of cropland. At each site, a composite soil sample and a composite crop sample, if available, are collected. Information on the kinds and amounts of pesticides applied to the site is also recorded.

Urban sites are 231 m^2. Composite soil samples are randomly collected at the rate of one site per 2.6 km^2 within the political boundaries of the city and one site per 51.8 km^2 in the surrounding suburbs.

All samples are analyzed for organochlorines and organophosphates by electron-capture gas chromatography (*4–6, 12*). For agricultural soils, additional analyses are performed for atrazine when use histories indicate recent

[1] This paper was presented at the 11th Congress of the International Society of Soil Science, Edmonton, Alberta, Canada, June 19–27, 1978.

[2] Ecological Monitoring Branch, Benefits and Field Studies Division, Office of Pesticide Programs, U.S. Environmental Protection Agency, TS-768, Washington, D.C. 20460.

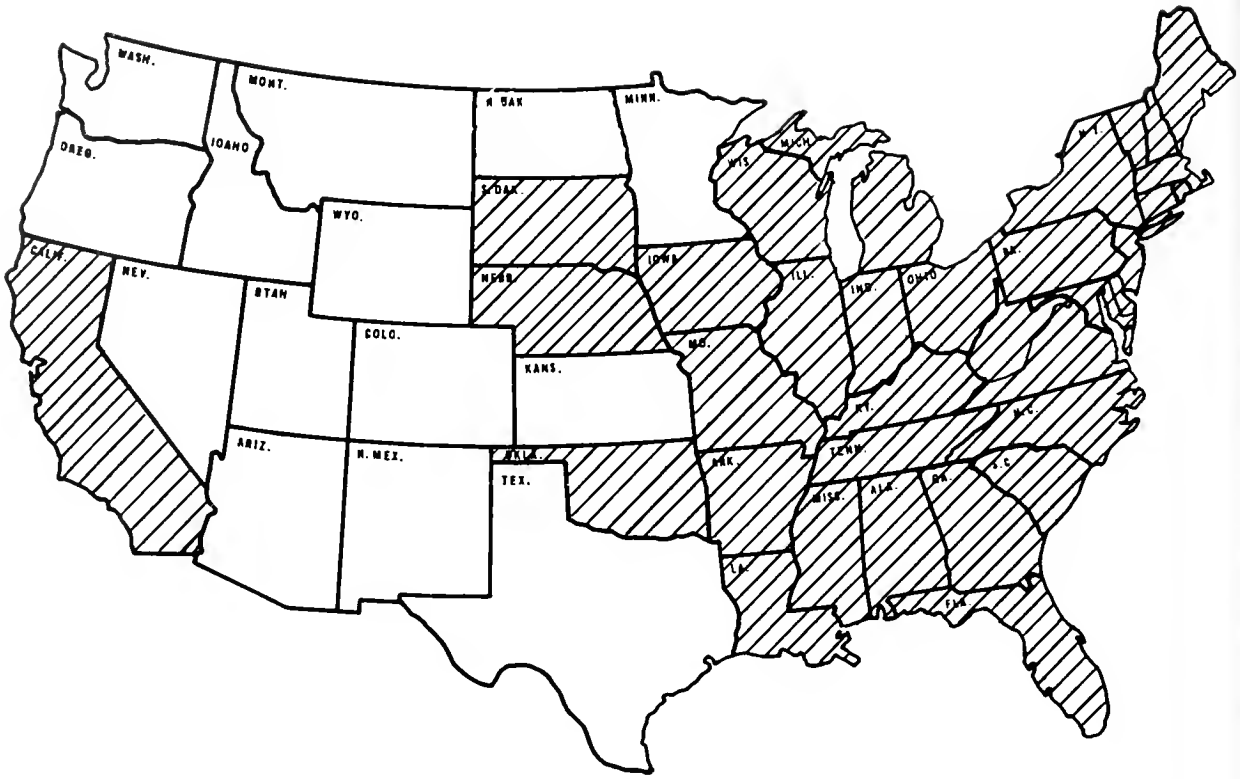


FIGURE 1. *States where agricultural soil and crops were sampled for pesticides during 1968–73—National Soils Monitoring Program, U.S. Environmental Protection Agency*

FIGURE 2. *Metropolitan areas where soils are currrently sampled during the Urban Soils Monitoring Program, U.S. Environmental Protection Agency*

application. Urban samples are also analyzed for mercury, cadmium, and lead (7). All samples for the programs are analyzed at the Pesticides Monitoring Laboratory, Bay St. Louis, Mississippi. The chemicals monitored are listed in Table 1.

TABLE 1. *Compounds monitored in agricultural and urban soils in the United States, National Soils Monitoring Program*

Organochlorines	
Alachlor	Endosulfan II
Aldrin	Endosulfan sulfate
BHC	Endrin
Chlordane	Endrin ketone
o,p'-DDT	Heptachlor
p,p'-DDT	Heptachlor epoxide
o,p'-DDE	Hexachlorobenzene
p,p'-DDE	Isodrin
o,p'-TDE	Lindane (γ-BHC)
p,p'-TDE	Methoxychlor
Dieldrin	PCBs
DCPA	Propachlor
Dicofol	Toxaphene
Endosulfan I	
Other Halogens	
Trifluralin	
Heavy Metals [1]	
Mercury	
Cadmium	
Lead	

[1] Monitored in urban soils only.

Results and Discussion

Representative results for organochlorine pesticides and mercury, cadmium, and lead are presented in Tables 2–7 for both the agricultural and urban soil monitoring programs. Most tables list the percent of positive detections, the arithmetic mean and/or the estimated geometric mean, and the extreme positive values detected. All data are presented as ppm dry weight, and all values have been corrected for percent recovery.

The estimated geometric mean is presented in many of the tables as an alternative to the arithmetic mean as a measure of central tendency of the data. Pesticide residue data frequently contain a large number of zero values, resulting from either the absence of pesticides or their presence at levels below analytical sensitivity. Such data are seldom distributed normally, but often approximate a log-normal distribution. Repeated tests for significant kurtosis and/or skewness resulted in use of the log (X + 0.01) transformation to determine the logarithmic means. The antilogs of these figures minus 0.01 were taken to estimate the geometric mean in the untransformed dimension. The estimated geometric mean was calculated only for those compounds with more than one positive detection.

TABLE 2. *Change in ΣDDT concentrations in United States agricultural soils of 34 states, 1968–73 —National Soils Monitoring Program*

		Residues, ppm Dry Weight			
			95% Confidence Interval		
Year	% of Positive Detections	Estimated Geometric Mean	Lower	Upper	Maximum Detected Value
1968	28.9	0.015	0.013	0.017	78.36
1969	23.8	0.013	0.011	0.015	113.09
1971	23.7	0.013	0.011	0.015	388.16
1972	21.3	0.010	0.008	0.012	29.45
1973	21.5	0.007	0.006	0.008	26.76

Table 2 presents the concentration changes of ΣDDT between 1968 and 1973 in United States agricultural soils. The 95 percent confidence intervals about the geometric mean are included to provide an estimate of the statistical significance of the means. The percent occurrence and the geometric mean level of ΣDDT in agricultural soils declined during the years shown. Widespread use of DDT had probably declined since the late 1960s as more reports documenting its effects were circulated in scientific and popular journals. Most uses of DDT in the United States ceased in 1973. Under the present pesticide law, the compound may still be used when considered necessary, but such uses are thoroughly reviewed by EPA before permission is granted. The confidence intervals for the geometric means for 1968 and 1973 do not overlap, indicating a probable significant difference. Additional *t*-tests on the log-transformed variates have shown that the means are significantly different.

Table 3 presents the concentration changes of aldrin, dieldrin, and toxaphene in agricultural soils sampled between 1968 and 1973. Aldrin gradually declined

TABLE 3. *Concentration changes in aldrin, dieldrin, and toxaphene in United States agricultural soils of 34 states, 1968–73—National Soils Monitoring Program*

	Residues, ppm Dry Weight					
	Aldrin		Dieldrin		Toxaphene	
Year	Geometric Mean	% Occurrence	Geometric Mean	% Occurrence	Geometric Mean	% Occurrence
1968	0.003	13.4	0.009	32.0	0.003	4.8
1969	0.003	14.2	0.010	32.3	0.001	2.0
1971	0.002	10.2	0.010	28.8	0.005	6.6
1972	0.002	9.4	0.009	28.1	0.004	5.4
1973	0.001	3.8	0.007	25.7	0.002	2.7

throughout the entire period. Dieldrin, its primary oxidation product, peaked about 1969, and then started to decline. Most agricultural uses of aldrin in the United States were cancelled in 1975. Toxaphene is still used today, but action is being considered to restrict or stop its use (*8*).

Table 4 presents a comparison of ΣDDT and chlordane concentrations in urban and agricultural soils sampled in 1973. To date, monitoring has shown that soils in urban areas are more heavily contaminated with the pesticides than are agricultural soils in the same locality. Only in the South, where DDT was used heavily in cotton cultivation, do the agricultural ΣDDT concentrations exceed urban concentrations.

Tables 5, 6, and 7, respectively, present concentrations of lead, cadmium, and mercury in soils from the urban and suburban portions of five metropolitan areas sampled in 1973. In general, concentrations observed for all three elements were much greater than the average background concentrations. The sources of such contamination are generally considered to be industrial processes and combustion of fossil fuels.

TABLE 4. *Comparison of ΣDDT and chlordane concentrations in United States urban and agricultural soils, 1973—National Soils Monitoring Program*

	Residues, ppm Dry Weight			
	ΣDDT		Chlordane	
Sample	% Occurrence	Geometric Mean	% Occurrence	Geometric Mean
Pittsfield, Mass.				
Urban	55.6	0.030	11.1	0.005
Agricultural	26.3	0.015	5.3	0.001
Washington, D.C.				
Urban	59.1	0.069	33.3	0.020
Agricultural	20.0	0.006	ND	—
Greenville, S.C.				
Urban	61.6	0.026	9.3	0.004
Agricultural	75.0	0.087	ND	—
Tacoma, Wash.				
Urban	34.7	0.015	14.7	0.009
Agricultural	30.2	0.010	ND	—

NOTE: ND = not detected.

TABLE 5. *Lead concentrations in urban and suburban soils of five United States cities, 1973*

	Residues, ppm Dry Weight			
			Range of Detected Values	
Sample	% of Positive Detections	Estimated Geometric Mean	Minimum	Maximum
Evansville, Ind.				
Urban	100.0	47.1	8.3	407.0
Suburban	100.0	16.1	6.3	733.0
Greenville, S.C.				
Urban	100.0	41.6	17.2	237.0
Suburban	100.0	15.9	5.0	172.1
Pittsfield, Mass.				
Urban	100.0	56.4	8.3	2136.4
Suburban	100.0	27.0	9.7	102.3
Tacoma, Wash.				
Urban	100.0	156.6	6.3	3141.4
Suburban	98.0	10.6	3.8	45.2
Washington, D.C.				
Urban	100.0	203.2	8.5	2310.0
Suburban	100.0	31.6	3.3	1840.0

TABLE 6. *Cadmium concentrations in urban and suburban soils of five United States cities, 1973*

	Residues, ppm Dry Weight			
			Range of Detected Values	
Sample	% of Positive Detections	Estimated Geometric Mean	Minimum	Maximum
Evansville, Ind.				
Urban	56.0	0.086	0.10	2.60
Suburban	28.0	0.017	0.11	1.41
Greenville, S.C.				
Urban	33.0	0.026	0.11	1.00
Suburban	3.0	0.001	0.22	0.22
Pittsfield, Mass.				
Urban	50.0	0.049	0.11	2.08
Suburban	40.0	0.029	0.11	0.75
Tacoma, Wash.				
Urban	87.0	0.378	0.13	18.00
Suburban	27.0	0.013	0.07	0.60
Washington, D.C.				
Urban	79.0	0.233	0.14	0.95
Suburban	25.0	0.010	0.14	0.83

TABLE 7. *Mercury concentrations in urban and suburban soils of five United States cities, 1973*

	Residues, ppm Dry Weight			
			Range of Detected Values	
Sample	% of Positive Detections	Estimated Geometric Mean	Minimum	Maximum
Evansville, Ind.				
Urban	100.0	0.156	0.04	3.55
Suburban	100.0	0.083	0.04	0.25
Greenville, S.C.				
Urban	100.0	0.121	0.06	1.19
Suburban	100.0	0.094	0.05	0.27
Pittsfield, Mass.				
Urban	100.0	0.249	0.11	2.51
Suburban	100.0	0.154	0.07	0.27
Tacoma, Wash.				
Urban	100.0	0.420	0.08	7.90
Suburban	100.0	0.172	0.10	0.59
Washington, D.C.				
Urban	100.0	0.246	0.07	7.81
Suburban	100.0	0.133	0.03	1.12

Conclusions

Monitoring of agricultural soils in the United States has shown that the soils are widely contaminated with low levels of the organochlorine pesticides. Residue concentrations are decreasing as applications of certain compounds decrease. Monitoring of urban areas has demonstrated that urban soils generally have higher pesticide residue concentrations than do agricultural soils in the same locations. High concentrations of mercury, cadmium, and lead have also been observed in urban soils.

Acknowledgments

The author gratefully acknowledges the work of Han Tai and all other employees of the EPA Pesticides Monitoring Laboratory, Bay St. Louis, Mississippi, for their chemical analyses of the soil samples.

LITERATURE CITED

(1) *Bennett, I. L. 1967.* Foreword. Pestic. Monit. J. 1(1).

(2) *Carey, A. E., G. B. Wiersma, and H. Tai. 1976.* Pesticide residues in urban soils from 14 U.S. cities, 1970. Pestic. Monit. J. 10(2):54–60.

(3) *Carey, A. E., P. Douglas, H. Hai, W. G. Mitchell, and G. B. Wiersma. 1979.* Pesticide residue concentrations in soils of five United States cities, 1971. Pestic. Monit. J. 13(1):17–22.

(4) *Carey, A. E., J. A. Gowen, H. Tai, W. G. Mitchell, and G. B. Wiersma. 1978.* Pesticide residue levels in soils and crops, 1971—National Soils Monitoring Program (III). Pestic. Monit. J. 12(3):117–136.

(5) *Carey, A. E., J. A. Gowen, H. Tai, W. G. Mitchell, and G. B. Wiersma. 1979.* Pesticide residue levels in soils and crops, 1972—National Soils Monitoring Program (IV). Pestic. Monit. J. 12(4):209–229.

(6) *Crockett, A. B., G. B. Wiersma, H. Tai, W. G. Mitchell, P. F. Sand, and A. E. Carey. 1974.* Pesticide residue levels in soils and crops, FY–1970—National Soils Monitoring Program (II). Pestic. Monit. J. 8(2):69–97.

(7) *Gowen, J. A., A. E. Carey, T. J. Forehand, H. Tai, and G. B. Wiersma. 1979.* Heavy metal concentrations in soils of five U.S. cities in 1972. J. Environ. Qual.

(8) Rebuttable Presumption Against Registration and Continued Registration of Pesticide Products Containing Toxaphene (OPP 3000/13), 42 Fed. Reg. 26860, May 25, 1977.

(9) *Wiersma, G. B., P. F. Sand, and E. L. Cox. 1971.* A sampling design to determine pesticide residue levels in soils of the conterminous United States. Pestic. Monit. J. 5(1):63–66.

(10) *Wiersma, G. B., P. F. Sand, and R. L. Schutzmann. 1971.* National Soils Monitoring Program—six states, 1967. Pestic. Monit. J. 5(2):223–227.

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

(12) *Wiersma, G. B., H. Tai, and P. F. Sand. 1972.* Pesticide residue levels in soil, FY 1969—National Soils Monitoring Program. Pestic. Monit. J. 6(3):194–228.

GENERAL

Organochlorine Residues in Fish, Water, and Sediment of American Falls Reservoir, Idaho, 1974[1]

James C. Kent [2] and Donald W. Johnson [3]

ABSTRACT

Organochlorine residues of TDE, DDE, and PCBs as high as 1.96, 2.79, and 28.74 μg/kg, respectively, have been found in sediments of American Falls Reservoir, Idaho. Residues of TDE, DDE, and dieldrin in the flesh of sport fish were as high as 52.3, 67.2, and 160.4 μg/kg, respectively. Maximum organochlorine residue levels found in sucker taken in the commercial fishery were 1.1 mg PCBs/kg, 781.7 μg TDE/kg, and 82.1 μg DDE/kg.

Introduction

American Falls Reservoir is located on the Snake River in Southeastern Idaho downstream from Idaho Falls and Pocatello, and is an important sport fishery for area residents. Water quality continues to be a problem in the reservoir. In 1970, the Idaho Department of Health reported that mercury concentrations in some reservoir fish exceeded the 0.5 mg/kg standard set by the Food and Drug Administration (FDA), U.S. Department of Health, Education and Welfare. The current FDA action level is 1.0 mg/kg. Officials recommended that sucker, bullhead, and yellow perch caught in the reservoir not be eaten (*29*). The fate of other pollutants, such as organochlorines, in American Falls Reservoir (AFR) and its fish had not been investigated.

The major source of pesticides has probably been contaminated sediment from irrigation and runoff. Adsorption to suspended particulate matter can place these compounds in a finely dispersed, available form which facilitates their transfer to benthic invertebrates and other silt-dwelling organisms and in turn to fish. Invertebrate populations could be affected, and in turn threaten fish populations which feed on the invertebrates (*12*).

[1]Funds provided by a grant from the Office of Water Research and Technology, in cooperation with Idaho Water Resources Research Institute, University of Idaho, Project A-043-IDA.
[2]Biology Department, Idaho State University, Pocatello, Idaho 83201.
[3]Hancock Biological Station, Murray State University, Murray, Ky. 42071.

PCBs have become ubiquitous in world ecosystems in quantities similar to those of DDT (*4*). They also may enter the aquatic environment as do organochlorine pesticides. Silt, laden with organochlorine residues, may be carried by stream flow until it is deposited in slow-moving waters, such as reservoirs, where the organochlorines can accumulate. Forage fish, such as the Utah sucker, are vulnerable to the contaminated sediment.

Sucker are often found in large numbers in disturbed habitats, such as reservoirs, where an abundance of detrital food sources is available. Fry of the sucker are important to the diet of the AFR game fish. The fry can contribute to biomagnification; higher concentrations of organochlorines accumulate in the fish which consume them.

Health problems resulting from PCBs in the environment have been established. PCBs interfere with reproduction in rodents, fish, fowl, and primates, and they cause intestinal ailments, enlarged livers, gastrointestinal lesions, and abnormalities in the lymphatic system (*20*).

Measuring pesticides in water alone does not determine the safety of fish populations in a given habitat (*13*). Both water and sediment samples should be analyzed (*15*). These values can be combined with other biological information such as fish residue values to give an accurate pesticide pollution index (*14*).

Data reported here were collected from AFR before failure of the Teton Dam in 1976. The resultant flood waters carried large containers of pesticides and possibly spills of PCBs into the Snake River above the reservoir. Information gathered prior to the flood may provide important comparative values to help evaluate flood impact.

The objectives of the present research were to deter-

mine the levels of organochlorines in fish, water, and sediment of American Falls Reservoir; to compare the levels with standards established to protect the aquatic biota and public health; and to determine the distribution of the pollutants in the reservoir.

Methods and Materials

Water and sediment samples were collected from four stations (Fig. 1); fish were collected throughout the reservoir. Water samples were collected with a Van Doren water bottle from the mud-water interface and were placed in 1-gallon glass jars which were sealed with aluminum foil-lined lids. Sediment samples were collected with an Ekman dredge to a depth of 15 cm and were placed in 1-quart glass jars which were sealed with aluminum foil. Water and sediment samples were kept frozen for 3 months until analyses were performed.

Fish collected for residue analysis included Utah chub (*Gilia atraria*), yellow perch (*Perca flavescens*), black crappie (*Pomoxis nigromaculatus*), black bullhead (*Ictalurus melas*), and Utah sucker (*Catostomus ardens*), a forage fish. They were collected with otter trawl, gill nets, seine, and an electrofishing unit mounted on a 19-ft work boat. Whole fish were frozen except for large sucker, from which sections of epaxial muscle were taken just anterior to the dorsal fin. Samples were wrapped in aluminum foil and frozen.

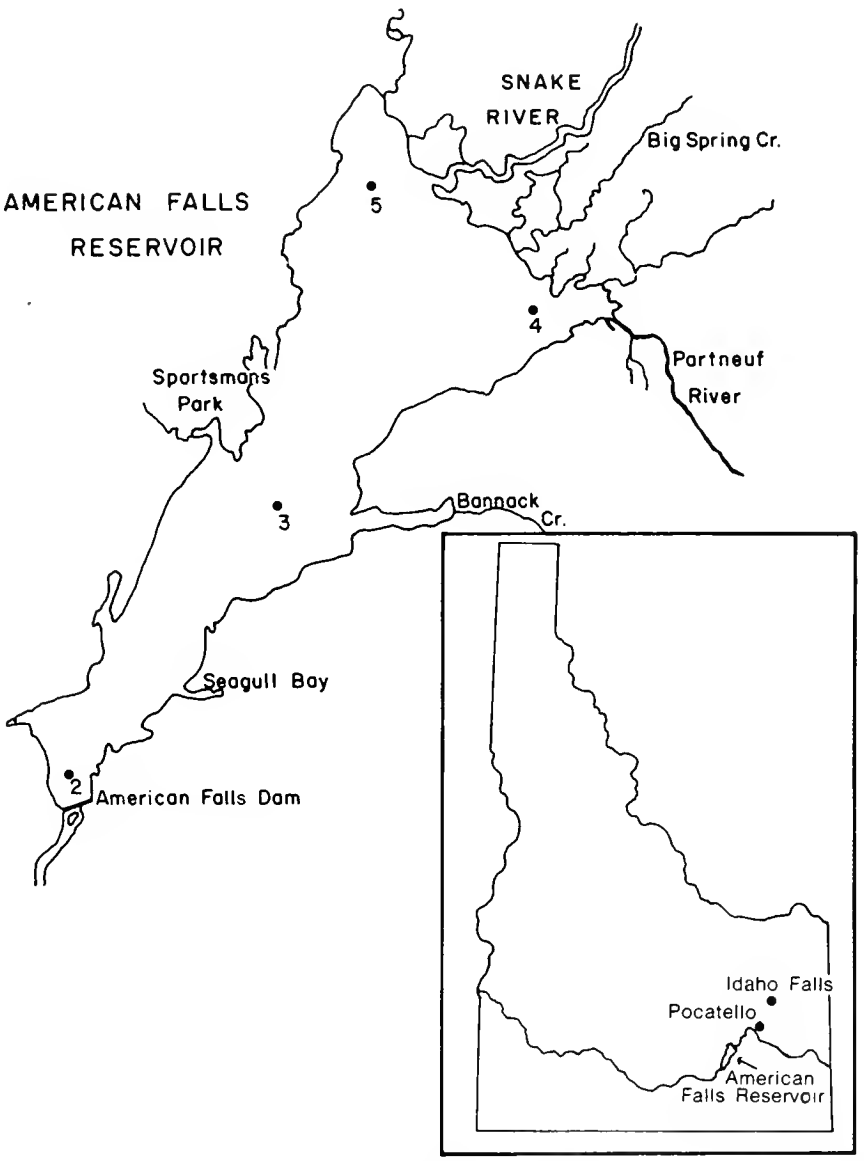


FIGURE 1. *American Falls Reservoir, Idaho, and stations sampled for organochlorine residues, 1974*

TABLE 1. *DDE, TDE, dieldrin, and PCB residues in flesh of fish over 2 years old, American Falls Reservoir, Idaho, 1974*

Species	Sample Size	Residues, µg/kg Wet Weight			
		DDE	TDE	Dieldrin	PCBs
Catostomus ardens	14	28.4±6.8[1] (1.1–82.1)	187.4±68.6 (13.9–781.7)	ND	671.7±89.0 (0–1144)
Perca flavescens	10	14.7±7.8 (2.3–28.6)	5.7±3.6 (1.2–13.4)	34.4±3.2 (0–160.4)	ND
Ictalurus melas	10	9.5±2.1 (1.0–22.6)	5.1±1.4 (0.9–14.0)	11.0±6.6 (0–48.4)	ND
Pomoxis nigromaculatus	20	20.7±4.0 (3.0–67.2)	14.0±3.1 (2.0–52.3)	ND	ND

NOTE: ND=not detected.
[1]Mean ± standard error (range).

Pesticides were separated as described by Hesselberg and Johnson (*11*). PCBs were separated from pesticides according to the method described in the *Manual of Analytical Methods* (*28*). Sulfur interference in sediment extracts was averted by adding copper.

Analyses were performed on a Hewlett-Packard, Series 7400, gas chromatograph (GC) with an electron-capture detector. Instrument parameters and operating conditions were as follows:

Column:	6-ft glass, 8 mm OD, 4 mm ID, packed with 100–120-mesh Supelcon AW-DMCS coated with a mixture of 1.5 percent SP-2250/1.95 percent SP-2401	
Temperatures, °C:	column	200
	detector	210
	injector	220
Carrier gas:	nitrogen flowing at 25 ml/minute	
Volume injected:	approximately 5 µl extract	

Each sample was analyzed for endrin, aldrin, dieldrin, hepatachlor, heptachlor epoxide, lindane, DDT, DDE, TDE, and PCBs. Compounds were quantified against an internal standard. Recovery was 85 percent, but values were not corrected for percent recovery. Quantitative and qualitative analyses of PCBs were performed by matching unknown peaks on the chromatogram to the nearest commercial preparation and by measuring the areas of four corresponding peaks with an electronic integrator (*3*). Linear regression was used in the analysis of data (*25*).

Sensitivity levels, in µg/kg, were as follows: DDT 25, DDE 5, TDE 5, endrin 50, dieldrin 2, heptachlor 2, and PCBs 2. Results were confirmed by comparison of relative retention times and by use of a dual column injected with known standards.

Results and Discussion

None of the water samples contained measurable quantities of organochlorines. This was expected because of the low solubilities of the compounds: 3.4 µg DDT/liter (*7*), 12.5 µg dieldrin/liter (*16*), and 100–1000 µg PCBs/liter (*21*).

DDE and TDE were found in all fish and sediment samples. Dieldrin was found in only two fish species, and PCBs were present in only one species. PCBs were also detected in the sediment (Tables 1, 2).

Sample areas 3, 4, and 5 had a larger mean concentration of DDE than of TDE. These areas are exposed to more turbulence, and anaerobic conditions do not develop; the reverse is true in area 2. EPA in 1973 found a similar distribution in area 2, but did not sample areas 3, 4, and 5 (personal communication). DDT and benzene hexachloride (BHC) degrade rapidly in anaerobic sediments (*6*, *19*), probably through reductive dechlorination by anaerobic bacteria (*6*). Consequently, bacteria in reservoirs are important in the degradation and removal of certain pesticides from the aquatic ecosystem. PCBs were not so ubiquitous as TDE and DDE in reservoir sediments, although two of the four areas sampled did contain a mixture of Aroclor 1248 and Aroclor 1254.

Quantities of DDT metabolites found in the present study in flesh of sucker from AFR were similar to those found in whole body samples of Ontario sucker (*5*). Dieldrin levels found in the muscle tissue of yellow perch from AFR were equal to those found in (whole body) samples of yellow perch taken from Lake Huron (*23*) and exceeded the 0.001–0.015 mg/kg levels found in yellow perch taken from lakes and streams in Ontario, Canada (*5*). Average sediment residues of DDE, TDE, and dieldrin in Ontario waters were usually much

TABLE 2. *TDE, DDE, and PCB residues in sediment of American Falls Reservoir, Idaho, 1974*

Area	Sample Size	Residues, µg/kg Wet Weight		
		TDE	DDE	PCBs
2	3	1.55[1] (1.42–1.79)	1.46 (1.18–1.73)	22.65[2]
3	3	1.04 (0.79–1.31)	2.13 (1.69–2.53)	ND
4	3	1.64 (0.53–3.60)	2.18 (1.09–3.80)	ND
5	3	1.68 (0.81–1.96)	2.21 (0.45–2.79)	28.74

NOTE: ND = not detected.
[1]Mean (range).
[2]Detected in a single sample.

higher than those found in AFR, yet sucker taken from AFR contained levels of DDE and TDE equal to or greater than those found in sucker from Ontario waters. There appears to be no correlation between sediment residue and bioconcentration in fish. Fish from McNary Refuge, Washington, contained 0.7–6.4 mg DDT and TDE/kg; 0.1–0.4 mg DDT and TDE/kg was found in associated sediments (*15*). At Deer Flat, Idaho, sediments contained 68.0–94.0 mg TDE/kg, and fish contained a maximum level of 0.2 mg TDE/kg (*15*). In a third reservoir, Tuttle Creek, Kansas, no DDT, DDE, TDE, or dieldrin was found in sediments, but all were present in fish at maximum levels of 0.17 mg DDT and dieldrin/kg (*17*). It is necessary to analyze several components of an aquatic ecosystem to establish an informative index of the pollution level.

The quantity and type of organochlorines varied considerably among species (Table 1). Dieldrin residues were detected in perch, but not in black crappie. The two species have similar diets, although mature yellow perch are more capable of bottom feeding (*22*). Consequently, perch may be more readily exposed to contaminated sediments than are black crappie. However, dieldrin was not present in sediment from the areas sampled (Table 2). Sediment analysis by the U.S. Environmental Protection Agency (EPA) in 1973 demonstrated the presence of dieldrin in one of the six areas sampled (personal communication). Presumably, exposure of fish to the contaminants depends on the areas which they inhabit and/or behavioral differences between species.

Utah sucker contained the highest concentration of organochlorines (Table 1). Constant contact of the detritus-feeding sucker with the sediment allows continuous exposure to the pesticides. This was the only species which contained PCBs, and the compound was not found in sucker less than 2 years old, possibly because the younger fish inhabit water near shore and may not be exposed to PCBs. Initial sampling indicates that PCBs are not ubiquitous in the sediments; therefore, absence of PCBs in the younger sucker may result simply from lack of exposure.

Suckers under 2 years had a greater concentration of DDE than TDE; older members of the species had a greater concentration of TDE than DDE (Table 3). This may result from metabolic changes associated with sexual maturation. Steroidogenesis may be particularly important in this metabolism (*13*). DDT metabolism has been increased by injecting rats with steroid hormones (*24*). The steroids induce the synthesis of nonspecific hepatic microsomal oxidases which increase the metabolism of DDT. The variation may also depend on the degree of exposure of the two age classes to different concentrations of DDE and TDE in the sediments. Behavioral and physiological parameters as well as availability could contribute to the residue differences observed in the fish.

Organochlorine residue levels in AFR fish were similar to residues found in fish taken from lakes and rivers used as sampling stations in the National Pesticide Monitoring Program (NPMP) conducted by EPA; however, NPMP values were calculated from whole-fish samples (*10*). American Falls Reservoir values are based on analyses of edible tissue only. The differences between values obtained for whole fish and edible tissue can be seen by comparing Tables 1 and 4. In all species except sucker and Utah chub, the concentration of pesticides in the whole fish was greater than concentrations in edible tissue. Fish used in determining whole-fish residues were younger and much smaller (1–10 g). Weights of fish analyzed for organochlorines in edible tissues were as follows: 21–2112 g, sucker; 196–600 g, black bullhead; 60–385 g, yellow perch; and 260–690 g, black crappie. Whole body residues in larger fish in the reservoir probably would be much higher than indicated by edible tissue values. The whole-fish samples analyzed indicate that residues in AFR fish exceed those reported by the NPMP. Information concerning whole-fish concentrations is most important in evaluating pesticide exposure of fish-eating birds, possible effects on the survival and maintenance of predatory game fish in the reservoir, and the exposure of animals fed rations composed of commercially caught reservoir fish. The human health threat is best evaluated by determining flesh residues which have been emphasized in the present study.

The continuance of a sport fishery in the reservoir depends on the reproductive success of all reservoir fish

TABLE 3. *DDE, TDE, and PCB residues in flesh of* Catostomus ardens *by age group, American Falls Reservoir, Idaho, 1974*

Age, Years	Sample Size	Residues, µg/kg (ppb) Wet Weight		
		DDE	TDE	PCBs
2	6	5.4±1.2 [1] (1.5–8.0)	3.0±1.1 (0–7.8)	ND
2–3	6	12.2±2.9 (1.1–19.3)	43.0±7.7 (13.9–71.4)	570±156 (0–1029)
3	8	40.5±9.8 (3.3–82.1)	295.6±106.5 (23.4–781.7)	748±104 (179–1144)

NOTE: ND = Not detected.
[1]Mean ± standard error (range).

TABLE 4. *DDE and TDE residues in whole fish samples from American Falls Reservoir, Idaho, 1974*

Species	Sample Size	Residues, µg/kg Wet Weight	
		DDE	TDE
Ictalurus melas	39	88.9[1]±11.6	127.0±26.7
Catostomus ardens	81	68.7±9.8	51.6±5.9
Pomoxis nigromaculatus	18	75.0±4.1	37.2±3.6
Perca flavescens	30	50.7±2.6	42.9±3.2
Gilia atraria	11	51.0±5.9	29.6±2.8

[1]Mean ± standard error.

populations. Several authors have studied the effects of organochlorine accumulation on the reproductive success, i.e., spermatogenesis, hatchability, time of hatching, survival, growth (*2, 8, 9, 18*). There was a direct correlation ($P < 0.05$) between the weight of the bullhead and total organochlorine residues (Fig. 2). Higher levels of organochlorine residues were found in the heavier fish. The increase in weight was associated with reproductive maturation (Fig. 2).

The Utah sucker is the predominant forage fish in the reservoir and is essential to the diet of many game spe-

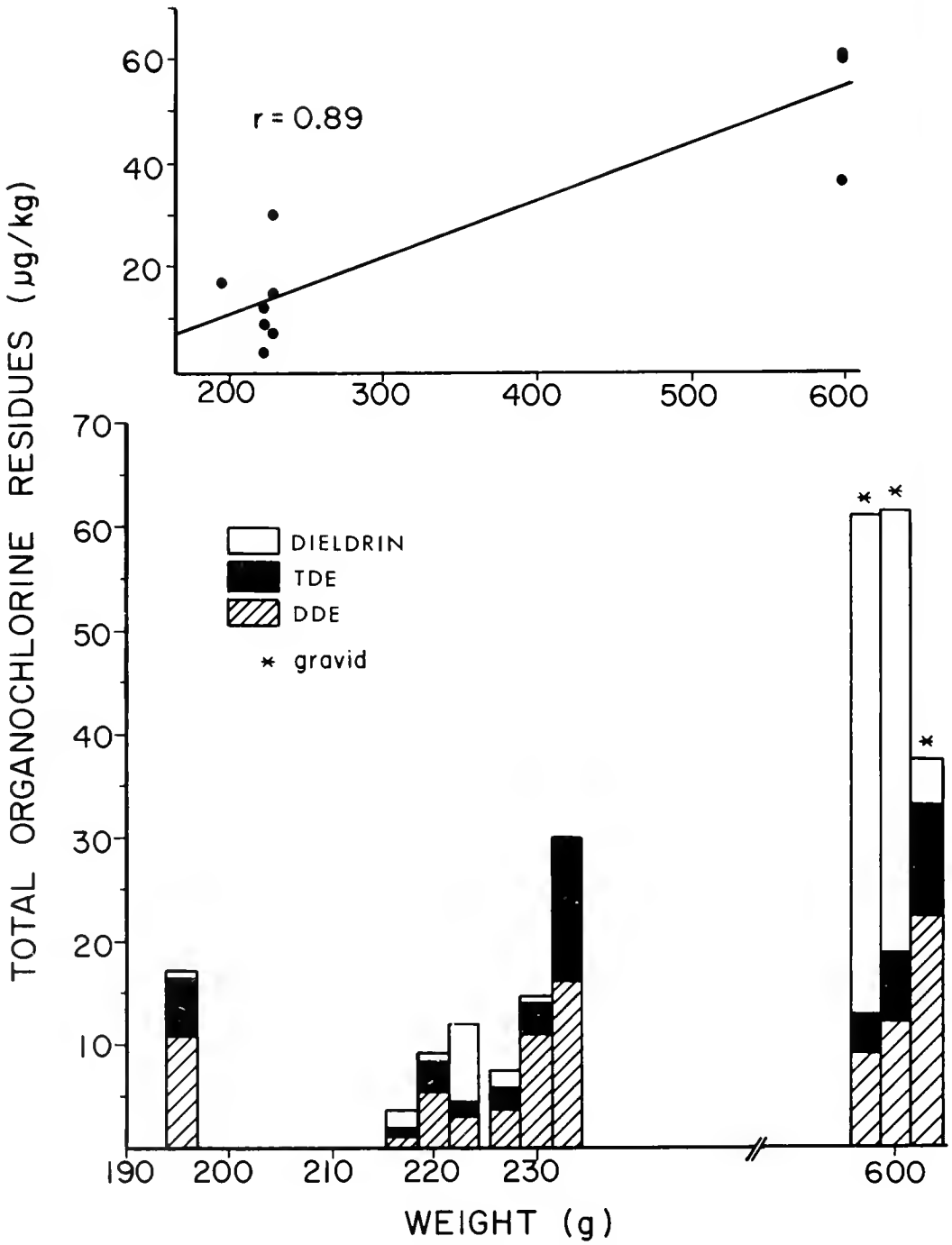


FIGURE 2. *Correlation ($P < 0.05$) between weight of the bullhead and total organochlorine residues*

cies. Reproductive success of the species is important in maintaining a stable community structure. Residues of DDT metabolites and PCBs are higher in the Utah sucker than in other reservoir species. Sucker are among the species most susceptible to organochlorines (*27*). Although no PCBs were found in AFR water, the possible effects of PCBs on reproduction remain.

During the summer of 1975, 75 percent of the sucker collected had fungus-like growths on their heads and sides. Similar symptoms developed when pinfish were exposed to 5 μg Aroclor 1254/liter (*26*). After the pinfish were returned to flowing water, free from PCBs, most died. Much higher concentrations were found in the larger sucker of American Falls Reservoir than in the experimentally exposed pinfish. Although PCBs in the reservoir were not demonstrated to have directly caused the lesions and fungus-like growths on the sucker, it is a possible explanation.

Chlorinated hydrocarbon residues in American Falls Reservoir did not exceed the FDA recommended action levels of 5 mg DDT/kg, 0.3 mg dieldrin/kg, and 5 mg PCBs/kg. In the larger sucker harvested by the commercial fishery, DDT approached 1 mg kg. At this level, EPA previously recommended that precautionary measures should be taken to avoid endangering the health of those who consume the fish (*21*). However, the current FDA and EPA view is that this level does not present a hazard (J. R. Wessel, FDA, personal communication, 1973).

EPA has recommended that PCB concentrations in any sample consumed by any bird or mammal be no greater than 0.5 mg/kg (*21*). The Fish and Wildlife Service, U.S. Department of the Interior, regards the presence of 0.5 mg PCBs/kg in a fish as indicative of pollution (*1*). Average PCB level in sucker from American Falls Reservoir was 0.67 mg/kg; hence consumption of fish from the reservoir may harm some of their predators.

Acknowledgments

The authors thank graduate students Virgil Moore, Don Campbell, and Gale Lewellen for assisting in field collections. Professional advice was provided by Joe Wylie and other members of the Idaho State Health Laboratory; John Heimer, Idaho Fish and Game Department; and Fred Rose and Richard Bowmer, Idaho State University.

LITERATURE CITED

(*1*) *Anonymous. 1976.* PCB's. Audubon 78(1):121.

(*2*) *Burdick, G. E., E. J. Harris, H. J. Dean, T. M. Walker, J. Skea, and D. Colby. 1964.* The accumulation of DDT in lake trout and the effect on reproduction. Trans. Am. Fish. Soc. 93(2):127–136.

(*3*) *Crump-Wiesner, H. J., H. R. Feltz, and M. L. Yates. 1974.* A study of the distribution of polychlorinated biphenyls in the aquatic environment. Pestic. Monit. J. 8(3):157–161.

(*4*) *Dustman, E. G., L. F. Stickle, L. J. Blue, W. L. Reichel, and S. N. Wiemeyer. 1971.* The occurrence and significance of polychlorinated biphenyls in the environment. 36th N. Am. Wildl. Nat. Res. Conf. pp. 118–133. Wildlife Management Institute, Washington, D.C.

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

(*6*) *Guenzi, W. D., and W. E. Beard. 1967.* Movement and persistence of DDT and lindane in soil columns. Soil Sci. Soc. Am. Progr. 31(5):664–674.

(*7*) *Gunther, F. A., W. E. Westlake, and P. S. Jaglan. 1968.* Reported solubilities of 738 pesticide chemicals in water. Residue Rev. 20:1–148.

(*8*) *Halter, M. T., and H. E. Johnson. 1974.* Acute toxicities of a polychlorinated biphenyl (PCB) and DDT alone and in combination to early life stages of coho salmon (*Onchorhynchus kisutch*). J. Fish. Res. Board Can. 31(9):1543–1547.

(*9*) *Hansen, D. J., S. C. Schimmel, and J. Forester. 1974.* Aroclor 1245 in eggs of sheephead minnows: effect on fertilization success and survival of embryos and fry. Proc. 27th Ann. Conf. S.E. Assoc. Game Fish Commissioners, 1973. pp. 420–426.

(*10*) *Henderson, C., A. Inglis, and W. L. Johnson. 1971.* Organochlorine insecticide residues in fish—fall 1969 National Pesticide Monitoring Program. Pestic. Monit. J. 5(1):1–11.

(*11*) *Hesselberg, R. J., and J. L. Johnson. 1972.* Column extraction of pesticides from fish, fish food and mud. Bull. Environ. Contam. Toxicol. 7(2/3):115–119.

(*12*) *Johnson, D. W. 1968.* Pesticides and fishes—a review of selected literature. Trans. Am. Fish Soc. 4(4):398–424.

(*13*) *Johnson, D. W. 1973.* Pesticide residues in fish. Pages 181–212 *in* Environmental Pollution by Pesticides. C. A. Edwards, ed. Plenum Press, New York, N.Y.

(*14*) *Keith, J. O. 1964.* Relation of pesticides to waterfowl mortality at Tule Lake Refuge. Fish Wildlife Serv., Denver Wildlife Res. Center, Ann. Progr. Rept. 14 pp.

(*15*) *Keith, J. O., M. H. Mohn, G. H. Ise, E. L. Flickinger, and C. W. Hall. 1964.* Relation of pesticides to waterfowl mortality at Tule Lake Refuge. (Movement and accumulation of pesticides in soil, water, and aquatic organisms in wetlands habitats). Wildlife Res. Center. Ann. Progr. Rep., Wildlife Res. Work Unit, Denver, Colo.

(*16*) *Khan, H. M., and M. A. Q. Chan.* as cited in Neudorf, S., and M. A. Q. Chan. 1975. Pick-up and metabolism of DDT, dieldrin, and photodieldrin by a freshwater alga (*Ankistrodesmus alamalloides*) and a microcrustacean (*Daphnia pulex*). Bull. Environ. Contam. *Toxicol.* 13(4):443–450.

(*17*) *Klaassen, H. E., and A. M. Kadoum. 1975.* Insecticide residues in the Tuttle Creek Reservoir ecosystem, Kansas—1970–71. Pestic. Monit. J. 9(2):89–93.

(*18*) *Krause, W. K., K. Hamm, and J. Weissmuller. 1975.* The effect of DDT on spermatogenesis of the juvenile rat. Bull. Environ. Contam. Toxicol. 14(2):171–179.

(*19*) *Lotse, G. E., D. A. Graetz, G. Chesters, G. B. Lee, and L. W. Newland. 1968.* Lindane adsorption by lake sediments. Environ. Sci. Technol. 2(5):353–357.

(20) *Maugh, T. H. 1975.* Chemical pollutants: polychlorinated biphenyls still a threat. Science 190(4220):1189.
(21) *National Academy of Sciences, National Academy of Engineering. 1973.* Water Quality Criteria 1972. Washington, D.C. 594 pp.
(22) *Pearse, A., and H. Actenberg. 1918.* Habits of the yellow perch in Wisconsin lakes. Bull. Bur. Fish. 36(1917–1918):318–336.
(23) *Reinert, R. E. 1970.* Pesticide concentrations in Great Lakes fish. Pestic. Monit. J. 3(4):233–240.
(24) *Sanchez, E. 1967.* DDT-induced metabolic changes in the rat liver. Can. J. Biochem. 45(12):1809–1818.
(25) *Sokal, R. R., and F. J. Rohlf. 1969.* Biometry. W. H. Freeman and Company, San Francisco, Calif. 776 pp.
(26) *Stickle, L. F. 1972.* Biological data on PCB's in animals other than birds. Patuxent Wildlife Res. Center, Laurel, Md.
(27) *Surber, E. W. 1948.* Chemical control agents and their effects on fish. Progr. Fish-Cult. 10(3):125–131.
(28) *Thompson, J. F. (ed.) 1972.* Analysis of pesticide residues in human and environmental samples. Primate and Pesticides Effects Laboratory, Environmental Protection Agency, Perrine, Fl. 328 pp.
(29) *U.S. Department of the Interior, Bureau of Reclamation. 1974.* Environmental statement: American Falls dam replacement and power plant. Minidoka Project, Idaho. 63 pp.

Mercury, Arsenic, and Cadmium in Fish, Water, and Sediment of American Falls Reservoir, Idaho, 1974[1]

James C. Kent [2] and Donald W. Johnson [3]

ABSTRACT

Mercury and cadmium were found in fish, water, and sediment of American Falls Reservoir (AFR), Idaho. Mercury and cadmium levels in some fish exceeded human health standards set by the Food and Drug Administration, U.S. Department of Health, Education and Welfare, and the World Health Organization. Analyses performed on the flesh of rainbow trout showed mercury residues of up to 1.20 mg/kg, which were higher than residues previously reported in trout collected in 1970 and 1971 from AFR. Cadmium residue levels were as high as 0.80 mg/kg. Although arsenic was found in reservoir sediment at levels of 1.36–2.40 mg/kg, it was not detected in fish.

Introduction

The pollution of aquatic ecosystems by heavy metals has received greater attention since the discovery of mercury as the cause of Minamata disease in Japan in the 1950s (*39*). Recent studies of fish from Idaho, California, Oregon, and Washington state revealed levels up to 1.9 mg mercury/kg (*11*), which were above the 1.0 mg/kg action level set by the Food and Drug Administration (FDA), U.S. Department of Health, Education and Welfare. Although mercury has received the most attention, other metals, such as arsenic and cadmium, may also contribute to pollution of aquatic ecosystems.

Cadmium—Isolated incidents of cadmium pollution have been reported. In 1970, cadmium was identified as the cause of the Japanese disease itai-itai. It was contracted by eating rice that had been irrigated with river water polluted by runoff from cadmium mines (*13*). A survey of 720 lakes and rivers in the United States revealed that water from only 4 percent of the samples contained more than 10 μg cadmium/liter (*1, 36*). Phosphate fertilizers contain 50–170 mg cadmium/kg (*2*). Waters in phosphate mining and processing areas of Idaho, as well as downstream reservoirs, have been monitored for potential cadmium pollution (*18*).

Arsenic—Arsenic was found in less than 6 percent of the waters sampled in 1962 by the Federal Water Quality Administration. In waters containing colloidal materials, the dissolved arsenic content may be decreased by adsorption. Water samples from Lake Erie contained an average of 38 μg arsenic/liter (*13*). Mean values of 5.6–80.0 μg arsenic/kg were found in 15 species of fish from the Great Lakes (*12*). However, the effect of arsenic accumulation in aquatic organisms is not well documented.

Mercury—Reservoirs act as a trap for silt and suspended particulate matter in runoff. Metals concentrated in the bottom sediments may be available to detrital-feeding organisms. Biomagnification of metals may produce fish unfit for repeated consumption. This has been the case in Idaho. In 1970, the Idaho Health Department collected 160 fish from Idaho waters and analyzed them for mercury. Nineteen percent of the samples exceeded the previous FDA standard of 0.5 mg/kg (*12*). Thirty percent of the fish taken from American Falls Reservoir (AFR), Idaho, had mercury levels exceeding 0.5 mg/kg. Similar mercury concentrations were found in fish taken from other impoundments in the lower and middle Snake River. Further investigations in 1971 revealed that rainbow trout (*Salmo gairdneri*) in AFR had a mean residue level of 0.33 mg mercury/kg and a maximum of 0.91 mg/kg (*12*). Elevated mercury levels were also detected in brown trout (*Salmo trutta*) and cutthroat trout (*Salmo clarki*). Yellow perch (*Perca flavescens*) from the reservoir had a mean concentration of 0.47 mg mercury/kg in muscle tissue; values ranged from 0.09 to 0.84 mg/kg; 57 percent of the yellow perch sampled contained residues at or above 0.5 mg/kg (*12*). A follow-up study in 1972 found a mean of only 0.19 mg mercury/kg in yellow perch (*19*).

The objectives of the present study were to determine mercury, arsenic, and cadmium concentrations in fish,

[1]Funds provided by a grant from the Office of Water Research and Technology, in cooperation with Idaho Water Resources Research Institute, University of Idaho, Project A-043-IDA.
[2]Biology Department, Idaho State University, Pocatello, Idaho 83201.
[3]Hancock Biological Station, Murray State University, Murray, Ky. 42071.

water, and sediment of AFR; to compare the concentrations of heavy metals with action levels established to protect aquatic biota and public health; and to determine the distribution of the pollutants within the fish community.

Study Area

American Falls Reservoir is located on the Snake River in southeastern Idaho downstream from Idaho Falls and Pocatello (Fig. 1). The upper Snake and Portneuf River watersheds are the major sources of reservoir waters; however, springs contribute as much as 22 percent of the reservoir inflow.

The most abundant game fish in the reservoir are yellow perch and hatchery-stocked rainbow trout. Black crappie (*Pomoxis nigromaculatus*) and black bullhead (*Ictalurus melas*) also enter the sport catch. Angling pressure at the reservoir is between 15,000 and 25,000 angler days annually (*15*). The most numerous native species include Utah sucker (*Catostomus ardens*) and chub (*Gilia atraria*). Introduced nongame species include redside shiner (*Richardsonius balteatus*) and carp (*Cyprinus carpio*). Carp and sucker are harvested commercially and sold for human consumption and as a component for fish food.

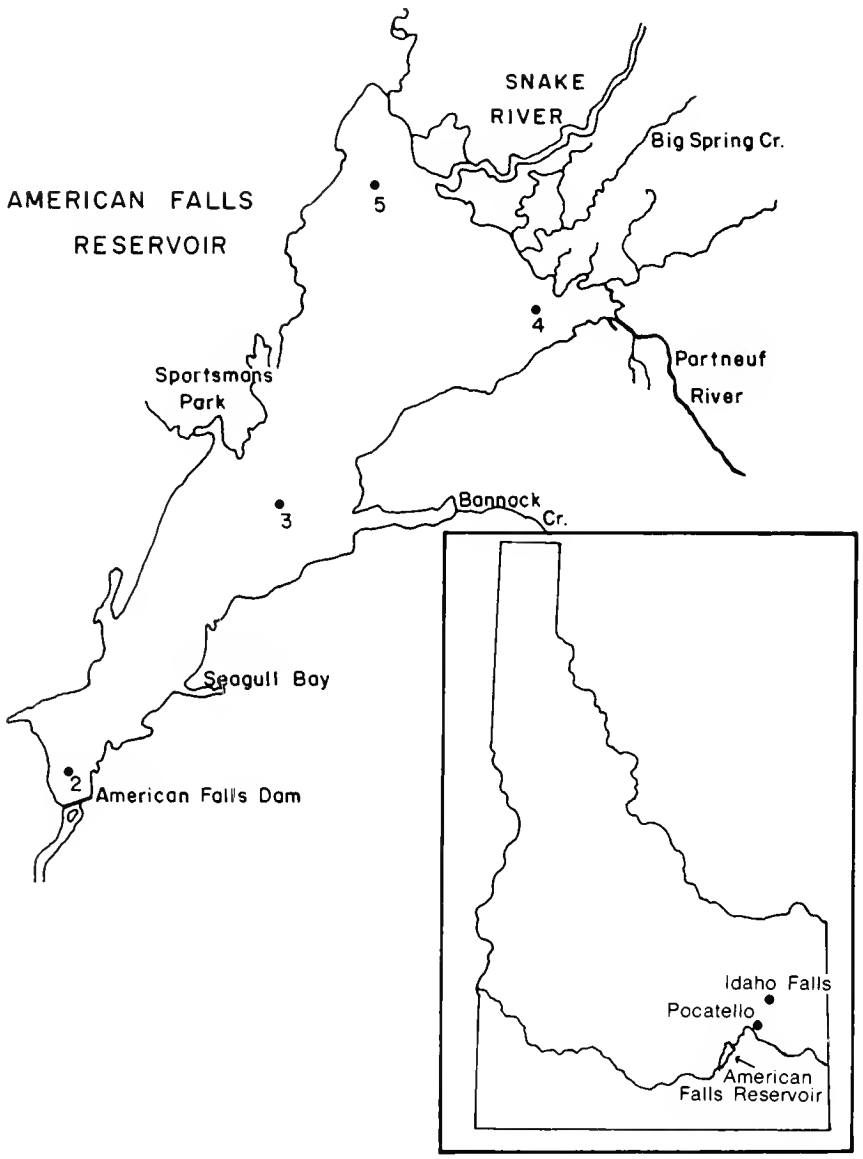


FIGURE 1. *American Falls Reservoir, Idaho, and stations sampled for heavy metal residues, 1974*

Methods of Study

Sediment and water samples were collected from four areas of the reservoir to determine the presence and distribution of cadmium, arsenic, and mercury (Fig. 1). Fish sampling was not restricted to these stations.

Water samples were collected with Van Dorn water bottles at the sediment-water interface and placed in 1-liter plastic containers to which concentrated nitric acid was added (*41*). Sediment samples were collected by Ekman dredge, to a depth of 15 cm, and placed in 1-quart glass jars which were sealed with aluminum foil.

The edible flesh of five species of fish was analyzed, including rainbow trout, yellow perch, black crappie, black bullhead, and the predominant forage fish, Utah sucker.

Analyses were performed on a Varian Model 1200 atomic absorption spectrophotometer equipped with a Model 63 carbon rod atomizer and the Model 64 As/Se/Hg Analysis Kit. A Neff Model 401 recorder was used to record results.

Mercury levels in fish, water, and sediment were determined by vapor generation (*28*). Arsenic was determined by the method of Duncan and Parker (*28*). Cadmium in water was determined by direct application of sample extracts to the carbon rod unit. Fish samples, 0.5 g, were first digested with 10 ml nitric acid (*9*). Sediment samples, 0.5 g, were digested with 10 ml nitric acid and diluted to 20 ml with distilled water. Fish and sediment samples were also analyzed directly on the carbon rod.

Spiked samples yielded 85 percent recoveries but results are reported at the conservative uncorrected values. Sensitivity for mercury, cadmium, and arsenic are, respectively, 2, 5, and 20 μg/kg.

Results and Discussion

The U.S. Environmental Protection Agency (EPA) in 1973 had determined the concentration of arsenic, mercury, and cadmium in AFR water (personal communication). Mercury accumulations in water, sediment, and trout, as well as other game fish, have also been determined (*35*). Each of the reports was based on analysis of only one component or one contaminant in the aquatic ecosystem. The present study on AFR has taken a broader approach (Tables 1–3). Cadmium and mercury were found in water, sediment, and fish. Arsenic was found only in the water and sediment. Examination of only one contaminant may fail to reveal hazards to the aquatic ecosystem. Synergistic or additive effects of multiple contaminants could render lethal so-called safe environmental levels of any single contaminant.

TABLE 1. *Mercury, cadmium, and arsenic residues in water and sediment, American Falls Reservoir, Idaho, 1974*

Location[1]	No. of Analyses	Mean Concentration (Range), Wet Weight		
		Mercury	Cadmium	Arsenic
Area 2				
Water[2]	3	0.72 (0.25–1.52)	9.23 (6.42–11.26)	12.60 (1.50–33.0)
Sediment[3]	3	350 (210–420)	620 (600–640)	2020 (1570–2400)
Area 3				
Water	3	0.70 (0.45–1.20)	14.64 (6.62–24.47)	15.67 (3.0–25.50)
Sediment	3	490 (420–530)	390 (360–640)	1830 (1380–2200)
Area 4				
Water	3	1.02 (0.55–1.78)	6.64 (1.67–10.63)	16.50 (3.50–30.50)
Sediment	3	530 (210–950)	430 (140–720)	1560 (1400–1750)
Area 5				
Water	3	1.02 (0.30–1.47)	5.95 (1.0–9.67)	4.67 (3.0–8.0)
Sediment	3	320 (320–320)	940 (640–1240)	1380 (1360–2040)

NOTE: Water values in excess of the following are considered by EPA to constitute an environmental threat: mercury, 0.2 μg/liter; cadmium, 2.0 μg/liter; arsenic, 50.0 μg/liter.

[1] See Figure 1.
[2] μg/liter.
[3] μg/kg.

TABLE 2. *Mercury residues in fish of American Falls Reservoir, Idaho, 1974*

Species	Sample Size	Residues, mg/kg (ppm), Wet Weight		
		Mean	Std Error	Range
Catostomus ardens	15	0.37	0.06	0.10–0.82
Perca flavescens	10	0.19	0.02	0.11–0.33
Ictalurus melas	10	0.17	0.03	0.10–0.34
Pomoxis nigromaculatus	14	0.37	0.06	0.12–0.80
Salmo gairdneri				
Hatchery stock (<20 cm)	16	0.13	0.02	0.05–0.30
Carry-over (>20 cm)	13	0.60	0.08	0.12–1.20

TABLE 3. *Cadmium residues in fish of American Falls Reservoir, Idaho 1974*

Species	Sample Size	Residues, mg/kg (ppm), Wet Weight		
		Mean	Std Error	Range
Catostomus ardens	16	0.19	0.04	0.08–0.60
Perca flavescens	9	0.23	0.03	0.14–0.44
Ictalurus melas	10	0.15	0.05	0.04–0.30
Pomoxis nigromaculatus	16	0.19	0.03	0.03–0.45
Salmo gairdneri (>20 cm)	12	0.51	0.04	0.32–0.80

Cadmium—Cadmium concentrations of 1.0–24.5 μg/liter were found in AFR water. Most lakes and rivers in the United States contain 10 μg/liter or less. Analysis of 720 lakes and rivers revealed that 41 percent had concentrations of 1–10 μg/liter, 4 percent of the waters contained 12–130 μg/liter (*7*). Values from AFR were similar to those from Foundry Cove, Hudson River, a known recipient of cadmium waste. The concentration in Foundry Cove ranged from 5 to 26 μg/liter (*36*). The National Academy of Sciences considered 3.0 μg/liter a threat to aquatic life (*26*).

Cadmium concentrations in the Illinois River were as follows: water, 0.10–2.0 μg/liter; sediment, 0.2–12.1 mg/kg, with a mean of 2.0 mg/kg; and fish, 0.03 mg/kg (*24*). Hudson River water contained little dissolved cadmium, 3.0–6.0 μg/liter, but the mud contained 162 mg/kg. Water from three Alabama rivers had 6.1, 65, and 90 μg cadmium/liter; however, cadmium was found only at the source and not downstream. Fish from the same rivers contained a maximum of 0.8 mg/kg, compared to 0.2–304 mg/kg found in Hudson River fish (*36*). This confirms the advisability of monitoring sediment concentrations, as well as levels in water. In these cases, no correlation was found between water and sediment concentrations. This was also true for AFR; linear regression analysis of cadmium in water and sediment indicates no correlation at the 0.05 significance level. Cadmium concentration in the AFR sediments was low (Table 1).

Cadmium was not mobilized from sediments as readily as mercury, nor was it concentrated in fish to the same degree (Table 3). The high calcium carbonate content of AFR water may decrease the availability and toxicity of cadmium to fish by forming a cadmium carbonate precipitate in sediments (*30*). Exposure to cadmium may depend on ingestion of contaminated biota or particulate matter. There is no evidence that cadmium is absorbed across the gill epithelia. Zinc values for rainbow trout, Utah sucker, yellow perch, and bullhead taken from AFR have been as high as 12.8, 9.2, 11.4, and 1.05 mg/kg, respectively (*27*). Cadmium appears to accumulate in larger amounts when absorbed with zinc than when it is absorbed alone as indicated by acute toxicity tests with cadmium alone (*8*).

Cadmium concentrations of 0.06–1.4 mg/kg were found in Great Lakes fish (*23*). Black bullhead, sucker, black crappie, and yellow perch from New York waters had mean levels of 27.3, 23.1, 14.7, and 51.0 μg cadmium/kg, respectively (*22*). In the present study and in the New York investigation, no correlation was found between size of fish and level of cadmium concentration. Data indicate that the 150–510 μg/kg values for cadmium in fish from AFR are high.

Daily intake of cadmium from all food sources averages 50 μg/day in the United States (*10*). The FDA has stated that at this level "we may have reached the safe upper limit for cadmium" (*3*). Consumption of fish from AFR would increase daily intake of cadmium in excess of the World Health Organization-suggested maximum intake of 70 μg/day.

Arsenic—Arsenic compounds occur naturally in some waters of the western United States (*25*). In AFR water, arsenic concentrations ranged from 1.5 to 33 μg/liter (Table 1). Similar values have been reported in other areas of the country. Water in Kansas contained 2.6 μg arsenic/liter, although Lake Erie and the St. Lawrence River contained only 0.308 and 0.58 μg/liter, respectively (*13, 29*).

Arsenic is readily adsorbed by colloidal and suspended matter and transported to the sediment (*26*). In AFR, a significant correlation ($P < 0.05$) existed between water turbidity and arsenic concentration. Arsenic in sediment ranged from 1.36 to 2.40 mg/kg.

Accumulation in fish depends on the valence state of arsenic. Fish collected from a lake 21 days after application of arsenic showed no significant increase in arsenic accumulation, although water concentrations reached a maximum of 7.0 mg/liter (*40*). Arsenic was not found in AFR fish.

Mercury—The maximum mercury level found in AFR water was 1.78 μg/liter. The Idaho Health Department found a maximum of 1.8 μg/liter, and Runyan found 1.3 μg/liter (*35*). Mercury concentrations were found in 27 of 73 rivers in the United States at levels of 0.1–1.0 μg/liter (*42*). Groundwaters have contained 0.02–0.07 μg/liter (*5*). Mercury levels in AFR were 70–100 times higher than levels found in Lake Powell (Colorado River) (*31*), although a higher level, 2.1 μg/liter, has been measured in surface waters of Lahontan Reservoir in Nevada (*33*). These values are far higher than the 0.03 μg/liter level presumed to be the mean natural content of uncontaminated water (*6*) and the EPA no-effect criterion of 0.05 μg/liter (*26*).

Mercury exhibits a distribution between water and sediment similar to that of cadmium. Mean mercury concentrations in AFR sediment ranged from 0.32 to 0.53 mg/kg, 300–700 times the concentration found in the water (Table 1). In Lake Powell, 0.03 mg/kg was found in the sediment, but concentrations in water were only 0.01 μg/liter (*31*). Values reported after California investigations ranged from 0.04 to 33.0 mg/kg in sediments (*4*). Methylation of mercury by bacteria in the sediment significantly increases the availability of mercury for absorption across the gills of fish (*34*).

Background levels of mercury in noncontaminated fish are generally less than 0.2 mg/kg (*6*). Mean values of mercury in AFR yellow perch, black bullhead, and hatchery-stocked trout did not exceed this value. Utah sucker, black crappie, and large rainbow trout have mean values greater than 0.2 mg/kg (Table 2). These values approach the previous FDA public health standard of 0.5 mg/kg for fish flesh (*11*). Thirteen percent of the Utah sucker, 21 percent of the black crappie, and 60 percent of the large rainbow trout exceeded this standard. The mean value of mercury for all fish from AFR was 0.30 mg/kg. By contrast, fish from Lake

Powell contained 0.23 mg/kg (*31*); from Ross Barnett Reservoir, Mississippi, 0.05–0.74 mg/kg; and from Lahontan Reservoir, Nevada, 0.20–2.72 mg/kg (*20, 33*). Mercury concentrations in hatchery trout and yellow perch from AFR were similar to those found in 1971 (*35*). However, the mean concentration in black bullhead was only 0.17 mg/kg compared to 0.36 mg/kg found in 1971, and the sucker value was 0.37 mg/kg compared to 0.11 mg/kg found in 1971.

Physical attributes of fish as well as chemical and physical characteristics of aquatic systems may limit, enhance, or modify the uptake and toxicity of heavy metals to fish. Runyan reported no correlation between weight and mercury concentration in rainbow trout from AFR, but a significant correlation was found between length and mercury concentration (*35*). Jarmon found a positive correlation between mercury concentration in muscle and the age and length of yellow perch from American Falls and Western Reservoirs in Idaho (*17*). Other authors have reported no correlation between either weight or length and concentration of mercury (*37, 43*). There was no significant correlation between weight, age, length, or condition factor and mercury concentration for any species analyzed in the present study. Chronic exposure to low levels of mercury may cause fish to acquire similar tissue concentrations regardless of size (*16*). Fish of the same size and species, exposed identically, have shown maximum concentrations up to 10 times the minimum (*14*).

Methylation of mercury by bacteria in sediments is a critical step toward increasing mercury availability to fish. These processes occur more readily under aerobic than anaerobic conditions. The rate of methylation has been directly related to the presence of nutrients such as carbon, phosphate, nitrogen, and other trace elements, presumably because they stimulate the growth of methylating bacteria (*21, 38*).

The amount of soluble inorganic mercury in the water absorbed by fish is also pH dependent. Under alkaline conditions, as in AFR, inorganic mercury is released from the sediment into the water (*38*). Noncomplexed inorganic mercury is, however, not readily absorbed by fish from water with a high pH. Halides, such as fluorides, present in AFR, may form complexes with inorganic mercury and facilitate its absorption by fish. Hydrogen sulfide which develops in the anaerobic bottom waters of the reservoir may be brought to the surface waters when overturn occurs in autumn. This would facilitate exposure and absorption of inorganic mercury at all levels of the water column (*38*). Increased temperature may also increase the uptake of both organic and inorganic mercury (*1, 32*). In rainbow trout, lethal levels of mercury decreased with increased water temperature, increased chloride ion content, or decreased oxygen (*1*). It appears, therefore, that ambient water conditions at the time of exposure are more significant to exposed fish than are age, weight, length, condition factor, or contaminant concentration.

Conclusions

Modification of toxicity by chemical and physical parameters emphasizes the need to redefine safe levels in aquatic environments. Each aquatic system is unique, and safe levels of contaminants should be determined which reflect the characteristics of the system.

Elevated mercury and cadmium levels have been identified in fish, sediment, and water. The levels present exceed those at which protection of aquatic species is recommended by EPA. The source of the pollutants is unidentified as is their potential to measurably degrade the health, growth, and reproductive success of the reservoir fishery.

Acknowledgments

The authors thank Virgil Moore, Don Campbell, and Gale Lewellen for assisting in field collections. Professional advice was provided by Joe Wylie and other members of the State Health Laboratory; John Heimer, Idaho Fish and Game Department; and Fred Rose and Richard Bowmer, Idaho State University.

LITERATURE CITED

(*1*) *Amend, D. F., W. T. Yasutsake, and R. Morgan. 1969.* Some factors influencing susceptibility of rainbow trout to the acute toxicity of an ethyl mercury phosphate formulation (Timsan). Trans. Am. Fish. Soc. 98(3):419–425.

(*2*) *Athanassiadis, Y. C. 1969.* Preliminary air pollution survey of cadmium and its compounds: a literature review. Litton Systems, National Air Pollution Control Administration, Washington, D.C.

(*3*) *Braude, G. L., C. F. Jelinek, and P. Corneliussen. 1975.* FDA's overview of the potential health hazards associated with the land application of municipal wastewater sludges. Proc. 1975 Nat. Conf. Municipal Sludge Management and Disposal—1975, Anaheim, Calif. Office of Research and Development, U.S. Environmental Protection Agency, Washington, D.C. pp. 214–217.

(*4*) *California State Health Department. 1971.* Mercury in the California environment. Environmental Health and Consumer Protection Program, Berkeley, Calif.

(*5*) *Dall'Aglio, M. 1968.* The abundance of mercury in 300 natural water samples from Tuscany and Latium (Central Italy). In Origin and Distribution of the Elements, L. H. Ahrens, ed. Pergamon Press, Oxford, England.

(*6*) *D'Itri, F. M. 1971.* The Environmental Mercury Problem. CRC Press, Cleveland, Ohio. 124 pp.

(*7*) *Durum, W. H., J. D. Hem, and S. G. Heidel. 1971.* Reconnaissance of selected minor elements in the surface waters of the United States, October 1970. Geological Survey Circular 643. U.S. Government Printing Office. Washington, D.C.

(*8*) *Eisler, R., and G. R. Gardner. 1973.* Acute toxicology to an estuarine teleost of mixtures of cadmium, copper, and zinc salts. J. Fish Biol. 5(2):131–142.

(9) *Finch, A. 1974.* Measurements of trace concentrations of metals in fish tissue. Atomic Absorption Application Notes. Varian Techtron Pty. Ltd., Springvale, Australia. 10 pp.

(10) *Friberg, L., M. Piscator, and G. Nordbery. 1971.* Cadmium in the Environment. CRC Press, Cleveland, Ohio. 248 pp.

(11) *Friberg, L., and J. Voslal. 1972.* Mercury in the Environment, CRC Press, Cleveland, Ohio. 215 pp.

(12) *Gebhards, S., J. Cline, F. Shields, and L. Pearson. 1970.* Mercury residue in Idaho fishes—1970. Idaho Fish and Game Department and Department of Health, Boise, Idaho. 13 pp.

(13) *Great Lakes Laboratory. 1971.* Chromium, cadmium, arsenic, selenium, mercury, and aquatic life: a brief literature review. State University College at Buffalo, N.Y. Rept. No. 9.

(14) *Hannerz, L. 1968.* Experimental investigations on the accumulation of mercury in water organisms. Rep. Inst. Freshwater Res. Dorttninghold 48:120–175.

(15) *Heimer, J. T. 1974.* American Falls Reservoir, forebay and Snake River fishery investigations. Idaho Fish and Game Department, Boise, Idaho. 30 pp.

(16) *Huckabee, J. W., C. Feldman, and Y. Talmi. 1974.* Mercury concentrations in fish from the Great Smokey Mountains National Park. Anal. Chim. Acta 70(1): 41–47.

(17) *Jarmon, T. L. 1973.* Mercury accumulation in yellow perch (*Perca flavescens*) correlated with age and growth. MS thesis, Idaho State University, Pocatello, Idaho.

(18) *Johnson, D. W., and J. C. Kent. 1978.* The source of American Falls Reservoir pollutants. Technical Completion Report Project A–043–IDA, OWRT. U.S. Dept. of the Interior, June 1978. 19 pp.

(19) *Kent, J. C. 1976.* Distribution and accumulation of pollutants in American Falls Reservoir. MS thesis, Idaho State University, Pocatello, Idaho.

(20) *Knight, L. A., Jr., and J. Herring. 1972.* Total mercury in largemouth bass (*Micropterus salmoides*) in Ross Barnett Reservoir, Mississippi—1970 and 1971. Pestic. Monit. J. 6(2):103–106.

(21) *Kromer, H. J., and B. Meidhart. 1975.* The behavior of mercury in the system water–fish. Bull. Environ. Contam. Toxicol. 14(6):699–704.

(22) *Lovett, R. J., W. H. Gutenmann, I. S. Pakkala, W. D. Youngs, D. J. Lisk, G. E. Burdick, and E. J. Harris. 1972.* A survey of the total cadmium content of 406 fish from 49 New York State freshwaters. J. Fish. Res. Board Can. 29(9):1283–1290.

(23) *Lucas, H. F., Jr., D. N. Edyington, and P. J. Colby. 1970.* Concentrations of trace elements in Great Lake fishes. J. Fish. Res. Board Can. 27(4):677–684.

(24) *Mathis, B. J., and T. F. Cummings. 1973.* Selected metals in sediments, water, and biota in the Illinois River. J. Water Pollut. Contr Fed. 45(7):1573–1583.

(25) *McKee, J. E., and H. W. Wolf. 1963.* Water Quality Criteria. 2nd ed. California State Water Quality Control Board, Sacramento, Calif. 548 pp.

(26) *National Academy of Sciences, National Academy of Engineering. 1973.* Water Quality Criteria 1972. Washington, D.C. 594 pp.

(27) *Neill, T. D. 1971.* Trace Elements in Idaho Game Animals. U.S. National Reactor Testing Station, Idaho Falls, Idaho. 83 pp.

(28) *Parker, C. R. 1972.* Determination of mercury by the vapor generation technique. Technical Topics. Varian Techtron Pty. Ltd., Springvale, Australia. 3 pp.

(29) *Pattison, E., I. V. Sollins, and E. E. Angio. 1970.* Arsenic and water pollution hazard. Science 170 (3960):870–872.

(30) *Pickering, Q. H., and M. H. Gast. 1972.* Acute and chronic toxicity of cadmium to the fathead minnow (*Pimephales promelas*). J. Fish. Res. Board Can. 29(8):1099–1106.

(31) *Potter, L., D. Kidd, and D. Standford. 1975.* Mercury levels in Lake Powell: biomagnification of mercury in a man-made desert reservoir. Environ. Sci. Technol. 9(1):41–46.

(32) *Reinert, R. E., L. J. Stone, and W. A. Willford. 1974.* Effect of temperature on accumulation of methylmercuric chloride and p,p'-DDT by rainbow trout (*Salmo gairdneri*). J. Fish. Res. Board Can. 31(10): 1649–1652.

(33) *Richins, R. T., and A. C. Risser, Jr. 1975.* Total mercury in water, sediment, and selected aquatic organisms, Carson River, Nevada—1972. Pestic. Monit. J. 9(1):44–54.

(34) *Rucker, R. R., and D. F. Amend. 1969.* Adsorption and retention of organic mercurials by rainbow trout and chinook and sockeye salmon. Progr. Fish-Culturist 31(4):197–201.

(35) *Runyan, K. W. 1972.* Mercury uptake in rainbow trout (*Salmo gairdneri*) in American Falls Reservoir. MS thesis, Idaho State University, Pocatello, Idaho.

(36) *Schroeder, H. A. 1974.* The poisons around us. Indiana University Press, Bloomington, Ind. 144 pp.

(37) *Scott, D. P. 1974.* Mercury concentration of white muscle in relation to age, growth, and condition in four species of fishes from Clay Lake, Ontario. J. Fish. Res. Board Can. 31(11):1723–1729.

(38) *Tsai, S.-C., G. M. Boush, and F. Matsurmara. 1975* Importance of water pH in accumulation of inorganic mercury in fish. Bull. Environ. Contam. Toxicol. 13(2):188–193.

(39) *Turney, W. G. 1971.* Mercury pollution: Michigan's action program. J. Water Pollut. Contr. Fed. 43(7): 1427–1438.

(40) *Ullmann, W. W., R. W. Schaefer, and W. W. Sanderson. 1961.* Arsenic accumulation of fish in lakes treated with sodium arsenite. J. Water Pollut. Contr Fed. 33(4):416–417.

(41) *U.S. Environmental Protection Agency. 1971.* Methods for chemical analysis of water and wastes, 1971 National Environmental Research Center, Analytical Quality Control Laboratory, Cincinnati, Ohio, 312 pp

(42) *Wershaw, R. L. 1970.* Source and behavior of mercury in surface waters in the U.S. Geological survey professional paper. 173:29–31.

(43) *Wobeser, G., N. O. Nielsen, R. H. Dunlop, and F. M Alton. 1970.* Mercury concentration in tissues of fish from the Saskatchewan River. J. Fish. Res. Board Can 27(4):830–834.

CALL FOR PAPERS

Abstracts due November 1, 1979

for conference

Application of Appropriate Technology

to Chemical Dose and Chemical Residue Monitoring

May 28–30, 1980

U.S. Environmental Protection Agency

Office of Research and Development

Washington, D.C.

CONFERENCE TOPICS

Environmental Monitoring Requirements

Types of Chemicals Monitored

Environmental Monitoring Procedures and Techniques

Review of Analysis Costs and Procedures

Sampling Methodology

Epidemiological Considerations

Techniques Designed to Simplify Analytic Procedures

Approaches Designed to Simplify or Decrease Monitoring

Address correspondence to:

Jack P. Keeve, Ph.D.
U.S. Environmental Protection Agency
Office of Research and Development (RD-683)
401 M Street, S.W.
Washington, D.C. 20460
(202) 755-0650

APPENDIX

Chemical Names of Compounds Discussed in This Issue

ALACHLOR	2-Chloro-2′,6′-diethyl-*N*-(methoxymethyl)-acetanilide
ALDRIN	Hexachlorohexahydro-*endo,exo*-dimethanonaphthalene 95% and related compounds 5%
AROCLOR 1016 or 1242	PCB, approximately 42% chlorine
AROCLOR 1248	PCB, approximately 48% chlorine
AROCLOR 1254	PCB, approximately 54% chlorine
BHC (Benzene Hexachloride)	1,2,3,4,5,6-Hexachlorocyclohexane (mixture of isomers)
CHLORDANE	1,2,3,4,5,6,7,8,8-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.
CHLORDENE	4,5,6,7,8,8-Hexachloro-3a,4,7,7a-tetrahydro-4,7-methano-1*H*-indene
DCPA	Dimethyl-2,3,5,6-tetrachloroterephthalate
DDE	Dichlorophenyl dicholoro-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-Chloro-2,2-bis(*p*-chlorophenyl) ethylene
DDT	Main component (*p,p′*-DDT): *o*-Bis(*p*-chlorophenyl) *β,β,β*-trichloroethane. Other isomers are possible and some are present in the commercial product. *o,p′*-DDT: 1,1,1-Trichloro-2-(*o*-chlorophenyl)-2-(*p*-chlorophenyl) ethane
DICOFOL	1,1-Bis(chlorophenyl)-2,2,2-trichloroethanol
DIELDRIN	Not less than 85% of 1,2,3,4,10,10-hexachloro-6,7-epoxy-1,4,4a,5,6,7:8,8a-octahydro-1,4-*endo-exo*-5,8-dimethanonaphthalene
ENDOSULFAN	Hexachlorohexahydromethano-2,4,3-benzodioxathiepin 3-oxide
ENDOSULFAN SULFATE	1,4,5,6,7,7-Hexachloro-5-norbornene-2,3-dimethanol cyclic sulfate
ENDRIN	Hexachloroepoxyoctahydro-*endo-endo*-dimethanonaphthalene
ENDRIN KETONE	1,8,9,10,11,11-Hexachloropentacyclo[6.2.1.$0^{2,7}$.$1^{3,6}$.$0^{5,9}$]dodecan-4-one
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-methanoindene
ISODRIN	Hexachlorohexahydro-*exo,exo*-dimethanonaphthalene
LINDANE	*Gamma* isomer of 1,2,3,4,5,6-hexachlorocyclohexane
METHOXYCHLOR	2,2-Bis(*p*-methoxyphenyl)-1,1,1-trichloroethane 88% and related compounds 12%

(Continued next page)

APPENDIX (*continued*)

MIREX	1,1a,2,2,3,3a,4,5,5,5a,5b,6-Dodecachlorooctahydro-1,3,4-metheno-1*H*-cyclobuta[cd]pentalene
NONACHLOR	1,2,3,4,5,6,7,8-Nonachlor-3a,4,7,7a-tetrahydro-4,7-methanoindan
OVEX	*p*-Chlorophenyl *p*-chlorobenzenesulfonate
OXYCHLORDANE	2,3,4,5,6,6a,7,7-Octachloro-1a,1b,5,5a,6,6a-hexahydro-2,5-methano-2*H*-indeno(1,2-*β*)oxirene
PCBs (Polychlorinated Biphenyls)	Mixtures of chlorinated biphenyl compounds having various percentages of chlorine
PCNs (Polychlorinated Naphthalenes)	Mixtures of chlorinated naphthalenes
PHOTODIELDRIN	3,4,5,6,7-Hexachloro-12-oxahexacyclo[6.5.0.0^{2,10}.0^{3,7}.0^{5,9}.0^{11,13}]tridecane
PHOTOMIREX	1,2,3,4,5,5,6,7,9,10,10-Undecachloropentacyclo[5.3.0.0^{2,6}.0^{3,9}.0^{4,8}]decane
PROPACHLOR	2-Chloro-*N*-isopropylacetanilide
TDE	2,2-Bis(*p*-chlorophenyl)-1,1-dichloroethane (including isomers and dehydrochlorination products)
TOXAPHENE	Chlorinated camphene (67–69% chlorine). Product is a mixture of polychlor bicyclic terpenes with chlorinated camphenes predominating.
TRIFLURALIN	*α,α,α*-Trifluoro-2,6-dinitro-*N,N*-dipropyl *p*-toluidine

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

Articles are grouped under seven headings. Five follow the basic environmental components of the National Pesticide Monitoring Program: Pesticide Residues in People; Pesticide Residues in Water; Pesticide Residues in Soil; Pesticide Residues in Food and Feed; and Pesticide Residues in Fish, Wildlife, and Estuaries. The sixth is a general heading; the seventh encompasses briefs.

Monitoring is defined here as the repeated sampling and analysis of environmental components to obtain reliable estimates of levels of pesticide residues and related compounds in these components and the changes in these levels with time. It can include the recording of residues at a given time and place, or the comparison of residues in different geographic areas. The Journal will publish results of such investigations and data on levels of pesticide residues in all portions of the environment in sufficient detail to permit interpretations and conclusions by author and reader alike. Such investigations should be specifically designed and planned for monitoring purposes. The Journal does not generally publish original research investigations on subjects such as pesticide analytical methods, pesticide metabolism, or field trials (studies in which pesticides are experimentally applied to a plot or field and pesticide residue depletion rates and movement within the treated plot or field are observed).

Authors are responsible for the accuracy and validity of their data and interpretations, including tables, charts, and references. Pesticides ordinarily should be identified by common or generic names approved by national or international scientific societies. Trade names are acceptable for compounds which have no common names. Structural chemical formulas should be used when appropriate. Accuracy, reliability, and limitations of sampling and analytical methods employed must be described thoroughly, indicating procedures and controls used, such as recovery experiments at appropriate levels, confirmatory tests, and application of internal standards and interlaboratory checks. The procedure employed should be described in detail. If reference is made to procedures in another paper, crucial points or modifications should be noted. Sensitivity of the method and limits of detection should be given, particularly when very low levels of pesticide residues are being reported. Specific note should be made regarding correction of data for percent recoveries. Numerical data, plot dimensions, and instrument measurements should be reported in metric units.

PREPARATION OF MANUSCRIPTS

——Prepare manuscripts in accord with the *CBE Style Manual*, third edition, Council of Biological Editors, Committee on Form and Style, American Institute of Biological Sciences, Washington, D.C., and/or the *U.S. Government Printing Office Style Manual*. For further enrichment in language and style, consult Strunk and White's *Elements of Style*, second edition, MacMillan Publishing Co., New York, N.Y., and *A Manual of Style*, twelfth edition, University of Chicago Press, Chicago, Ill.

——On the title page include authors' full names with affiliations and addresses footnoted; the senior author's name should appear first. Authors are those individuals who have actually written or made essential contributions to the manuscript and bear ultimate responsibility for its content. Use the Acknowledgment section at the end of the paper for crediting secondary contributors

——Preface each manuscript with an informative abstract not to exceed 200 words. Construct this piece as an entity separate from the paper itself; it is potential material for domestic and foreign secondary publications concerned with the topic of study. Choose language that is succinct but not detailed, summarizing reasons for and results of the study, and mentioning significant trends. Bear in mind the literature searcher and his/her need for key words in scanning abstracts.

——Forward original manuscript and three copies by first-class mail in flat form: do not fold or roll.

——Type manuscripts on 8½-by-11-inch paper with generous margins on all sides, and end each page with a completed paragraph. Recycled paper is acceptable if it does not degrade the quality of reproduction. Double-space all copy, including tables and references, and number each page.

——Place tables, charts, and illustrations, properly titled, at the end of the article with notations in the text to show where they should be inserted. *Treat original artwork as irreplaceable material.* Lightly print author's name and illustration number with a ballpoint pen on the back of each figure. Wrap in cardboard to prevent mutilation; do not use paperclips or staples.

——Letter charts distinctly so that numbers and words will be legible when reduced. Execute drawings in

Information continued

black ink on plain white paper. Submit original drawings or sharp glossy photographs: no copies will be accepted.

—Number literature citations in alphabetical order according to author. For journal article include, respectively, author, year, title, journal name as abbreviated in *Chemical Abstracts Service Source Index*, and volume, issue, and page numbers. For book references cite, respectively, author, year, chapter title, pages, and editor if pertinent, book title, and name and city of publisher. For Government manuals list originating agency and relevant subgroup, year, chapter title and editor if pertinent, manual title, and relevant volume, chapter, and/or page numbers. Do not list private communications among Literature Cited. Insert them parenthetically within the text, including author, date, and professional or university affiliation indicating author's area of expertise.

The Journal welcomes brief papers reporting monitoring data of a preliminary nature or studies of limited scope. A section entitled Briefs will be included as necessary to provide space for short papers which present timely and informative data. These papers must be limited to two published pages (850 words) and should conform to the format for regular papers accepted by the Journal.

Manuscripts require approval by the Editorial Advisory Board. When approved, the paper will be edited for clarity and style. Editors will make the minimum changes required to meet the needs of the general Journal audience, including international subscribers for whom English is a second language. Authors of accepted manuscripts will receive edited typescripts for approval before type is set. After publication, senior authors will receive 100 reprints.

Manuscripts are received and reviewed with the understanding that they have not been accepted previously for publication elsewhere. If a paper has been given or is intended for presentation at a meeting, or if a significant portion of its contents has been published or submitted for publication elsewhere, notations of such should be provided. Upon acceptance, the original manuscript and artwork become the property of the *Pesticides Monitoring Journal*.

Every volume of the Journal is available on microfilm. Requests for microfilm and correspondence on editorial matters should be addressed to:

Paul Fuschini (TS-793)
Editorial Manager
Pesticides Monitoring Journal
U.S. Environmental Protection Agency
Washington, D.C. 20460

For questions concerning GPO subscriptions and back issues write:

Superintendent of Documents
U.S. Government Printing Office
Washington, D.C. 20402

The Administrator of the U.S. Environmental Protection Agency has determined that the publication of this periodical is necessary in the transaction of public business required by law of this Agency. Use of funds for printing this publication approved by the Director of the Office of Management and Budget, May 19, 1976.

ORDER BLANK
FOR PMJ

To: Superintendent of Documents
Government Printing Office
Washington, D.C. 20402

Please enter my Subscription for Pesticides Monitoring Journal. I am enclosing Money Order ☐ Check ☐ for this subscription. ($7.90 a year; $2.00 additional for foreign mailing)

*Please address the PMJ as follows:*_____

_____

_____

UNITED STATES GOVERNMENT PRINTING OFFICE, WASHINGTON, D. C. 1967

For sale by the Superintendent of Documents, U.S. Government Printing Office, Washington, D. C. 20402. Subscription price $7.90 a year, $2.00 additional for foreign mailing. Price for a single copy of this issue is $2.00.

United States
Environmental Protection
Agency
(TS-793)
Washington DC 20460

Official Business
Penalty for Private Use
$300

Fourth-Class Mail
Postage and Fees Paid
EPA
Permit No. G-35

FEDERAL WORKING GROUP ON PEST MANAGEMENT
(RESPONSIBLE TO THE COUNCIL ON ENVIRONMENTAL QUALITY)

If you do not desire to continue receiving this publication, please CHECK HERE ☐; cut off this label and return it to the above address. Your name will be removed from the mailing list.

PESTICIDES MONITORING JOURNAL

SEPTEMBER 1979

VOLUME 13 NUMBER 2

PEMJAA (13)47–80 (1979)

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

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

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

The *Pesticides Monitoring Journal* is published by the Chemical Information Division, Office for Program Integration and Information, Office of Pesticides and Toxic Substances, U.S. Environmental Protection Agency.

Pesticide monitoring activities of the Federal Government, particularly in those agencies represented on the Monitoring Panel which participate in operation of the national pesticides monitoring network, are expected to be the principal sources of data and articles. However, pertinent data in summarized form, together with discussions, are invited from both Federal and non-Federal sources, including those associated with State and community monitoring programs, universities, hospitals, and nongovernmental research institutions, both domestic and foreign. Results of studies in which monitoring data play a major or minor role or serve as support for research investigation also are welcome; however, the Journal is not intended as a primary medium for the publication of basic research. Publication of scientific data, general information, trade names, and commercial sources in the *Pesticides Monitoring Journal* does not represent endorsement by any Federal agency.

Manuscripts received for publication are reviewed by an Editorial Advisory Board established by the Monitoring Panel. Authors are given the benefit of review comments prior to publication. For further information on Journal scope and manuscript preparation, see Information for Contributors at the back of this issue.

Address correspondence to:

Paul Fuschini (TS-793)
Editorial Manager
Pesticides Monitoring Journal
U. S. Environmental Protection Agency
Washington, D.C. 20460

Editor
Martha Finan

CONTENTS

Volume 13 September 1979 Number 1

HUMANS

Organochlorine Pesticide Residues in Human Milk Samples from Women Living in Northwest and Northeast Mississippi, 1973–75 [1]

Rai W. Barnett,[2] A. Joseph D'Ercole,[3] Jimmie D. Cain,[2] and Robert D. Arthur[4]

ABSTRACT

nochlorine pesticide analyses were performed on human samples obtained from 34 women living in the Mississi Delta, a high pesticide usage area, and from six women g in Starkville, Mississippi, a low pesticide usage area. women collected samples before and after their babies nursed so that fat levels and ΣDDT levels could be pared on whole milk and milk fat bases. ΣDDT values independent of collection time if calculated on a milk asis, but not if calculated on a whole milk basis. Thus, nost consistent indicator of DDT residues were values lated on a milk fat basis. Residue levels for p,p'-DDE, DDT, and ΣDDT were significantly different (P <0.01) mples from the two areas. Residues of o,p'-DDT, β-', and oxychlordane in milk samples from women living e high pesticide usage area also were significantly dift (P < 0.05). A mean value of 19.17 ppm ΣDDT, d in the milk fat of samples from the high pesticide area, is the highest ever reported. Samples from the esticide usage area contained a mean level of 2.36 ppm T.

Introduction

ng the past several years, concern about pesticides he ecosystem has developed. Although several es have been conducted to determine pesticide ue levels in human blood and other tissues, only tly has there been an interest in pesticide residues man milk. Researchers have reported similar pesti- residue levels in human milk samples collected in the United States (*2, 3, 6, 9, 15, 17*), Australia (*8, 12, 13*), France (*7*), Germany (*5*), Japan (*10*), and Uruguay (*1*). Several residue levels reported in these papers were above the World Health Organization's recommended maximum concentration of 0.05 ppm ΣDDT in cow's milk. Previous work has been concerned primarily with DDT residues, but other organochlorine pesticides and their metabolites should be considered. Also, some data were reported on a whole milk basis (WB) and others were reported on a fat basis (FB); the data cannot be compared directly unless the fat content of the milk is also reported. Many studies in the United States have been conducted in areas where pesticide usage is about 0.3 kg/ha/year, which is low compared to the estimated 6.72 kg/ha/year in the agricultural areas of Mississippi.

The present study identifies and quantitates organochlorine pesticides and their metabolites in human milk from women living in the Mississippi Delta, a high pesticide usage area, and compares the levels with those found in human milk samples collected in a low pesticide use area.

The Delta is an alluvial plain which occupies most of the northwest quadrant of Mississippi. The low pesticide usage area residents were women living in Starkville, Mississippi, located in the northeast quadrant of Mississippi close to the Alabama state line. Pesticide usage in these two areas of Mississippi is quite different. The Mississippi Delta, comprised of 10 counties, produces 60 percent of the cotton, 50 percent of soybeans, and all the rice grown in Mississippi. It has been estimated that 6.72 kg (active ingredients) of all pesticides were applied per hectare of land in the Mississippi Delta in 1974, whereas only 0.27 kg/ha were applied in the area of Starkville, Oktibbeha County, Mississippi. (Robert D. Arthur, University of Mississippi, 1974: unpublished data).

---

ssippi Agricultural and Forestry Experiment Station, Mississippi Miss. 39762, Paper No. 3297. This study was supported by the iiologic Studies Program, Technical Services Division, Office ticide Programs, U.S. Environmental Protection Agency, under t No. EPA 68-02-0669.

ssippi State Chemical Laboratory, Epidemiologic Studies Pro- Mississippi State University, Mississippi State, Miss. 39762. inquiries to this author.

it address: Department of Pediatric Endocrinology, University th Carolina, Chapel Hill, N.C. 27514.

it address: Department of Animal Industries, Southern Illinois ity, Carbondale, Ill. 62901.

Concern has been expressed in the literature (*17*) over the difference in DDT levels found in human milk collected before and after a baby has nursed. Wilson et al. (17) reported respective levels of 0.15 ppm and 0.22 ppm ΣDDT in milk samples collected before and after a baby nursed. Thus in the present study authors sought the reason for the difference.

Sample Collection

From 1973 to 1975, human milk samples were collected from 34 women living in the Mississippi Delta, a high pesticide usage area, and from six women living in Starkville, Mississippi, a low pesticide usage area. Nine women supplied samples collected before (fore-milk) and after (hind-milk) their babies nursed. Four of the nine women were from the high pesticide usage area.

Samples were obtained from nursing mothers who participated in the Maternal Child Health Care Program in the high pesticide usage area. The only criterion used to select donors was residence for at least five years in the established area. Samples from the low pesticide usage area were obtained from volunteers who were known to be breast feeding, who had been residing there for at least three years, and who were known to the authors. Single samples were received from each of the mothers except for the nine women who supplied both fore-milk and hind-milk samples.

Each woman expressed approximately 100 ml of milk with a clean plastic nylon breast pump which the investigators had washed with soap and water and rinsed with petroleum ether and hexane. Solvent washes were examined by gas-liquid chromatography (GLC) for contaminants; none were found. Milk was stored at −20°C in a pesticide-free glass bottle sealed with a Teflon-lined screw cap until analysis.

Analytical Methods

Each milk sample was prepared and fat was determined according to the *Pesticide Analytical Manual* (*4*). Liquid-liquid partitioning and Florisil fractionation cleanup was conducted according to the *Manual of Analytical Methods* (*16*). Pesticides were identified and quantitated on a Micro-Tek MT–220 gas chromatograph with two columns having different resolution characteristics. No other confirmatory tests were used. Polychlorinated biphenyl (PCB) interference was circumvented where possible by diluting the samples and rechromatographing. When this technique was not feasible due to a low pesticide/PCB ratio, the pesticide level was corrected by subtracting interference due to PCBs. Instrument parameters and operating conditions were as follows:

Columns:	(A) borosilicate glass, 6 ft × ¼ inch, packed with a mixture of 1.5 percent OV-17 and 1.95 percent QF-1 on 80–100-mesh Gas-Chrom Q
	(B) borosilicate glass, 6 ft × ¼ inch, pac with a mixture of 4 percent SE-30 an percent QF-1 on 80–100-mesh Gas-Ch Q
Detector:	electron capture, equipped with a 130 mCi ium ionizing source
Temperatures:	injector 230°C column 200°C detector 215°C
Carrier gas:	prepurified nitrogen flowing at 60 ml/mi (column A) and 90 ml/minute (column B)

Within these parameters, the sensitivity limit for ald was 20 pg for half scale deflection at 1.25×10^{-10} A Samples were examined specifically for the follow pesticides and metabolites: *p,p′*-DDE, *o,p′*-DDE, *p* TDE, *o,p′*-TDE, *p,p′*-DDT, *o,p′*-DDT, α-BHC, β-BH lindane, heptachlor, heptachlor epoxide, oxychlorda dieldrin, endrin, and mirex. Results were not correc for recovery.

The laboratory maintained both internal and exte quality assurance programs. The internal program u human milk with natural contamination and the ternal program used spiked fat samples which were of a national program.

Statistical Methods

Differences in fat levels in fore-milk and hind-m samples, and changes in ΣDDT levels in milk w expressed on a whole milk basis versus a milk fat b were determined by use of the Student t-metho paired observations (*14*). The high pesticide and pesticide usage area samples were compared by us the Mann-Whitney U Test (*11*) which is a nonp metric alternative to the t-test for two indepen samples.

Results and Discussion

Wilson et al. (*17*) expressed concern over differe in ΣDDT levels in fore-milk and hind-milk sam They reported ΣDDT levels of 0.15 ppm (WB) in milk samples and 0.22 ppm (WB) in hind-milk ples, a significant difference ($P < 0.01$). In most ing mammals, the hind-milk has a higher fat co than the fore-milk. Because pesticide residues lipophilic and homogeneously distributed throu fat, increased fat content of the milk yields incr pesticide residues in the milk. Therefore, author that the difference reported by Wilson et al. (*17*) have been due to the fat content of the milk san Kroger (*6*) was aware of the potential problem analyzed samples on a fat basis.

To determine whether differences in the present were due to the fat content, nine fore-milk and hind-milk samples were analyzed on a fat basis ΣDDT on a whole milk basis was then calculat multiplying FB values times the percent fat i sample as shown in Table 1.

Milk fat was significantly higher ($P < 0.05$) in milk samples, which was reflected in ΣDDT leve

ted on a whole milk basis (*14*). For example, in ıple No. 7 in Table 1, the fat level increased from 7 percent pre-nursing to 4.75 percent post-nursing. a fat basis, ΣDDT concentrations in pre- and post-sing samples were 3.11 ppm and 3.32 ppm, respec-ly, whereas ΣDDT concentrations in whole milk e 0.07 ppm and 0.15 ppm, respectively. The average erence in ΣDDT of hind-milk residues minus fore-k residues on a fat basis was not significant, whereas average difference in ΣDDT on a whole milk basis significant ($P < 0.05$) (*14*). ΣDDT values are ependent of collection time if reported on a fat s, but not if reported on a whole milk basis. There-, the most consistent indicator of DDT residues is ı on a fat basis. The other pesticide residues found ne samples show the same trend. From this evidence, must conclude that the differences which Wilson l. (*17*) reported were due to the increased fat con-of the milk collected after nursing.

BLE 1. *Comparison of ΣDDT on fat and whole milk ıses in human milk samples from women living in northwest and northeast Mississippi, 1973–75*

MPLE UMBER	% FAT	ΣDDT, PPM	
		FAT BASIS	WHOLE MILK BASIS[1]
1	3.80	B 11.300	0.429
	3.60	A 10.680	0.384
2	5.80	B 20.430	1.185
	7.20	A 21.340	1.536
3	3.30	B 14.360	0.474
	2.40	A 16.380	0.393
4	2.20	B 37.620	0.828
	2.80	A 37.910	1.061
5	0.81	B 2.240	0.018
	5.50	A 1.580	0.087
6	2.41	B 3.010	0.073
	3.66	A 3.070	0.112
7	2.17	B 3.110	0.067
	4.75	A 3.320	0.153
8	0.75	B 2.470	0.019
	7.38	A 2.010	0.148
9	5.04	B 3.360	0.169
	6.18	A 4.250	0.262

: B = fore-milk; A = hind-milk.
ılated by multiplying fat basis values times percent fat in .

lue values, extreme values, and percent positive les of the FB milk samples collected from women th pesticide usage areas are presented in Table 2. ɔesticides and their metabolites were found in the samples. Percent positive samples varied little be-ı the two areas for *p,p′*-DDE, *o,p′*-DDT, *p,p′*-, α-BHC, β-BHC, lindane, heptachlor epoxide, ieldrin, as shown in Table 2.

:e et al. (*9*) reported similar data for percent posi-samples for *p,p′*-DDE, *o,p′*-DDE, *o,p′*-DDT,)DT, and β-BHC in human milk samples col-in Colorado. However, they found dieldrin in 45 ıt of the samples and heptachlor epoxide in 25 ıt of the samples. In the present study both resi-vere found in all samples collected from the high de usage area. PCB residues were reported in rcent of the Colorado samples (*9*). Most of the samples from the Mississippi Delta contained PCBs, but no attempt was made to quantitate them. No residues of *o,p′*-DDE, *o,p′*-TDE, α-BHC, heptachlor, endrin, or mirex were found in any of the samples analyzed in the present investigation. Mean values of all pesticide residues were higher in samples from the Mississippi Delta than in samples from the low pesticide usage area, although some differences were quite small.

A comparison in Table 2 of samples from the high pesticide usage area with samples from the low pesticide usage area on the fat basis shows that *p,p′*-DDE, *p,p′*-DDT, and ΣDDT were significantly different ($P < 0.01$). Residues of *o,p′*-DDT, β-BHC, and oxychlordane in milk samples from the high pesticide usage area were significantly different ($P < 0.05$). Average levels of *p,p′*-TDE, α-BHC, heptachlor epoxide, lindane, and dieldrin were not significantly different between the two groups.

Table 3 shows the same residue values as Table 2 but expressed on a ppm whole milk basis. Again values for milk samples from the high pesticide usage area were higher than values for samples from the low pesticide usage area. The mean ΣDDT residue for samples from the high pesticide usage area was 19.17 ppm (FB) and 0.69 ppm (WB). Kroger (*6*) analyzed 53 samples from the Philadelphia, Pennsylvania, area and found ΣDDT levels of 2.40 ppm (FB). Wilson et al. (*17*) analyzed 138 samples from different areas of the United States and found a mean of 0.17 ppm ΣDDT (WB). Human milk samples from Colorado (*9*), Atlanta, Georgia (*2*), and Texas (*3*) contained ΣDDT levels of 0.06–0.12 ppm (WB). Pesticide levels in those studies were similar to levels found in the milk from the low pesticide usage area sampled in the present study. None of the previous studies reported residue values as high as those detected in the high pesticide usage area of the present study. Also, except for 12 samples in the Texas study (*3*), all samples in previous studies were collected in areas of low pesticide usage. The 12 Texas samples were collected in an agricultural area with high pesticide usage, but contained only 0.14 ppm *p,p′*-DDE plus *p,p′*-DDT (WB) (*3*). Strassman and Kutz (*15*) analyzed 57 samples from selected rice-growing counties in Arkansas and Mississippi. They found ΣDDT equivalent levels to be 0.344 ppm (WB).

ΣDDT levels of 0.06–0.43 ppm (WB) have been found in human milk in Germany (*5*), Japan (*10*), Uruguay (*12*), and Australia (*13*). Luquet et al. (*7*) from France reported finding an average of 3.24 ppm ΣDDT (FB). Miller and Fox (*8*) compared human milk samples from urban and rural areas of Australia. ΣDDT levels in the rural area were 3.17–30.90 ppm with a mean of 16.90 ppm (FB); the range of ΣDDT in the urban area was 3.26–21.00 ppm with a mean of 8.60 ppm (FB). In the rural area of Australia, large amounts of pesticides were used on tobacco. The residue values

TABLE 2. *Organochlorine pesticide residues in human milk, on a ppm fat basis, from women living in northeast and northwest Mississippi, 1973–75*

Residue	High Pesticide Usage Area				Low Pesticide Usage Area			
	Mean[1]	Minimum	Maximum	% Positive Samples	Mean[1]	Minimum	Maximum	% Positive Samples
p,p'-DDE	14.67 ± 2.59[2]	2.46	73.83	100	1.920 ± 0.160	1.47	2.45	100
p,p'-TDE	0.04 ± 0.02	0	0.43	31.6	0.002 ± 0.002	0	0.01	16.7
o,p'-DDT	0.21 ± 0.04[3]	0	1.08	97.4	0.050 ± 0.020	0.02	0.14	100
p,p'-DDT	4.25 ± 0.74[2]	0.34	18.45	100	0.390 ± 0.050	0.26	0.53	100
ΣDDT	19.17 ± 3.30[2]	2.95	92.46	100	2.360 ± 0.185	1.84	2.89	100
α-BHC	0.02 ± 0.01	0	0.27	31.6	0.003 ± 0.002	0	0.01	33.3
β-BHC	0.53 ± 0.07[3]	0.08	1.69	100	0.270 ± 0.100	0.11	0.75	100
Lindane	0.03 ± 0.01	0	0.29	55.3	0.008 ± 0.005	0	0.03	50.0
Heptachlor epoxide	0.08 ± 0.01	0.02	0.37	100	0.050 ± 0.010	0.01	0.08	100
Oxychlordane	0.13 ± 0.02[3]	0.03	0.70	100	0.050 ± 0.020	0	0.12	67.0
Dieldrin	0.15 ± 0.02	0.04	0.62	100	0.120 ± 0.020	0.03	0.17	100
% Fat	3.75	1.63	10.10		3.53	1.79	4.50	

[1] Means are ppm ± standard error of the mean, $N = 34$, high pesticide usage area; $N = 6$, low pesticide usage area.
[2] $P < 0.01$.
[3] $P < 0.05$.

TABLE 3. *Organochlorine pesticide residues in human milk, on a ppm whole milk basis, from women living in northwest and northeast Mississippi, 1973–75*

Residue	High Pesticide Usage Area			Low Pesticide Usage Area		
	Mean[1]	Min.	Max.	Mean[1]	Min.	Max
p,p'-DDE	0.550 ± 0.130	0.056	3.946	0.067 ± 0.010	0.041	0.110
p,p'-TDE	0.002 ± 0.001	0	0.019	< 0.001	0	< 0.001
o,p'-DDT	0.008 ± 0.001	0	0.027	0.002 ± 0.001	0.001	0.005
p,p'-DDT	0.159 ± 0.030	0.010	0.810	0.014 ± 0.002	0.008	0.022
ΣDDT	0.719 ± 0.162	0.069	4.801	0.083 ± 0.012	0.051	0.130
α-BHC	< 0.001	0	0.009	< 0.001	0	< 0.001
β-BHC	0.020 ± 0.004	0.002	0.105	0.009 ± 0.001	0.003	0.011
Lindane	0.001 ± 0.001	0	0.012	< 0.001	0	0.001
Heptachlor epoxide	0.003 ± 0.001	<0.001	0.020	0.002 ± <0.001	<0.001	0.003
Oxychlordane	0.005 ± 0.001	0.001	0.022	0.002 ± 0.001	0	0.004
Dieldrin	0.006 ± 0.001	0.001	0.042	0.004 ± 0.001	0.001	0.007

[1] Means are ppm ± SEM; N = 34, high pesticide usage area; N = 6, low pesticide usage area.

from Australia are the only ones in the literature similar to those reported here.

Pesticide residues reported in Tables 2 and 3 indicate that women living in the Mississippi Delta, a high pesticide usage area, have one of the highest reported concentrations of ΣDDT residues in their milk. Although the appearance of pesticide residues in human tissues and milk is recognized as potentially hazardous, it is important to note that no adverse effects to infants due to this exposure have been documented.

Acknowledgment

The Mississippi Delta milk samples were collected by the Maternal Child Health Program at the South Washington County Hospital, Hollandale, Mississippi.

LITERATURE CITED

(1) *Bauza, C. A. 1975.* Organochlorine pesticide residues in mother's milk in Montevides. Arch. Pediatr. Uruguay 46(1):31–42. Pestic. Abstr. 75–2325 (1975).

(2) *Curley, A., and R. Kimbrough. 1969.* Chlorin hydrocarbon insecticides in plasma and milk of p nant and lactating women. Arch. Environ. Health (February):156–164.

(3) *Dyment, P. G., L. M. Herbertson, W. J. Decker, J. Gomes, and J. S. Wiseman. 1971.* Relationship tween levels of chlorinated hydrocarbon insecti in human milk and serum. Bull. Environ. Cor Toxicol. 6(5):449–452.

(4) *Food and Drug Administration. 1972.* Pest Analytical Manual. Vol. 1. Sect. 211.13h (1). Department of Health, Education, and Welfare, V ington, D.C.

(5) *Knoll, W., and S. Jayaraman. 1973.* On the contar tion of human milk with chlorinated hydrocar Nahrung. 17(5):599–615. Pestic. Abstr. 74- (19/4).

(6) *Kroger, M. 1972.* Insecticide residues in human J. Pediatr. 80(3):401–405.

(7) *Luquet, F. M., J. Gaursaud, and J. Casalis.* Pollution of French human milk by organochl pesticide residues. Aliment. Vie. 62(1):40–69. Abstr. 59001b (1974).

(8) *Miller, G. J., and J. A. Fox. 1973.* Chlorinate drocarbon pesticide residues in Queensland h milk. Med. J. Aust. 2:261–264.

(9) *Savage, E. P., J. D. Tessari, J. W. Malberg, H. Wheeler, and J. R. Bagby. 1973.* Organochlorine cide residues and polychlorinated biphenyls in h milk, Colorado—1971–72. Pestic. Monit. J. 7(1)

(10) *Shirakawa, M. 1974.* On the results of investi of the pesticide residues in the milk from lac woman of coastal areas in Waykayama prefe Jap. Hyg. 29(1):94. Pestic. Abstr. 74–1574 (1

(11) *Siegel, S. 1956.* Nonparametric Statistics for th havioral Sciences. McGraw-Hill Book Co., Inc. York, N.Y. p. 123.

(12) *Siyali, D. S. 1973.* Polychlorinated biphenyls, chlorobenzene and other organochlorine pestici human milk. Med. J. Aust. 2:815–818.

(13) *Stacey, C. I., and B. W. Thomas. 1975.* O chlorine pesticide residues in human milk, w Australia—1970–71. Pestic Monit. J. 9(2):64–

(14) *Steel, R. G. D., and J. H. Torrie. 1960.* Pri and Procedures of Statistics. McGraw-Hill Boo Inc., New York, N.Y. Chapt. 5, pp. 79–80.

) *Strassman, S. C., and F. W. Kutz. 1977.* Insecticide residues in human milk from Arkansas and Mississippi, 1973–74. Pestic. Monit. J. 10(4):130–133.

) *U.S. Environmental Protection Agency. 1974.* Manual of analytical methods for the analysis of pesticide residues in human and environmental samples. Prepared for the Epidemiologic Study Program by the Pesticides and Toxic Substances Effects Laboratory, National Environmental Research Center, Research Triangle Park, N.C. Section 5, A (1), VII, VIII. pp. 6–8.

(17) *Wilson, D. J., D. J. Locker, C. A. Ritzen, J. T. Watson, and W. S. Schaffner. 1973.* DDT concentrations in human milk. Am. J. Dis. Child. 125(June):814–817.

Pesticide Residues in Human Milk, Alberta, Canada—1966–70, 1977–78[1]

Robert A. Currie, V. William Kadis, Walter E. Breitkreitz,
George B. Cunningham,[2] and Gary W. Bruns

ABSTRACT

Organochlorine pesticide residues were determined in human milk of residents of Alberta, Canada, during 1966–70 and 1977–78. Levels of polybrominated biphenyls (PBBs), polychlorinated biphenyls (PCBs), and some common organophosphorus pesticides were also monitored during 1977–78. Average residue levels were generally lower in 1977–78 samples, whereas the percent incidence of residues was generally lower in 1966–70 samples. β-BHC was found in all 1977–78 samples, but was not detected in 1966–70 samples. PCBs were detected in all but two of the 1977–78 samples. Average levels of p,p'-*DDT and its metabolites were substantially lower during the second period than during the first. Large increases in the average levels and percent incidences of heptachlor epoxide and* o,p'-*DDT have been attributed to refinements in both cleanup and gas chromatographic analysis. Although no PBBs or organophosphorus pesticides were detected in 1977–78 samples, an unidentified hydrocarbon similar to dicofol was found in all samples of that period. No correlation between donor age groups and average pesticide residue levels could be inferred.*

Introduction

Pesticide residues in human milk were first reported in 1951 by Laug et al. (*7*) who found DDT in 30 of their 32 samples. Since 1951, and particularly since the introduction of multiresidue screening by gas chromatography, numerous studies on levels of organochlorine pesticides and polychlorinated biphenyls (PCBs) in human milk have been reported throughout the world.

The present report describes two surveys of pesticide residue levels in human milk of residents of Alberta, Canada, during 1966–70 and 1977–78. The 1966–70 samples were analyzed only for residues of the common lipid-soluble organochlorine pesticides. During the second study, analysis included more organochlorine pesticides, some industrial chemicals, polybrominated biphenyls (PBBs) and PCBs, and the more comm lipid-soluble organophosphorus pesticides.

Sampling and Analysis

Human milk samples for the 1966–70 study were lected at the University of Alberta Hospital, Edmon Alberta, from women hospitalized for childbirth. samples were obtained 2–10 days postpartum (m four days for the 53 donors who supplied this infor tion) on a strictly voluntary basis, using a breast pu of unknown make. Samples were formalinized imm ately after collection and stored upon receipt by laboratory at −10°C until analysis. The majority samples, 51 of 59, were from residents of the city Edmonton; the balance came from residents of var parts of the Province of Alberta. The lipid content of milk was 0.41–4.29 percent, based on 27 determ tions, with a mean value of 1.86 percent. No cor tion was evident between lipid percent and days p partum. The maximum lipid value, 4.29 percent, found in a sample obtained at three days postpart Information on racial origin of the donors or e ordinary exposure to pesticides was not available.

The lipid portion of the milk was extracted by method of Kadis (*5*). Cleanup of an accura weighed portion of the lipid material was perfor on a Florisil column according to the method of K et al. (*6*).

Residues were determined by electron-capture (tri foil) gas chromatography of a 1.8 m × 3 mm borosilicate glass column packed with 25 percent 200/QF–1 (2:3) on 60–80-mesh Gas-Chrom Q. sults were confirmed on a gas chromatograph equi with a Dohrmann microcoulometric detector in halogen mode or by thin-layer chromatography silica gel and $AgNO_3$ spray for detection. Alth formalin used for initial preservation of the samples not tested for possible interfering compounds, no p lems were evident with the cleaned extracts at the chromatography stage.

[1] Food Laboratory Services Branch, Alberta Agriculture, 6909—116 Street, Edmonton, Alberta, Canada, T6H 4P2.
[2] Present address: R. M. Hardy & Associates Ltd., 4810—93 Street, Edmonton, Alberta, Canada, T5J 2L4.

nples for the second study were submitted to the oratory by public health offices throughout the vince of Alberta between December 1977 and March 1978, in direct response to a television program ling with PCB and DDT residues in human milk. in the first study, the majority of the samples, 24 of originated in the city of Edmonton. Lipid content samples was 0.27–5.45 percent on the basis of 24 erminations, with a mean value of 1.99 percent. nples were collected 17–309 days postpartum (mean, days); 27 of 33 donors made this information avail-. As in the first study, no correlation between milk l percent and days postpartum was evident. Resi-cy information from 25 donors showed that 17 had n residents of the Province of Alberta longer than 5 rs. Age was noted for 27 of 33 donors. No other demiological information was available. The samples e analyzed immediately upon receipt.

ds were extracted from the milk using Bureau of ry Industries (BDI) reagent described in *Standard hods for the Examination of Dairy Products* (*1*). umetric flasks of suitable size were substituted for test bottles, and the amounts of milk and reagent e scaled up proportionately. No solvents were added he fat layer. The fat layer was drawn off with a osable Pasteur pipet, dissolved in petroleum ether, dried over anhydrous sodium sulfate. Following ation and removal of the solvent, a weighed portion he lipids, not exceeding 5 g, was partitioned four s between equal volumes of petroleum ether and onitrile to remove the bulk of the lipids. The ace-rile extracts were partitioned back into petroleum r, and the solvent was removed by drying over um sulfate. Samples were cleaned on Florisil and d in three fractions according to the method of ie (*4*). For samples which yielded less than 1 g the dried lipid material was diluted in 25 ml petro-ether and applied directly to the Florisil column out acetonitrile partitioning.

nohalogen residues were determined by electron-ure gas chromatography using modulated-pulse Ni-etectors. Fraction 1 from the Florisil column was ined for PBB residues on a 0.46 m × 6 mm OD silicate glass column packed with 6.8 percent DC-QF-1 (2:3) on 80–100-mesh Gas-Chrom Z at C. This fraction was further examined for PCBs, T, and other organochlorine pesticides known to in the fraction, on a 1 m × 6 mm OD borosilicate column packed with 12.5 percent OV-101/QF-1) on 80–100-mesh Gas-Chrom Q. When PCBs encountered, they were separated from other pesti-by the method of Snyder and Reinert (*9*).

ion 2 from the Florisil column was examined for rochlorine pesticides on a 1 m × 6 mm OD boro-te glass column packed with 12.5 percent OV-QF-1 (2:3) on 80–100-mesh Gas-Chrom Q.

Fraction 3 from the Florisil column was examined for lipid-soluble organophosphorus pesticides by alkali-flame ionization detection on a 0.9 m × 6 mm OD borosilicate glass column packed with 5 percent QF-1 on 80–100-mesh Gas-Chrom Q.

Pesticides were partially confirmed by Florisil graded-elution described above. However, identities of pesticides in approximately every fourth sample were also confirmed by calculation of p-values (*2*).

Recoveries for the common lipid-soluble organochlorine and organophosphorus pesticides, PBBs, and PCBs exceeded 80 percent, except hexachlorobenzene (HCB). A 50 percent loss of HCB occurred during the acetonitrile-petroleum ether partitioning stage used to remove the bulk of the lipids from 1977–78 samples.

Quantitation was accomplished by the peak height comparison technique after adjusting pesticide concentrations in samples to values similar to those in the standards. Reliable quantitation limits were 0.001 ppm for the common lipid-soluble organochlorine pesticides, 0.01 ppm for PBBs and PCBs, and 0.02 ppm for common lipid-soluble organophosphorus pesticides. Organochlorine pesticides detected in 1966–70 samples included aldrin, α-BHC, *p,p'*-TDE, *p,p'*-DDE, *o,p'*-DDT, *p,p'*-DDT, dieldrin, endrin, heptachlor, heptachlor epoxide, and lindane. Samples from 1977–78 included the above compounds plus β-BHC, *cis*- and *trans*-chlordane, chlordene, *o,p'*-TDE, *o,p'*-DDE, HCB, kelthane, methoxychlor, mirex, PCNB, pentachlorobenzene (QCB), perthane, TCNB, and thiodan I. The following organophosphorus pesticides were sought in 1977–78 samples: ciodrin, diazinon, dursban, EPN, ethion, leptophos, leptophos phenol analog, malathion, methyl parathion, parathion, and phorate. Measured values of residues were not corrected for recoveries except values for HCB which were corrected to 100 percent.

Results and Discussion

Mean pesticide levels, on an extractable lipid basis, found in all samples for both 1966–70 and 1977–78 surveys of human milk are given in Table 1. Trace quantities were arbitrarily assigned a value of zero for computational purposes. With a few exceptions, individual average residue levels are lower in the second survey than in the first, as is the total average pesticide residue load, i.e., the sum of the individual pesticides. However, in general, the incidence of pesticide residues increased during the time between the two surveys. The increase may, in part, be due to improvements in analytical technique. Although the primary result of these improvements has been greater assurance of pesticide identity, they could have played a small role in effecting generally lower residues in 1977–78. Differences in the sampling periods postpartum may also have influenced the generally lower residue levels in 1977–78. However,

TABLE 1. *Incidence and mean level of pesticide residues in extracted lipids of human milk samples, Alberta, Canada, 1966–70, 1977–78*

Pesticide	Mean, ppm[1]		Incidence, %	
	1966–70 $N = 59$	1977–78 $N = 33$	1966–70 $N = 59$	1977–78 $N = 33$
α-BHC	0.107	0.002	37	76
β-BHC	—[2]	0.232	—[2]	100
p,p'-TDE	0.151	0.023	83	48
p,p'-DDE	2.23	1.09	100	100
o,p'-DDT	0.003	0.031	5	70
p,p'-DDT	1.14	0.437	97	100
Dieldrin	0.180	0.025	39	97
Heptachlor epoxide	0.002	0.028	5	94
Hexachlorobenzene	—[2]	0.091	—[2]	94
PCBs	—[2]	0.085	—[2]	100
Lindane	0.006	ND	3	0
Unidentified hydrocarbon[3]	—[2]	0.072	—[2]	100
Total average pesticide load	3.819	2.116	—	—

NOTE: ND = not detected.
[1] On extractable lipid basis.
[2] Not within the scope of the analytical procedure.
[3] Quantity estimated versus detector response for heptachlor epoxide.

Quinby et al. (*8*) found essentially no change in DDT and DDE levels in whole human milk sampled two to seven months postpartum from three individual donors. On the other hand, Curley and Kimborough (*3*) reported a 24 percent increase in the average ΣDDT in whole human milk sampled from five donors over 90–96 days postpartum.

No satisfactory explanation can be offered for the dramatic universal appearance of β-BHC in 1977–78. Although GC column analysis in the 1966–70 survey could not distinguish between lindane and β-BHC, lindane was found in only two of the 1966–70 samples, and the level in one of those was sufficiently high for its identity to be confirmed by thin-layer chromatography (TLC) using a silver nitrate reagent for detection.

As with lindane and β-BHC, the earlier GC column technology would not have allowed distinguishing between HCB and α-BHC except in certain cases. However, even if HCB was present in all the samples in which α-BHC was detected in the 1966–70 survey, it is obvious that the incidence of both HCB and α-BHC has more than doubled over the intervening years between the two surveys.

PCBs were detected in all but two of the 33 samples examined during the 1977–78 survey. However, during the earlier survey an awareness of the presence of PCBs and the methods for determining them were just being developed.

An unidentified hydrocarbon was found in all the second fractions from the graded-elution Florisil column used for cleanup of 1977–78 samples. At present t compound is thought to be structurally similar to dic which also elutes in fraction 2 of the Florisil colu The unknown has the same p-value as dicofol and t same retention time as dicofol on the 2:3 OV–101/(1 GC column. However, significant differences were o served between dicofol and the unknown on TLC an their retention times on a 1:4 OV–101/QF–1 GC umn. Although the unknown was not reported du the 1966–70 survey, its presence cannot be preclu because the single-fraction elution system used du the early survey may have allowed it to be masked other residues. An attempt will be made to identify unknown by means of GC-mass spectrometry.

The large increases in the average levels and the cent incidences of heptachlor epoxide and *o,p'*-D are perhaps the most striking results of the two surv Use of DDT and heptachlor epoxide had been gre curtailed during the years between the two surveys, one would normally have expected both the percen cidences and the average levels to have followed a tern similar to that of dieldrin. The usage patter dieldrin closely approximated that of heptachlor epo during these years, and although dieldrin's percent dence is up, its average level is substantially lowe one might expect. Also, the average levels of *p,p'*-D and its metabolites are substantially lower in the se survey than in the first survey. At the present time most satisfactory explanation for these apparent ar alies is the improvement and refinement in cle and GC column technology.

The ranges of pesticides found in both surveys, their percent incidences, are given in Table 2. C

TABLE 2. *Incidence and range of pesticide residu extracted lipids of human milk samples, Alberta, Ca 1966–70, 1977–78*

Pesticide	Range, ppm[1]		Incidence, %	
	1966–70	1977–78	1966–70 $N = 59$	197 N
α-BHC	ND–0.733	ND–0.016	37	
β-BHC	—[2]	0.009–0.393	—[2]	1
p,p'-TDE	ND–1.45	ND–0.348	83	
p,p'-DDE	0.173–8.12	0.258–5.18	100	1
o,p'-DDT	ND–0.072	ND–0.169	5	
p,p'-DDT	ND–11.25	TR–8.35	97	1
Dieldrin	ND–4.66	ND–0.081	39	
Heptachlor epoxide	ND–0.060	ND–0.113	5	
Hexachlorobenzene	—[2]	TR–5.13	—[2]	
Lindane	ND–0.340	ND	3	
PCBs	—[2]	ND–0.751	—[2]	1
Unidentified hydrocarbon[3]	—[2]	0.014–0.258	—[2]	1
Maximum range	ND–11.25	ND–8.35	—	

NOTE: ND = Not detected; TR = trace.
[1] On extractable lipid basis.
[2] Not within scope of the analytical procedure.
[3] Quantity estimated versus detector response for heptachlor ep

BLE 3. *Distribution of mean pesticide residue level in racted lipids of human milk according to age of donor, Alberta, Canada, 1966–70*

E GROUP	<21	21–25	26–30	31–35	>35
OF DONORS	4	18	21	10	6
ESTICIDE			MEAN, PPM[1]		
HC	0.195	0.135	0.075	0.087	0.114
TDE	0.189	0.129	0.197	0.101	0.114
DDE	2.31	2.13	2.24	2.12	2.64
DDT	ND	ND	0.008	ND	ND
DDT	1.34	0.866	1.29	0.973	1.46
drin	0.089	0.066	0.174	0.049	0.81
achlor oxide	ND	ND	0.033	ND	0.016
lane	ND	ND	0.010	0.034	ND
l average id	4.123	3.326	4.027	3.364	5.154

E: ND = not detected.
extractable lipid basis.

TABLE 4. *Distribution of mean pesticide residue levels in extracted lipids of human milk according to age of donor, Alberta, Canada, 1977–78*

AGE GROUP	<21	21–25	26–30	31–35	UNKNOWN
NO. OF DONORS	1	10	11	5	6
PESTICIDE			MEAN, PPM[1]		
α-BHC	0.001	0.003	0.002	0.002	0.003
β-BHC	0.014	0.072	0.536	0.094	0.092
p,p'-TDE	ND	0.028	0.012	0.070	ND
p,p'-DDE	0.699	1.10	1.01	1.41	1.03
o,p'-DDT	ND	0.016	0.042	0.066	0.014
p,p'-DDT	TR	0.134	0.218	0.275	1.55
Dieldrin	0.015	0.018	0.032	0.030	0.023
Heptachlor epoxide	0.016	0.015	0.040	0.025	0.030
Hexachlorobenzene	0.009	0.057	0.110	0.107	0.081
PCB	ND	0.044	0.052	0.250	0.121
Unidentified hydrocarbon	0.065	0.061	0.056	0.082	0.109
Total average load	0.819	1.548	2.111	2.411	3.053

NOTE: ND = not detected; TR = trace.
[1] On extractable lipid basis.

ıts made regarding average levels of pesticides also ly to the ranges of levels.

ıples collected for the second survey were also yzed for PBBs and the common lipid-soluble or- ɔphosphorus pesticides, but none was detected.

distribution of mean pesticide residue levels in extracted lipids of human milk for both the 1966– ınd 1977–78 surveys are shown in Tables 3 and 4, ectively, according to age of donor. No correla- between donor age groups and average pesticide lue levels could be inferred. It is possible, however, other factors such as the number of previous lren the donor had nursed and the donor's dietary ts may have a greater influence on pesticide residue s than does age alone.

LITERATURE CITED

Bianco, L. J., P. B. Manning, R. W. Mykleby, W. Roth, and J. A. Burke, 1972. Supplementary chemical control methods *In* Standard Methods for the Examination of Dairy Products. W. J. Hausler (ed.). American Public Health Association, Washington, D.C. pp. 217–218.

Bowman, M. C., and M. Beroza. 1965. Extraction *p*-values of pesticides and related compounds in six binary solvent systems. J. Assoc. Off. Agric. Chem. 48(5):943–952.

(3) *Curley, M. S., and R. Kimborough. 1969.* Chlorinated hydrocarbon insecticides in plasma and milk of pregnant and lactating women. Arch. Environ. Health 18(Feb.):156–164.

(4) *Currie, R. A. 1977.* Florisil as prepared and used in the food laboratory. Report on the 12th Annual Workshop on Pesticide Residue Analysis, Western Canada. Health Protection Branch, Health and Welfare Canada, Winnipeg, Manitoba. pp. 42–54.

(5) *Kadis, V. W. 1966.* Preparation, extraction, and cleanup of samples. Report of the First Pesticide Residue Analysis Seminar, Western Canada. Health Protection Branch, Health and Welfare Canada, Vancouver, British Columbia. pp. 24–28.

(6) *Kadis, V. W., O. J. Jonasson, and W. E. Breitkreitz. 1968.* Determination of organochlorine pesticide residues in human tissues. Can. J. Public Health 59(9): 357–361.

(7) *Laug, E. P., F. M. Kunze, and C. S. Prickett. 1951.* Occurrence of DDT in human fat and milk. Arch. Ind. Hyg. Occup. Med. 3(3):245–246.

(8) *Quinby, G. E., J. F. Armstrong, and W. F. Durham. 1965.* DDT in human milk. Nature 207(4998):726–728.

(9) *Snyder, D., and R. Reinert. 1971.* Rapid separation of polychlorinated biphenyls from DDT and its analogs on silica gel. Bull. Environ. Contam. Toxicol. 6(5): 385–390.

FISH, WILDLIFE, AND ESTUARIES

Organochlorine Residues in Six Species of Estuarine Birds, South Carolina, 1971–75

Lawrence J. Blus[1] and Thair G. Lamont[2]

ABSTRACT

In South Carolina between 1971 and 1975, authors evaluated the occurrence of organochlorine residues in the laughing gull (Larus atricilla), *white ibis* (Eudocimus albus), *glossy ibis* (Plegadis falcinellus), *American oystercatcher* (Haematopus palliatus), *willet* (Catoptrophorus semipalmatus), *and ruddy turnstone* (Arenaria interpres). *Tissues of birds found dead and eggs were analyzed, eggshell thicknesses were measured, and incidental observations were made of reproductive success and population status. Eggshell thicknesses of the white ibis, American oystercatcher, and laughing gull were not significantly different* ($P < 0.05$) *from the pre-1947 norms. DDE and polychlorinated biphenyls (PCBs) were found most frequently and at the highest concentrations in eggs. DDE residues declined significantly in oystercatcher eggs, and declined slightly in laughing gull eggs; no change was noted in white ibis eggs. No consistent trends were found for dieldrin and PCBs. Authors found no obvious problems with reproductive success of any species. Populations of the five species breeding in South Carolina appear stable. The white ibis and laughing gull in South Carolina have experienced population explosions over the past 50 years; the glossy ibis has increased substantially since the first documented breeding records in 1947.*

Introduction

Authors' studies of the effects of pollutants on estuarine birds in the southeastern United States have focused on the brown pelican (*Pelecanus occidentalis*), a sensitive indicator species for certain organochlorine pollutants (*1, 3*). However, studies in South Carolina included other estuarine birds which appeared to be less sensitive to organochlorines than is the pelican (*6*). Six of the species included the laughing gull (*Larus atricilla*), white ibis (*Eudocimus albus*), glossy ibis (*Plegadis falcinellus*), American oystercatcher (*Haematopus palliatus*), willet (*Catoptrophorus semipalmatus*), and ruddy turnstone (*Arenaria interpres*). The purposes of the present study were to analyze eggs and tissues for organochlorine residues, to measure eggshell th nesses, and to obtain incidental information on bree biology and population status of several of the spec

Procedure for Sampling, Necropsy, and Field S

From 1971 to 1975 authors visited islands in S Carolina estuaries during the breeding season to co eggs and dead birds and to record incidental info tion on breeding biology and population status. of the research was conducted on or near the Romain National Wildlife Refuge (CRNWR).

Addled and viable eggs in all stages of incubation collected. One egg was usually taken from each selected for sampling. Eggs were weighed and m ured. Their contents were removed and placed in ch cally cleaned glass bottles that had been rinsed acetone, hexane, deionized water, and dilute nitric filled bottles were placed in a freezer. Eggshells thoroughly rinsed with tap water and were allowe dry. Shell thickness, shell plus shell membranes, measured at three sites on the waist of the egg w micrometer graduated in units of 0.01 mm.

Two oystercatchers found dead were collected frozen. The specimens were removed from the fr several months later, allowed to thaw, and subsequ necropsied. Tissues for histological study were fix 10 percent formalin, embedded in paraffin, secti and stained (*15*). The entire brain was removed placed in a chemically cleaned glass bottle. The re ing carcasses, except for skin, feet, wings, liver, ki and gastrointestinal tract, were wrapped in foil refrozen. The brains and carcasses were later ana for organochlorine residues.

Analytical Procedures

Contents of each egg collected in 1971 were ho enized, and a 20-g portion was mixed with anhy sodium sulfate in a blender and extracted for 7 with hexane in a Soxhlet apparatus. The extrac

[1] Pacific Northwest Field Station, 480 SW Airport Road, Corvallis, Ore. 97330.
[2] Fish and Wildlife Service, U.S. Department of the Interior, Patuxent Wildlife Research Center, Laurel, Md. 20811.

BLE 1. *Eggshell thickness of four species of estuarine birds, South Carolina, 1947–75*

Species	Eggshell Thickness, mm [1]				
	Pre-1947	1971	1972	1974	1975
te ibis	0.334[2]± 0.005 (27)		0.335± 0.011 (10)	0.335± 0.005 (10)	
rican oystercatcher	0.308± 0.001 (192)	0.290± 0.013 (5)	0.313± 0.006 (11)		0.303± 0.005 (13)
ghing gull	0.280± 0.007 (4)	0.271± 0.003 (15)			0.268± 0.007 (11)
sy ibis			0.290± 0.008 (10)		

an ± standard error; sample size in parentheses.
ckness means were not significantly different ($P > 0.05$). Means separated by multiple range tests (*11, 13*).

ined by acetonitrile partitioning and was eluted on tially deactivated Florisil. For pesticide analysis, dues in the cleaned extract were separated and re- ved in four fractions from a silica gel thin-layer e (*15*). Each thin-layer fraction was analyzed by tron-capture gas chromatography (GC) on a column 3 percent OV-1 or 3.8 percent UCW-98 on Chromo- W(HP). DDT and its metabolites in fractions III V were confirmed on a column of 3 percent XE-60 3 percent QF-1 on Gas-Chrom Q. Polychlorinated ienyls (PCBs) were identified and measured semi- ntitatively by thin-layer chromatography (*14*).

eggs collected between 1972 and 1975, the metho- gy was modified as described by Cromartie et al. The extract of the 10-g portion was cleaned on a isil column. Pesticides and PCBs were separated three fractions on a SilicAR column and analyzed GC on a 4 percent SE-30/6 percent QF-1 column. his method, authors could detect additional pesti- s, including toxaphene, *cis*-chlordane or *trans*- achlor, and *cis*-nonachlor. In 1972, there was no dard for quantitating *cis*-nonachlor and in 1973, ocedure was first developed to estimate toxaphene s. For the eggs collected during 1974–75, the lipids removed either on a Florisil column or by auto- d gel permeation chromatography. In 1974, authors ated and quantitated *cis*-chlordane and *trans*- chlor on a 1.5 percent OV-17/1.95 percent QF-1 nn.

lues in 10 percent of the samples were confirmed by nass spectrometry. Average recoveries from spiked les were 75–112 percent. Residues were not cor- d for recovery. Weights of egg contents were cor- d for moisture loss by use of egg volume (*21*); ues are expressed as fresh wet weight.

Results

HELL THICKNESS

ells of the white ibis, American oystercatcher, laughing gull, and glossy ibis were measured for thickness (Table 1). No pre-1947 thickness data for the glossy ibis from South Carolina were available, and only a small sample was located for the laughing gull. Eggshell thickness means of eggs collected during the 1970s were not significantly different ($P > 0.05$; range, −4.3 to +1.6 percent) from pre-1947 norms (Table 1). In Texas, eggshell thinning averaged <4 percent for the laughing gull and white ibis in 1970 (*12*). In the present study, authors did not observe any obviously thin-shelled, cracked, or crushed eggs.

ORGANOCHLORINE RESIDUES

Residues of 10 organochlorines were found in 84 eggs of four species (Tables 2–5). DDE and PCBs were detected most frequently and at the highest levels; DDE was detected in all eggs, PCBs in 68 percent, and dieldrin in 33 percent. Residues in laughing gull (Table 4) and glossy ibis (Table 5) eggs were slightly higher than residues in eggs of the oystercatcher (Table 2) or white ibis (Table 3). The highest residues found in individual

TABLE 2. *Residues of organochlorines in eggs of the American oystercatcher, South Carolina, 1971–75*

Year	Residues, µg/g Fresh Wet Weight	
	DDE	PCBs
1971	1.10	—
	0.96[1]	—
	1.10[2]	—
	0.74	—
	0.77	—
Geometric mean	0.92	—
95% Confidence limits	0.73–1.17	—
Range	0.74–1.10	ND
1972	0.44	1.0
	0.54	0.9
	0.71	—
	0.30	0.9
	0.38	1.0
	0.40	1.0
	0.74	0.9
	0.41	0.8
	0.45	0.9
	0.42	0.8
Geometric mean	0.46	0.8
95% Confidence limits	0.39–0.56	0.6–1.1
Range	0.30–0.74	ND–1.0
1975	0.28	0.5
	0.25	0.5
	0.24	0.6
	0.25[3]	0.5
	0.20	—
	0.25	0.5
	0.45	0.7
	0.33	0.5
	0.21	—
	0.33	0.5
	0.24	0.5
	0.25	0.5
	0.15	0.5
Geometric mean	0.26	0.5
95% Confidence limits	0.22–0.30	0.4–0.6
Range	0.15–0.45	ND–0.7

[1] 0.12 µg/g of dieldrin.
[2] 0.13 µg/g of dieldrin.
[3] 0.63 µg/g of toxaphene.

TABLE 3. *Residues of organochlorine pollutants in eggs of the white ibis, South Carolina, 1972, 1974*

Year	Residues, µg/g Fresh Wet Weight			
	DDE	Dieldrin	Mirex	PCBs
1972	0.19	—	0.12	—
	0.68	0.10	—	1.2
	1.02	—	0.21	0.6
	0.45	—	0.20	—
	1.27[1]	—	0.13	—
	0.20	—	—	—
	0.42	—	—	1.1
	1.46[2]	—	—	0.8
	0.32	—	0.39	—
	0.19	—	—	—
Geometric mean	0.48	—	—	—
95% Confidence limits	0.27–0.83	—	—	—
Range	0.19–1.46	ND–0.10	ND–0.39	ND–1.2
1974	0.88	0.10	—	1.8
	0.85	0.11	—	1.0
	0.35	—	—	0.5
	0.43	—	—	—
	0.14	—	—	—
	0.68	—	—	0.5
	0.53	—	—	—
	0.43	—	—	0.5
	0.83	—	—	—
	0.65[3]	—	—	0.5
Geometric mean	0.52	—	—	0.6
95% Confidence limits	0.35–0.77	—	—	0.4–0.8
Range	0.14–0.88	ND–0.11	ND	ND–1.8

[1] 0.10 µg/g of DDT.
[2] 0.18 µg/g of DDT.
[3] 0.28 µg/g of *trans*-nonachlor.

TABLE 4. *Residues of organochlorine pollutants in eggs of the laughing gull, South Carolina, 1971, 1975*

Year	Residues, µg/g Fresh Wet Weight		
	DDE	Dieldrin	PCBs
1971	1.55	—	—
	1.81	0.14	4.8
	2.08	0.24	2.0
	0.70	—	—
	1.04	0.14	5.9
	1.05	0.12	2.4
	1.54	1.83	2.7
	1.29	0.14	2.1
	0.55	0.24	6.3
	3.33	0.18	9.5
	2.25[1]	0.17	3.9
	2.57	0.29	4.7
	1.18	0.10	1.0
	1.46	0.19	1.9
	1.09	—	3.4
Geometric mean	1.41	0.16	2.6
95% Confidence limits	1.08–1.84	0.11–0.25	1.6–4.2
Range	0.55–2.57	ND–1.83	ND–9.5
1975	2.00	0.11	2.2
	1.10	0.25	4.8
	0.65	—	1.9
	0.85	—	2.1
	1.30	—	1.5
	0.65	—	1.0
	1.20	0.17	1.2
	1.40[2]	0.22	1.7
	2.20[3]	1.50	4.3
	0.83	0.23	—
	1.40	0.14	2.8
Geometric mean	1.14	0.14	1.6
95% Confidence limits	0.87–1.50	0.07–0.27	1.1–2.4
Range	0.65–2.20	ND–1.50	ND–4.8

[1] 0.29 µg/g of mirex.
[2] 0.10 µg/g of toxaphene.
[3] 0.18 µg/g of heptachlor epoxide, 0.18 µg/g of oxychlordane, 0.12 µg/g of *cis*-chlordane, 0.19 µg/g of *trans*-nonachlor, and 0.11 µg/g of toxaphene.

TABLE 5. *Residues of organochlorines in eggs of th glossy ibis, South Carolina, 1972*

Year	Residues, µg/g Fresh Wet Weight			
	DDE	DDT	Dieldrin	PCBs
1972	2.26	0.19	1.72	0.6
	1.12	—	—	—
	0.27	—	—	—
	1.57	—	0.15	—
	0.94	0.17	—	—
	7.70[1]	0.21	0.33	0.5
	3.44[2]	2.64	2.16	—
	1.28	—	—	0.6
	4.54	0.14	—	—
	0.34	—	—	—
Geometric mean	1.49			
95% Confidence limits	0.69–3.19			
Range	0.27–7.70	ND–2.64	ND–2.16	ND–0.6

[1] 0.12 µg/g of mirex.
[2] 0.72 µg/g of TDE.

eggs were: 7.70 µg/g DDE, glossy ibis; 2.16 µ dieldrin, glossy ibis; and 9.5 µg/g PCBs, laughing g DDE residues declined significantly in oystercat eggs (Table 2), declined slightly in laughing gull e (Table 4), and were unchanged in white ibis eggs (T 3). There were no consistent trends for dieldrin PCBs.

DDE and PCBs were the only residues detected in br and carcasses of seven birds found dead in South C lina (Table 6). Residues were generally very low. D and PCBs were detected in three of seven brains. C two oystercatchers were necropsied; one died of a cholera (*2*) and the other of nephrosis (Table 6).

BREEDING SITES AND POPULATION STATUS

Except for the ruddy turnstone, all of the species b in South Carolina. Authors found the willet, a soli nester that builds a well concealed nest, nesting on Key (Stono River), Deveaux Bank, and on islands the CRNWR including Cape Island, Raccoon Key, Bank, and Marsh Island. Authors observed only young willet. Population status of the species is in nite; the willet is widespread on the coastal islands, is not numerous in any area.

The oystercatcher is essentially a solitary nester, though nests may be found close together at times. like willet eggs, oystercatcher eggs are laid in a s cavity or scrape that the birds dig in sand or shells with few exceptions, the scrapes are dug in sites no vegetative cover. Authors found oystercatcher on a number of coastal islands and on the spoil de ited along the banks of the Intracoastal Waterwa South Carolina. The oystercatcher population is ap ently in good condition, although quantitative dat establish trends are unavailable.

The glossy ibis was first found nesting in South Car in 1947 (*18*), and the population had increased to a 700 pairs by 1975 (*10*). Nesting sites ranged barrier islands with small shrubs, specifically, M

TABLE 6. *Residues of organochlorines in tissues of three species of estuarine birds, South Carolina, 1971–74*

cies	Year	Age	Sex	Residues, µg/g Fresh Wet Weight			Cause of Death
				Tissue	DDE	PCBs	
ldy							
rnstone	1974	Ad	Unk	Brain	0.27	3.0	Open
		Ad	Unk	Brain	—	3.4	Open
		Ad	Unk	Brain	—	7.0	Open
et	1973	Ad	Unk	Brain	0.20	—	Open
erican							
stercatcher	1971	Ad	F	Brain	0.10	—	Nephrosis
				Carcass	0.40	—	
	1973	Ad	Unk	Brain	—	—	Open
		Ad	F	Brain	—	—	Avian cholera
				Carcass	0.45	—	

TE: Open = unknown at this time.

nd and White Banks on the CRNWR and Deveaux nk, to a large wooded island, Drum Island, in the oper River at Charleston.

thors found white ibis nesting in three colonies in 75; inactive nests from the previous year were ob- ved in another colony on Hilton Head Island. Since 22 when the species was first found nesting in South rolina (*19*), the population had increased to about 000 breeding pairs by 1975. The colony on Pumpkin- d Island near Georgetown contained 19,000 pairs l the Drum Island colony consisted of 12,000 pairs; y two pairs were located in an inland swamp colony ır Conway (*10*).

tory of the laughing gull in South Carolina is similar that of the white ibis. There is only one nesting rec- for this species before 1933, although adults were n in previous years in South Carolina estuaries ɔughout the usual breeding season (*20*). Since the ɔrded nesting in South Carolina in 1933 (*7*), the s have undergone a population explosion. Rough mates in 1975 indicated more than 10,000 breeding s in the state. Laughing gulls nest on almost all of South Carolina barrier islands.

neral observations indicated that the laughing gull, te ibis, and glossy ibis experienced excellent repro- tive success. There were insufficient observations to mate reproductive success in the oystercatcher and et, but there were no obvious problems.

Discussion

organochlorine residues in the oystercatcher prob- reflect low residues in the oyster (*Crassostrea vir- ca*), another shellfish consumed by this species. dues in oysters in South Carolina were declining in late 1960s. So few oysters contained detectable ls of organochlorine pesticides in 1969 that monitor- was discontinued (*8*). The decline in DDE residues ystercatcher eggs from 1971 to 1975 apparently cts a further decline in residues in food of the ercatcher. Authors have noted significant declines of E in eggs of other birds from South Carolina estu- aries including the brown pelican (*4*) and the least tern (*Sterna albifrons*) (*5*) which parallel decreases of organochlorine pollutants in certain estuarine fish.

The low mean residues found in eggs of the white ibis and laughing gull from South Carolina differed from means in the same species from other areas. Laughing gull eggs collected in Texas in 1970 (*12*) contained more DDE (~ 10 µg/g), dieldrin (0.52 µg/g), and PCBs (3.00 µg/g) than did South Carolina eggs. White ibis eggs collected in Texas in 1970 (*12*) and in the southeastern United States in 1972–73 (*17*) contained lower DDE (< 0.4 µg/g) and PCB (< 0.2 µg/g) residues than did South Carolina eggs.

Laughing gulls are most numerous on islands such as Bird Bank, Marsh Island, and Deveaux Bank where royal terns (*Sterna maxima*) and Sandwich terns (*Sterna sandvicensis*) nest. Gulls catch live fish and other prey animals, but they also obtain food regurgitated by terns, particularly by chicks. Large numbers of tern eggs that are washed out of nests by tidewaters can be a substantial food source for the gulls. Laughing gulls seldom preyed on royal and Sandwich tern eggs; however, laughing gull depredation of eggs of the black skimmer (*Rynchops niger*) and gullbilled tern (*Gelochelidon nilotica*) was apparently the major factor in reproductive failure of those species on Deveaux Bank from 1972 to 1975.

Laughing gulls, together with royal and Sandwich terns, deserted Marsh Island in 1976 and nested on Bird Bank. On June 16, 1973, a partial count revealed 629 laughing gull nests on several of the small islands known collectively as White Banks (CRNWR); the actual number was probably near 1000 nests. Royal and Sandwich terns did not nest at White Banks during the present study. The laughing gulls nesting on White Banks seemed to feed extensively on shrimp heads, waste fish, pieces of crab, and other materials originating from shrimp trawlers on nearby Five Fathom Creek, from a nearby crab processing plant, and from other commercial fishing activities.

The low organochlorine residues in eggs and tissues of the birds apparently exerted negligible effects on eggshell thickness, reproductive success, and adult survival.

Populations of the five species breeding in South Carolina appear stable. Alterations of the estuarine environment through dredging, commercial fishing, or other activities may have created conditions that favored population increases in the glossy ibis, white ibis, and laughing gull. The increases in the glossy ibis and white ibis populations may be related to a general northward expansion of the breeding range in combination with continued recovery of populations decimated by human disturbance early in this century (*16*). Authors feel that this explanation may suffice for the population increase of glossy ibis; however, the increase in white ibis seems related primarily to changes in the habitat, particularly creation of dredge islands for nesting. The population dynamics of the laughing gull seem distinct from the other two species in that there has been no general latitudinal expansion in the Atlantic coast population. Thus, at this point, we have little real insight into the mechanisms underlying fluctuations in populations of the three species in South Carolina.

Acknowledgments

We thank A. S. Federighi and H. M. Ohlendorf for critical editing of the manuscript, L. N. Locke for necropsy reports, the numerous individuals who assisted with the field work, and E. E. Klaas and H. M. Ohlendorf for provision of pre-1947 eggshell thickness data.

LITERATURE CITED

(*1*) *Blus, L. J., R. G. Heath, C. D. Gish, A. A. Belisle, and R. M. Prouty. 1971.* Eggshell thinning in the brown pelican: implication of DDE. Bioscience 21 (24):1213–1215.

(*2*) *Blus, L. J., L. N. Locke, and E. Cromartie. 1978.* Avian cholera and organochlorine residues in an American oystercatcher. Estuaries 1(2):128–129.

(*3*) *Blus, L. J., B. S. Neely, Jr., A. A. Belisle, and R. M. Prouty. 1974.* Organochlorine residues in brown pelican eggs: relation to reproductive success. Environ. Pollut. 7(2):81–91.

(*4*) *Blus, L. J., B. S. Neely, Jr., T. G. Lamont, and B. Mulhern. 1977.* Residues of organochlorines and heavy metals in tissues and eggs of brown pelicans, 1969–73. Pestic. Monit. J. 11(1):40–53.

(*5*) *Blus, L. J., and R. M. Prouty. 1979.* Organochlorine pollutants and population status of least terns in South Carolina. Wilson Bull. 91(1):62–71.

(*6*) *Blus, L. J., R. C. Stendell, S. N. Wiemeyer, H. M. Ohlendorf, J. A. Kerwin, and L. F. Stickel. 1977.* Impact of estuarine pollution on birds. Estuarine lution Control and Assessment, Vol. I. Proc. Environmental Protection Agency Conf. Feb. 11- t975. Pensacola, Fla., pp. 57–71.

(*7*) *Burton, E. M., and E. B. Chamberlain. 1933.* La ing gull breeding on the South Carolina coast. 50(3):360.

(*8*) *Butler, P. A. 1973.* Organochlorine residues in es rine mollusks, 1965–72—National Pesticide Moni ing Program. Pestic. Monit. J. 6(4):238–362.

(*9*) *Cromartie, E., W. L. Reichel, L. N. Locke, A. Belisle, T. E. Kaiser, T. G. Lamont, B. M. Mulh R. M. Prouty, and D. M. Swineford. 1975.* Resi of organochlorine pesticides and polychlorinated phenyls and autopsy data for bald eagles, 1971- Pestic. Monit. J. 9(1):11–14.

(*10*) *Custer, T. W., and R. G. Osborn. 1977.* Wading b as biological indicators: 1975 colony survey. Fish Wildlife Service, U.S. Department of the Inte Washington, D.C., Spec. Sci. Rep.-Wildl. No. 206 pp.

(*11*) *Duncan, D. B. 1955.* Multiple range and multip tests. Biometrics 11(1):1–42.

(*12*) *King, K. A., E. L. Flickinger, and H. H. Hildebr 1978.* Shell thinning and pesticide residues in T aquatic bird eggs, 1970. Pestic. Monit. J. 12(1) 21.

(*13*) *Kramer, C. Y. 1956.* Extensions of multiple r tests to group means with unequal numbers of r cations. Biometrics 12(2):307–310.

(*14*) *Mulhern, B. M., E. Cromartie, W. L. Reichel, A. A. Belisle. 1971.* Semiquantitative determina of polychlorinated biphenyls in tissue samples by layer chromatography. J. Assoc. Off. Anal. C 54(3):548–550.

(*15*) *Mulhern, B. M., W. L. Reichel, L. N. Locke, T Lamont, A. A. Belisle, E. Cromartie, G. E. Ba and R. M. Prouty. 1970.* Organochlorine residues autopsy data from bald eagles, 1966–68. Pestic. M J. 4(3):141–144.

(*16*) *Ogden, J. C. 1978.* Recent population trends of nial wading birds on the Atlantic and Gulf co plains. Pages 137–153 *in* A. Sprunt IV, J. C. O and S. Winkler, eds., Wading Birds, National A bon Society, New York, N.Y.

(*17*) *Ohlendorf, H. M., E. E. Klaas, and T. E. Kaiser.* Organochlorine residues and eggshell thinnin anhingas and waders. Proc. 1977 Conf. Col Waterbird group, DeKalb, Ill., pp. 185–195.

(*18*) *Sass, H. R. 1948.* Glossy ibis breeding in South lina. Auk 65(4):459–460.

(*19*) *Sprunt, A., Jr. 1944.* Northward extension of breeding range of the white ibis. Auk 61(1):144-

(*20*) *Sprunt, A., Jr., and E. B. Chamberlain. 1949.* Carolina bird life. University of South Carolina Columbia, S.C., 858 pp.

(*21*) *Stickel, L. F., S. N. Wiemeyer, and L. J. Blus.* Pesticide residues in eggs of wild birds: adjustmen loss of moisture and lipid. Bull. Environ. Co Toxicol. 9(4):193–196.

Shell Thinning and Residues of Organochlorines and Mercury in Seabird Eggs, Eastern Canada, 1970–76

Peter A. Pearce,[1] David B. Peakall,[2] and Lincoln M. Reynolds[3]

ABSTRACT

ganochlorine and mercury concentrations are reported for 2 eggs of Leach's storm-petrel (Oceanodroma leucorhoa), *uble-crested cormorant* (Phalacrocorax auritus), *common ler* (Somateria mollissima), *common tern* (Sterna hirdo), *razorbill* (Alca torda), *common murre* (Uria aalge), *ack guillemot* (Cepphus grylle), *and Atlantic puffin* ratercula arctica) *from the Bay of Fundy, the Gulf of Lawrence, and the open Atlantic shore of Canada during 70–76. Concentrations of all organochlorines except DDE d polychlorinated biphenyls (PCBs) were low. DDE, Bs, and mercury residues were highest in cormorant and rel, intermediate in alcids, and lowest in eider and tern. mporal and spatial aspects of contamination patterns discussed. Authors conclude that only in cormorants re DDE residues high enough to cause, through eggshell nning, local population declines.*

Introduction

ring the past century marked changes have occurred some seabird populations of the western Atlantic 9). Leach's storm-petrel (*Oceanodroma leucorhoa*) decreased in the Bay of Fundy, the Gulf of Maine, d the Gulf of St. Lawrence. Populations of doublested cormorant (*Phalacrocorax auritus*) have inased considerably since the turn of the century, apently due to decreased human predation; however, ent declines have occurred in the Gulf of St. Lawce. Terns have declined on the North American antic seaboard although three species of gulls have reased. Alcid populations generally have declined; reases of the razorbill (*Alca torda*) in the Gulf of Lawrence have been particularly marked.

v chemical pollutant residue data have been pubed for seabirds off the northeastern coast of North erica. Organochlorine concentrations in petrels and ds in Newfoundland, and in marine double-crested morants in the Gulf of Maine-Bay of Fundy region have been reported (*14, 16, 35*). Major sources of pollutant contamination of the Gulf of St. Lawrence have been discussed (*33*). DDE contamination of that basin in the late 1960s was thought to be high enough to have contributed to low productivity of gannets (*Morus bassanus*) (*18*). PCB and DDE concentrations in the eggs of seabirds of western Canadian coastal waters were given in a review of the exposure of marine birds to environmental pollutants (*20*). In the present paper authors present organochlorine and mercury residue concentrations found in seabird eggs collected on the Canadian Atlantic seaboard during 1970–76, and attempt to assess the implications of the contamination on the productivity of the birds.

Sampling, Materials, and Methods

Eggs of Leach's storm-petrel, double-crested cormorant, common eider (*Somateria mollissima*), common tern (*Sterna hirundo*), razorbill, common murre (*Uria aalge*), black guillemot (*Cepphus grylle*), and Atlantic puffin (*Fratercula arctica*) were collected from various sites in eastern Canada (Fig. 1) between 1970 and 1976. At most sites, eggs were taken early in the nesting season. Eggs were taken from first clutches at cormorant and tern colonies because the species re-lay if the first clutch is destroyed. One egg was taken from each of five or ten nests near the center of the colony. The maximum length and width of each egg was measured and, after the contents had been removed, the eggshell was washed, dried, and weighed. Eggshell thickness indices, weight(mg)/length(mm) $\times$ width(mm), were calculated. Pending analysis, egg contents were stored frozen.

Analytical Procedures

ORGANOCHLORINES

The frozen egg sample was thawed, and homogenized in a Waring Blendor. A 2–5-g aliquot of the blend was weighed to the nearest milligram and was oven-dried for about 24 hours at 45°C with slight vacuum (water aspirator) to constant weight. The dried sample was ground with 5–10 g anhydrous sodium sulfate. The

[1] nadian Wildlife Service, Department of the Environment, Frederic- New Brunswick, Canada E3B 4Z9.
[2] nadian Wildlife Service, Department of the Environment, Ottawa, rio, Canada K1A 0E7.
[3] ario Research Foundation, Sheridan Park, Ontario, Canada L5K

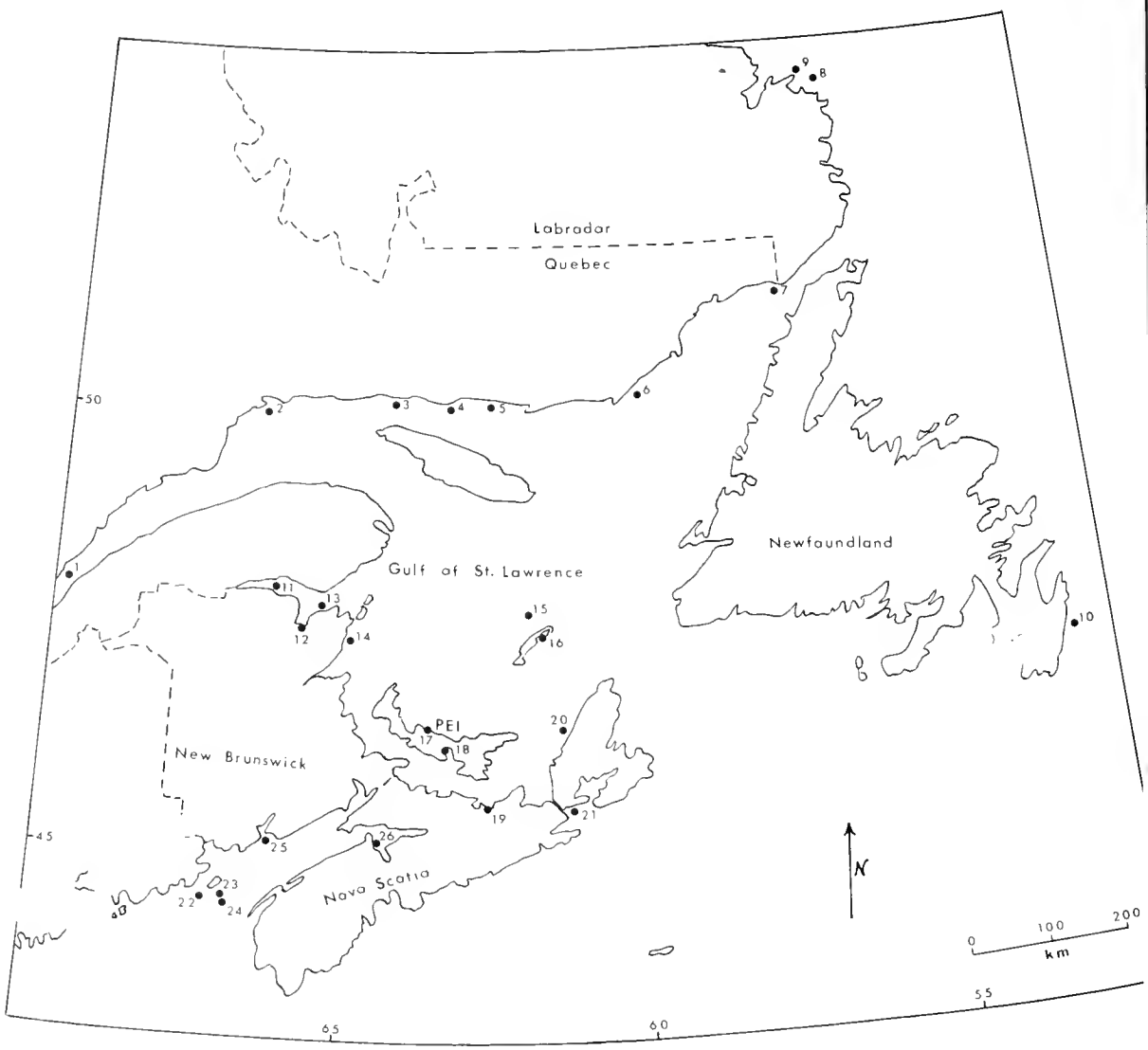


FIGURE 1. *Locations of seabird egg-sampling sites in the Atlantic Provinces and eastern Quebec, 1970–76*

1. Ile-aux-Pommes, Quebec.
2. Carrousel Island, Quebec.
3. Inner Birch Island, Quebec.
4. Betchouane, Quebec.
5. Watshishu, Quebec.
6. Ile Ste-Marie, Quebec.
7. Perroquet Island, Quebec.
8. Gannet Island, Newfoundland.
9. Bird Island, Newfoundland.
10. Great Island, Newfoundland.
11. Heron Island, New Brunswick.
12. Bathurst, New Brunswick.
13. Riorden, New Brunswick.
14. Tabusintac, New Brunswick.
15. Brion Island, Quebec.
16. Magdalen Islands, Quebec.
17. Cape Tryon, Prince Edward Island.
18. Charlottetown, Prince Edward Island.
19. Pictou, Nova Scotia.
20. Margaree Island, Nova Scotia.
21. Campbell Island, Nova Scotia.
22. Machias Seal Island, New Brunswick.
23. Low Duck Island, New Brunswick.
24. Kent Island, New Brunswick.
25. Manawagonish Island, New Brunswick.
26. Boot Island, Nova Scotia.

sample was extracted in a Soxhlet apparatus for 2 hours with 150 ml of a 1:3 mixture of ether-hexane at a rate of 10 siphonings/hour. After extraction, the solvent was removed in a Rotovapor flash evaporator, the dried flask was weighed, and the percent fat was calculated.

Some minor modifications were made during the vestigation. For eggs collected during 1970–71, cle involved the cold precipitation of fats with filtra through a carbon-Celite pad at —70°C (*34*). Prio the present study, the authors became aware of presence of PCBs in other wildlife samples, and th

: developed a Florisil separation method (*28*). Thus organochlorine residue data reported here are free PCB interference. PCB estimations were made ı Aroclor 1260 as the reference standard, and are averages of calculations for peaks No. 8 and No. 10. he cleanup of extracts of samples collected during 2–73, an alumina-Celite pad was substituted for the ›on-Celite pad used in the cold filtration process to rove PCB recoveries (*7*). Cleanup procedures for 1974–76 specimens were based on the use of 2 per- : water-deactivated Florisil (*29*).

hromatographic glass column was packed with 15 of regular grade Florisil which had been heated to °C and then deactivated with 2 percent water. The isil was topped with 1 cm sodium sulfate and the mn was washed with 100 ml hexane. A maximum).5 g oil or fat from the sample extract was mixed ı approximately 5 ml hexane and placed in the mn. Two fractions were eluted successively at roximately 5 ml/minute as follows: Fraction I, ed with 130–135 ml hexane, contained DDE, hexa›robenzene (HCB), and PCBs; Fraction II, eluted ı 300 ml of . . . rcent dichloromethane in hexane, tained TDE, . . dieldrin, endrin, and heptachlor xide.

lyses were performed on a Hewlett-Packard Model 0 gas chromatograph equipped with linear Ni^{63} elec-capture detector, a Model 7671A automatic sample ctor, and a Model 7123A recorder. Instrument ımeters and operating conditions follow:

Column:	0.64 cm × 183 cm × 4 mm ID, glass spiral, packed with a mixture of 3 percent OV-101 and 5 percent OV-210 on 80–100-mesh Chromosorb W (HP)
Temperatures:	injector 215°C detector 300°C column 215°C
Carrier gas:	5 percent methane in argon flowing at 60 ml/minute

sensitivity of the method was 0.001 ppm organo›rine pesticides and 0.01 ppm PCBs, on a wet-weight s. For practical purposes, values lower than 0.01 ı are not reported since the present mode of con›ation by differential gas chromatography (GC) or /mass spectrometry (MS) was not applicable at :r concentrations. Recoveries at concentrations of 1.0 ppm were above 90 percent except for HCB, for which they were 60 percent. Only HCB residues were corrected for recovery. As part of general quality control during the study, authors participated in several check sample programs, including those conducted by the Canada Committee on Pesticide Usage in Agriculture and the Organization for Economic Cooperation and Development.

MERCURY

Total mercury in 1970–73 samples was determined by wet digestion followed by flameless atomic absorption spectrophotometry (AAS) (*10*). About 0.5 g of the homogenate was weighed into a 50-ml Erlenmeyer flask to which 10 ml concentrated sulfuric acid was added. The flask was placed in a hot water shaker bath until everything dissolved. The cooled mixture was oxidized by the addition of 15 ml of 6 percent potassium permanganate ($KMnO_4$).

AAS was performed on a Varian Techtron Model AA–120 spectrophotometer as follows: Excess $KMnO_4$ was reduced by the dropwise addition of 20 percent aqueous hydroxylamine hydrochloride; the solution was diluted to 50 ml with distilled water. The dilute solution was placed in a Drechsel gas washing bottle with 1 ml 40 percent tin dichloride and, by use of the air purging method, absorption at 2537A was read. Authors used a mercury hollow cathode lamp as an energy source and a 15-cm-long absorption cell. Curve height was monitored on a Varian Model G2500 recorder and compared with a standard curve. The 1[illegible] samples were analyzed in essentially the same manner except that absorption was read by use of Pharmacia Fine Che[illegible]cals Ultraviolet Mercury Monitor equipped with a[illegible] long absorption cell. Sensitivity of the present method was 0.005 μg mercury. When 0.5 g of tissue was used, sensitivity was as low as 0.01 ppm. Many comparative studies have shown that the present method is reliable within ± 10 percent of the actual value, and spiked samples showed essentially total recoveries (*10*).

Results and Discussion

Organochlorine and mercury concentrations in the eggs of Leach's storm-petrel, double-crested cormorant, common eider, common tern, alcids other than Atlantic puffin, and Atlantic puffin are given in Tables 1–6,

TABLE 1. *Organochlorine and mercury concentrations in Leach's storm-petrel eggs collected in eastern Canadian coastal waters, 1972–76*

Site (Map ference)	Year	No. of Eggs	Arithmetic Mean		Geometric Mean (Range), ppm Wet Weight				Ratio of PCB/DDE
			% Fat	% Moisture	DDE	PCBs	Dieldrin	Mercury	
Island	1972	5	16.8	69.2	6.81 (4.61–8.38)	11.1 (7.51–15.4)	0.05 (0.05–0.07)	0.30 (0.26–0.35)	1.6
	1976	5	10.3	74.1	1.75 (1.37–2.35)	3.45 (2.80–4.66)	0.04 (0.03–0.05)	0.38 (0.25–0.51)	2.0
Island	1972	4	17.0	68.2	2.48 (1.19–8.35)	2.68 (1.81–4.04)	0.07 (0.05–0.13)	0.32 (0.26–0.45)	1.1
	1976	4	7.3	73.7	0.75 (0.52–1.69)	1.92 (1.37–5.06)	0.04 (0.03–0.07)	0.39 (0.31–0.48)	2.6

TABLE 2. *Organochlorine and mercury concentrations in double-crested cormorant eggs collected in eastern Canadian coastal waters, 1970–76*

Site (Map Reference)	Year	No. of Eggs	Arithmetic Mean		Geometric Mean (Range), ppm Wet Weight				Rati PCB/
			% Fat	% Moisture	DDE	PCBs	Dieldrin	Mercury	
Riorden (13)	1970	5	4.3	84.3	8.57 (4.82–17.7)	8.17 (5.10–19.7)	0.12 (0.05–0.59)	0.50 (0.40–0.60)	1.
Heron Island (11)	1970	10	3.8	84.6	5.93 (1.11–18.8)	8.63 (1.34–30.2)	0.15 (0.01–0.68)	0.27 (0.10–0.51)	1.
	1973	5	4.4	83.9	7.37 (4.03–17.9)	14.3 (9.86–26.1)	0.21 (0.14–0.27)	0.32 (0.26–0.44)	1.
Watshishu (5)	1972	5	6.3	85.1	7.56 (2.15–14.8)	13.8 (5.44–24.3)	0.19 (0.05–0.31)	0.34 (0.27–0.48)	1.
Ile Ste-Marie (6)	1972	10	7.7	83.8	4.99 (2.50–10.6)	9.45 (3.00–20.2)	0.12 (0.05–0.34)	0.25 (0.15–0.36)	1.
Pictou (19)	1972	5	3.6	83.1	4.21 (2.52–7.84)	11.4 (4.56–22.7)	0.15 (0.11–0.33)	0.26 (0.20–0.35)	2.
Magdalen Islands (16)	1973	5	4.6	84.0	7.44 (3.76–13.6)	19.3 (7.13–59.5)	0.16 (0.08–0.26)	0.30 (0.20–0.52)	2.
Cape Tryon (17)	1973	5	4.7	83.8	5.93 (2.56–11.0)	11.8 (3.67–21.0)	0.20 (0.06–0.30)	0.25 (0.19–0.31)	2.
Ile-aux-Pommes (1)	1972	5	2.0	85.3	2.85 (0.18–12.8)	11.5 (4.62–22.7)	0.12 (0.08–0.39)	0.32 (0.26–0.40)	4.
	1976	5	3.1	83.6	2.18 (1.16–3.25)	14.3 (9.13–18.7)	0.07 (0.02–0.17)	0.36 (0.16–0.54)	6.
Manawagonish Island (25)	1972	10	9.9	83.2	6.51 (3.46–20.0)	14.6 (9.88–22.3)	0.15 (0.05–0.36)	0.22 (0.14–0.39)	2.
	1976	5	3.8	83.1	1.49 (0.48–3.15)	6.31 (2.73–11.9)	0.06 (0.01–0.17)	0.24 (0.10–0.50)	4.
Boot Island (26)	1972	5	4.0	83.7	4.41 (2.16–13.1)	8.45 (6.13–22.3)	0.14 (0.08–0.44)	0.27 (0.17–0.52)	1.
	1976	5	3.5	83.0	1.66 (1.08–2.44)	5.66 (1.62–9.65)	0.07 (0.03–0.13)	0.25 (0.19–0.44)	3.
Campbell Island (21)	1976	5	4.0	83.6	1.61 (1.23–2.68)	9.71 (7.79–11.5)	0.10 (0.07–0.14)	0.21 (0.15–0.26)	6.

TABLE 3. *Organochlorine and mercury concentrations in common eider eggs collected in eastern Canadian coastal waters, 1972*

Site (Map Reference)	Year	No. of Eggs	Arithmetic Mean		Geometric Mean (Range), ppm Wet Weight				Rati PCB/
			% Fat	% Moisture	DDE	PCBs	Dieldrin	Mercury	
Inner Birch Island (3)	1972	5	17.6	66.7	0.38 (0.17–0.54)	1.83 (0.45–3.17)	0.02 (0.01–0.03)	0.08 (0.05–0.21)	4.
Watshishu (5)	1972	5	21.1	66.7	0.29 (0.25–0.34)	0.52 (0.36–0.67)	0.01 (0.01–0.01)	0.08 (0.05–0.12)	1.
Ile Ste-Marie (6)	1972	10	21.4	66.0	0.29 (0.21–0.69)	0.57 (0.35–2.03)	0.01 (ND–0.02)	0.03 (0.01–0.06)	2.
Low Duck Island (23)	1972	5	16.6	66.4	0.59 (0.36–0.96)	4.67 (1.94–30.0)	0.02 (0.01–0.04)	0.05 (0.04–0.09)	7.

NOTE: ND = not detected = <0.001 ppm.

TABLE 4. *Organochlorine and mercury concentrations in common tern eggs collected in eastern Canadian coastal waters, 1970–73*

Site (Map Reference)	Year	No. of Eggs	Arithmetic Mean		Geometric Mean (Range), ppm Wet Weight				Rati PCB/
			% Fat	% Moisture	DDE	PCBs	Dieldrin	Mercury	
Bathurst (12)	1970	10	9.6	77.1	0.88 (0.70–1.61)	1.99 (1.12–6.93)	0.04 (0.03–0.11)	—[1]	2.
	1972	10	13.3	76.0	0.62 (0.45–1.19)	1.96 (1.17–4.79)	0.03 (0.01–0.05)	0.12 (0.08–0.20)	3.
	1973	10	7.8	76.8	0.49 (0.26–0.61)	1.48 (0.90–2.09)	0.02 (0.01–0.05)	0.08 (0.04–0.14)	3.
Tabusintac (14)	1973	5	8.6	76.0	0.52 (0.37–0.61)	1.37 (1.22–1.61)	0.03 (0.01–0.05)	0.06 (0.04–0.10)	2.
Magdalen Islands (16)	1973	5	9.1	76.8	0.54 (0.15–1.52)	1.95 (1.33–3.23)	0.08 (0.04–0.13)	0.11 (0.08–0.17)	3.
Charlottetown (18)	1973	5	8.5	76.2	1.11 (0.80–3.36)	1.95 (0.77–3.91)	0.05 (0.03–0.11)	0.16 (0.08–0.31)	1.
Margaree Island (20)	1973	5	9.6	76.3	0.95 (0.44–1.44)	1.86 (1.15–2.59)	0.04 (0.03–0.06)	0.09 (0.07–0.15)	1.

[1] Not examined for mercury.

respectively. Lipid and moisture content are also given. Because of the strongly skewed distribution of residue levels, residue data are given as geometric means. The unskewed distribution of fat and moisture data allows their more conventional presentation as arithm means.

Organochlorine pesticide and other pollutant con

TABLE 5. *Organochlorine and mercury concentrations in eggs of the razorbill, common murre, and black guillemot from eastern Canadian coastal waters, 1971–73*

Site (Map eference)	Year	No. of Eggs	Arithmetic Mean		Geometric Mean (Range), ppm Wet Weight				Ratio of PCB/DDE
			% Fat	% Moisture	DDE	PCBs	Dieldrin	Mercury	
RAZORBILL									
ousel land (2)	1972	5	14.4	71.4	4.54 (2.30–14.9)	21.7 (12.8–37.3)	0.15 (0.08–0.52)	0.08 (0.01–0.19)	4.8
Ste- arie (6)	1972	5	17.2	72.4	2.75 (1.82–3.28)	9.34 (6.29–15.0)	0.10 (0.06–0.15)	0.12 (0.08–0.15)	3.4
n Island 5)	1973	3	12.5	72.0	2.55 (2.14–3.10)	8.37 (7.72–12.1)	0.12 (0.01–0.16)	0.11 (0.04–0.25)	3.3
COMMON MURRE									
Ste- arie (6)	1971	4	17.0	67.6	2.03 (1.28–3.81)	2.21 (0.94–7.00)	0.02 (0.02–0.03)	0.12 (0.08–0.17)	1.1
BLACK GUILLEMOT									
dalen lands (16)	1973	3	9.9	73.8	1.04 (0.75–1.27)	2.13 (2.06–3.82)	0.02 (0.01–0.05)	0.13 (0.10–0.17)	2.0

TABLE 6. *Organochlorine and mercury concentrations in Atlantic puffin eggs collected in eastern Canadian coastal waters, 1972–76*

Site (Map eference)	Year	No. of Eggs	Arithmetic Mean		Geometric Mean (Range), ppm Wet Weight				Ratio of PCB/DDE
			% Fat	% Moisture	DDE	PCBs	Dieldrin	Mercury	
houane)	1972	5	16.2	71.4	1.19 (0.75–2.28)	4.42 (2.76–7.40)	0.06 (0.05–0.10)	0.15 (0.10–0.22)	3.7
Ste- arie (6)	1972	9	16.7	71.1	0.99 (0.62–1.72)	2.89 (1.20–5.11)	0.06 (0.04–0.10)	0.16 (0.07–0.24)	2.9
oquet land (7)	1972	5	14.8	69.9	1.49 (1.22–1.70)	3.99 (3.08–5.08)	0.07 (0.05–0.09)	0.16 (0.08–0.20)	2.7
net land (8)	1972	5	13.7	70.7	0.57 (0.43–0.73)	2.32 (1.69–2.90)	0.05 (0.04–0.06)	0.18 (0.16–0.21)	4.1
Island)	1972	5	17.5	72.0	0.58 (0.48–0.90)	1.90 (1.48–3.06)	0.04 (0.03–0.05)	0.18 (0.10–0.34)	3.3
n Island 5)	1973	1	10.2	73.2	1.46	4.19	0.06	0.16	2.9
t Island 0)	1972	3	15.8	68.7	0.76 (0.52–0.89)	1.67 (1.49–1.99)	0.05 (0.04–0.06)	0.26 (0.21–0.33)	2.2
	1976	5	10.2	71.5	0.59 (0.43–0.87)	1.86 (1.63–2.00)	0.04 (0.04–0.05)	0.23 (0.14–0.28)	3.2
hias al Island 2)	1972	5	13.0	71.5	2.57 (1.97–3.89)	7.20 (5.80–8.19)	0.09 (0.07–0.11)	0.20 (0.18–0.26)	2.8
	1976	5	11.3	70.7	1.27 (0.75–1.76)	6.10 (4.73–6.59)	0.08 (0.06–0.13)	0.09 (0.06–0.12)	4.8

ions in eggs can be adjusted for loss of lipid and isture during incubation (*30*). The problem of how t to express organochlorine residues in homogenized an eggs has been further addressed by Peakall and man (*25*). They showed that in the herring gull *urus argentatus*) the lipid and moisture contents of combined yolk and albumin remain fairly constant r the incubation period, as do lipid and moisture tents of the developing embryo. The yolk-plus-umin:embryo ratio shifts continuously as the em-o grows. The lipid content of the total egg decreases one fifth during incubation, and the moisture con-t decreases to about four fifths. One can conclude m the data of Peakall and Gilman (*25*) that, where ge of incubation varies from sample to sample, nparisons of residues of whole egg contents will be re accurate on a wet-weight than on a lipid-weight is. Moisture content of samples in the present study ied little within species, and residue data are ex-ssed on a wet-weight basis.

In the present study, all organochlorine residues except DDE and PCBs are low in all samples. Mean DDE ranged from 0.29 ppm in common eider to 8.57 ppm in double-crested cormorant. Mean PCBs ranged from 0.52 ppm in common eider to 21.7 ppm in razorbill. Authors found TDE and *p,p'*-DDT in most samples frequently at < 0.01 ppm and < 0.10 ppm, respectively, *p,p'*-DDT exceeded 0.10 ppm only in eggs of Leach's storm-petrel, mean concentrations being 0.33 ppm and 0.39 ppm in Kent Island eggs in 1972 and 1976, respectively, and 0.17 ppm and 0.15 ppm in eggs from Great Island in 1972 and 1976, respectively. Dieldrin was present in most eggs. The highest concentration, 0.68 ppm, was found in eggs of the double-crested cormorant collected in 1970 on Heron Island. HCB was found in all eggs, corrected residue concentrations being < 0.10 ppm except in alcids, in which they ranged to 0.23 ppm in razorbill and puffin, and to 0.27 ppm in murre. Heptachlor epoxide occurred at low concentrations in most eggs, exceeding 0.05 ppm in

less than 5 percent of the total. Endrin was found only in 1972 samples, at < 0.10 ppm except in the eggs of razorbill in which it ranged from 0.10 to 0.21 ppm. *cis*-Chlordane and oxychlordane residues of < 0.10 ppm were found in all eggs in 1976, but only in that year. The lowest mean mercury concentration, 0.03 ppm, was noted in common eider eggs collected in 1972 at Ile Ste-Marie. The highest mean mercury level, 0.50 ppm, was recorded for double-crested cormorant eggs collected in 1970 at Riorden.

DDE and PCB concentrations in the eggs of several species collected in the Bay of Fundy were compared. Although Leach's storm-petrel is pelagic and feeds on small crustaceans and cephalopods (*21*) at low trophic levels, eggs of that species contained the highest residues. Presumably that is because petrels feed at the interface of the air and water where organochlorines first reach the oceans and where they may be held by a thin oily film on the surface.

The relatively high organochlorine concentrations in cormorants would be expected; cormorants eat fish of considerable size and are essentially coastal. Other Bay of Fundy double-crested cormorant colonies were reported to be more heavily contaminated in 1971 (*35*) than those sampled in the present study. When compared on a lipid-weight basis, DDE and PCB residues in double-crested cormorant eggs from most of the sites sampled in the present study were higher than those reported in eggs of that species from the Strait of Georgia, British Columbia (*20*).

Residues were low in eider eggs, despite the predominance in their diet of mollusks (*22*), which are considered to be good accumulators of chemical pollutants (*26*) and which may reflect local levels of contamination where exposure is chronic. At Ile Ste-Marie, in the Gulf of St. Lawrence, residues were highest in double-crested cormorants and lowest in eiders; no petrel eggs were collected there. Among the Alcidae at that site, residues were highest in the razorbill, and lowest in the Atlantic puffin. As with organochlorines, mercury concentrations were lowest in eiders and terns, intermediate in alcids, and highest in cormorants and petrels.

Changes in contaminant concentrations in eggs between 1972 and 1976 can be compared in three species at six sites: Leach's storm-petrel at Kent Island and Great Island; double-crested cormorant at Manawagonish Island, Boot Island, and Ile-aux-Pommes; and Atlantic puffin at Machias Seal Island and Great Island. In all cases DDE residues decreased, but significantly only in petrels at Kent Island ($P < 0.01$), puffins at Machias Seal Island ($P < 0.01$), and cormorants at Manawagonish Island ($P < 0.05$). PCB concentrations decreased significantly ($P < 0.01$) in petrels at Kent Island and cormorants at Manawagonish Island increased significantly ($P < 0.01$) in puffins at G Island. The ratio of PCBs to DDE increased betv 1972 and 1976 in all cases, indicating that DDE centrations in the foods of those birds decreased r rapidly than PCB concentrations. There was little i cation of changes in mercury contamination of the over that time period. Authors feel that the ab reported analytical refinements were minor and do invalidate comparisons of changes in residue con trations over time.

DDE and PCB residues in Atlantic puffin eggs colle from the Bay of Fundy were considerably higher < 0.01) in 1972 and 1976 than residues in eggs f an open-ocean colony off Newfoundland. Winte areas of puffins inhabiting those colonies are unkn and females returning there from the open ocean not carry equivalent contaminant loads. If contami loads of such birds were equivalent the uptake organochlorines between arrival of females and formation, a period of about four weeks in G Britain (*17*), would have to be much more rapi the Bay of Fundy, presumably reflecting a more taminated environment there. In the present study, D residues in Leach's storm-petrel eggs were also hi in the Bay of Fundy than they were in Newfoundl in 1972 ($P < 0.05$) and in 1976 ($P < 0.01$). Ag the interval between arrival at the colony and egg la was about a month (*21*).

TABLE 7. *DDE concentrations associated with 20% shell thinning in the eggs of Procellariiformes, Pele formes, Ciconiiformes, and Charadriiformes*

Species	DDE, ppm Wet Weight	Referen
Procellariiformes		
Leach's storm-petrel (*Oceanodroma leucorhoa*)	12[1]	This stu
Pelecaniformes		
Brown pelican (*Pelecanus occidentalis*)	8	(*3*)
Gannet (*Morus bassanus*)	11[2]	(*23*)
Great cormorant (*Phalacrocorax carbo*)	10	(*15*)
Double-crested cormorant (*Phalacrocorax auritus*)	10	This stu
Ciconiiformes		
Great blue heron (*Ardea herodias*)	47[3]	(*9*)
Grey Heron (*Ardea cinerea*)	25	(*5*)
Charadriiformes		
Herring gull (*Larus argentatus*)	160[4]	(*32*)
Common tern (*Sterna hirundo*)	25	(*31*)
Razorbill (*Alca torda*)	45[1]	This stu
Atlantic puffin (*Fratercula arctica*)	30[1]	This stu

[1] Extrapolated. Linear regressions were used and correlation c cients were calculated using the Pearson product-moments form
[2] Assuming 10 percent lipid.
[3] Assuming 10 percent lipid, level associated with 16 percent thin
[4] Assuming water content of 80 percent.

he present study, DDE and PCB residues in razor- eggs were one to two orders of magnitude lower ı residues in razorbill eggs collected from the Baltic in 1970–72 (*2*). DDE and PCB levels in Atlantic in eggs from the colonies in Newfoundland-Labra- were high compared to samples collected at St. la in 1969 (*24*). DDE residues in Leach's storm- el eggs from Kent Island and Great Island in 1968) were similar to 1972 samples in the present study reflect the same contrast between sites. When com- ed on a lipid-weight basis, DDE concentration in ch's storm-petrel eggs from the west coast of Van- ver Island in 1970 (*20*), the only other literature ıe apparently available, was similar to the values orted here, but the present PCB residues were con- rably higher. DDE and PCB concentrations in the s of the fork-tailed storm-petrel (*O. furcata*) from Queen Charlotte Islands (*20*) were similar to the ıes reported here, but DDE residues in ashy storm- el (*O. homochroa*) eggs from the California coast were much higher.

significance of elevated mercury concentrations in ine birds is not yet known. The most serious effect DDE on the reproduction of birds is eggshell thin- g, which has been demonstrated in a variety of cies (*4*). Laboratory experiments and field investi- ons indicate that, in the absence of effects caused eggshell thinning, high concentrations of organo- orines are required to impair reproductive success. ring gulls on Lake Huron and Lake Superior re- duce normally despite residues of 15–20 ppm DDE 50–60 ppm PCBs in their eggs (*11*), whereas ble-crested cormorants showed severe declines and ere eggshell thinning at 7–11 ppm DDE and 10–12 ı PCBs (*27*). DDE caused eggshell thinning in the ble-crested cormorant in prairie states and provinces, was related to a severe colony decline in Wisconsin . Laboratory studies have shown that most organo- orines are relatively nontoxic when injected into cken eggs at concentrations up to 250 ppm (*8*).

DDE concentration associated with eggshell thin- g varies greatly among species. Residues of DDE ociated with 20 percent eggshell thinning, considered be the population damage threshold, have been ulated for six species (*14*). That amount of thinning been correlated with population declines of several cies of fish-eating and raptorial birds (*13*). In Table ıe published data relating DDE in eggs to 20 per- t eggshell thinning in aquatic birds are summarized.

gshell thickness indices were plotted against DDE centrations in eggs. For the Leach's storm-petrel, in ch the relationship showed a correlation coeffi- ıt of −0.74, extrapolation of the regression analysis icates that 12 ppm DDE (wet weight) would be expected to be associated with 20 percent eggshell thinning. Although Leach's storm-petrel is apparently sensitive to DDE, that level of contamination was not reached in any of the eggs of that species taken during the present survey. In the case of the double-crested cormorant, 10 ppm DDE was related to 20 percent eggshell thinning, a value which corresponds well with those found by other investigators for the double-crested cormorant (*1, 12*) and closely related species (*15*). DDE residues exceeded 10 ppm in one-fifth of the cormorant eggs analyzed in the present study. Regression plots of eggshell thickness indices against DDE for two species of Alcidae, the razorbill and the Atlantic puffin, gave low correlation coefficients of −0.40 and −0.47, respectively. The razorbill sample was small, DDE exceeding 5 ppm in only one egg. The occurrence of significant eggshell thinning could not be related to much higher levels of ΣDDT in razorbill eggs from the Baltic Sea (*2*). The present Atlantic puffin data varied significantly, like data on the common tern (*31*). It appears that alcids, like other members of the Charadriiformes (*13, 32*), are relatively insensitive to DDE.

Authors conclude that among the species investigated some populations of double-crested cormorants probably have been adversely affected by DDE, through shell thinning, and that the margin of safety for Leach's storm-petrel is narrow. The other species investigated probably were unaffected.

Acknowledgments

Authors wish to thank the following for their direct or indirect assistance in collecting the samples: H. P. Barkhouse, W. R. Barrow, G. Boyd, J. V. Dobell, N. R. Garrity, S. Homer, B. C. Johnson, D. N. Nettleship, A. Reed, and A. D. Smith. Useful comments on the manuscript were made by A. J. Erskine, J. A. Keith, and S. W. Speller.

LITERATURE CITED

(*1*) *Anderson, D. W., J. J. Hickey, R. W. Risebrough, D. F. Hughes, and R. E. Christensen. 1969.* Significance of chlorinated hydrocarbon residues to breeding pelicans and cormorants. Can. Field Nat. 83(2):91–112.

(*2*) *Andersson, A., T. Odsjö, and M. Olsson. 1974.* Breeding success of razorbill in the Archipelago of Stockholm in relation to eggshell thickness and levels of DDT, PCB and mercury in eggs. Statens Naturvärdsverk PM 483. 30 pp.

(*3*) *Blus, L. J., G. D. Gish, A. A. Belisle, and R. M. Prouty. 1972.* Logarithmic relationship of DDE residues to eggshell thinning. Nature 235(5338):376–377.

(4) *Cooke, A. S. 1973.* Shell thinning in avian eggs by environmental pollutants. Environ. Pollut. 4(2):85–152.

(5) *Cooke, A. S., A. A. Bell, and I. Prestt. 1976.* Egg shell characteristics and incidence of shell breakage for grey herons (*Ardea cinerea*) exposed to environmental pollutants. Environ. Pollut. 11(1):59–84.

(6) *Coulter, M. C., and R. W. Risebrough. 1973.* Shell-thinning in eggs of the ashy petrel (*Oceanodroma homochroa*) from the Farallon Islands. Condor 75 (2):254–255.

(7) *Dilworth, T. G., J. A. Keith, P. A. Pearce, and L. M. Reynolds. 1972.* DDE and eggshell thickness in New Brunswick woodcock. J. Wildl. Manage. 36(4):1186–1193.

(8) *Dunachie, J. F., and W. W. Fletcher. 1969.* An investigation of the toxicity of insecticides to birds' eggs using the egg-injection technique. Ann. Appl. Biol. 64(2):409–423.

(9) *Faber, R. A., and J. J. Hickey. 1973.* Eggshell thinning, chlorinated hydrocarbons, and mercury in inland aquatic bird eggs, 1969 and 1970. Pestic. Monit. J. 7(1):27–36.

(10) *Fimreite, N., and L. M. Reynolds. 1973.* Mercury contamination of fish in northwestern Ontario. J. Wildl. Manage. 37(1):62–68.

(11) *Gilman, A. P., G. A. Fox, D. B. Peakall, S. M. Teeple, T. R. Carroll, and G. T. Haymes. 1977.* Reproductive parameters and egg contaminant levels of Great Lakes herring gulls. J. Wildl. Manage. 41 (3):458–468.

(12) *Gress, F., R. W. Risebrough, D. W. Anderson, L. F. Kiff, and J. R. Jehl, Jr. 1973.* Reproductive failures of double-crested cormorants in southern California and Baja California. Wilson Bull. 85(2):197–208.

(13) *Hickey, J. J., and D. W. Anderson. 1968.* Chlorinated hydrocarbons and eggshell changes in raptorial and fish-eating birds. Science 162(3850):271–273.

(14) *Keith, J. A., and I. M. Gruchy. 1972.* Residue levels of chemical pollutants in North American birdlife. Proc. 15th Intern. Ornithol. Congr. Brill, Leiden. pp. 437–454.

(15) *Koeman, J. H., T. Bothof, R. De Vries, H. Van Velzen-Blad, and J. G. Vos. 1972.* The impact of persistent pollutants in piscivorous and molluscivorous birds. TNO-nieuwas 27(10):561–569.

(16) *Kury, C. R. 1969.* Pesticide residues in a marine population of double-crested cormorants. J. Wildl. Manage. 33(1):91–95.

(17) *Lockley, R. M. 1962.* Puffins. Doubleday, New York, N.Y., pp. 19–68.

(18) *Nettleship, D. N. 1975.* A recent decline of gannets, *Morus bassanus*, on Bonaventure Island, Quebec. Can. Field Nat. 89(2):125–133.

(19) *Nettleship, D.N. 1977.* Seabird resources of eastern Canada: status, problems and prospects. *In* Canada's Threatened Species and Habitats. T. Mosquin ar Suchal, Eds. pp. 96–108. Canadian Nature Fe tion, Ottawa, Ontario, Canada.

(20) *Ohlendorf, H. M., R. W. Risebrough, and K. Ver 1978.* Exposure of marine birds to environm pollutants. Fish and Wildlife Service, U.S. Depart of the Interior, Wildlife Research Report 9. 40 p

(21) *Palmer, R. S. 1962.* Handbook of North Ame Birds, Vol. 1. Yale University Press, New Ha Conn. pp. 230–234.

(22) *Palmer, R. S. 1972.* Handbook of North Ame Birds, Vol. 3. Yale University Press, New Ha Conn. pp. 80–82.

(23) *Parslow, J. L. F., and D. J. Jeffries. 1977.* Ga and toxic chemicals. Brit. Birds 70(9):366–372.

(24) *Parslow, J. L. F., D. J. Jeffries, and M. C. Fre 1972.* Ingested pollutants in puffins and their Bird Study 19(1):18–33.

(25) *Peakall, D. B., and A. P. Gilman. 1979.* Limita of expressing organochlorine levels in eggs on a l weight basis. Bull. Environ. Contam. Toxicol. press).

(26) *Phillips, D. J. H. 1977.* The use of biological cator organisms to monitor trace metal pollutio marine and estuarine environments—a review. viron. Pollut. 13(4):281–317.

(27) *Postupalsky, S. 1971.* Toxic chemicals and decli bald eagles and cormorants in Ontario. Can. W Serv. Pesticide Section Manuscript Rept. No. 20.

(28) *Reynolds, L. M. 1969.* Polychlorobiphenyls (PC and their interference with pesticide residue anal Bull. Environ. Contam. Toxicol. 4(3):128–143.

(29) *Reynolds, L. M., and T. Cooper. 1975.* The ana of organochlorine residues in fish. ASTM W Quality Parameters. STP 573, pp. 196–205.

(30) *Stickel, L. F., S. N. Wiemeyer, and L. J. Blus. 1* Pesticide residues in eggs of wild birds: adjustr for loss of moisture and lipid. Bull. Environ. C tam. Toxicol. 9(4):193–196.

(31) *Switzer, B., V. Lewin, and F. H. Wolfe. 1973.* I and reproductive success in some Alberta com terns. Can. J. Zool. 51(10):1081–1086.

(32) *Teeple, S. M. 1977.* Reproductive success of her gulls nesting on Brothers Island, Lake Ontario 1973. Can. Field Nat. 91(2):148–157.

(33) *Trites, R. W. 1972.* The Gulf of St. Lawrence fro pollution viewpoint. Marine pollution and sea FAO and Fishing News (Books) Ltd., Surrey, l land. pp. 59–72.

(34) *Vermeer, K., and L. M. Reynolds. 1970.* Orga chlorine residues in aquatic birds in the Cana prairie provinces. Can. Field Nat. 84(2):117–130

(35) *Zitko, V., and P. M. K. Choi. 1972.* PCB and p DDE in eggs of cormorants, gulls, and ducks from Bay of Fundy, Canada. Bull. Environ. Contam. T col. 7(1):63–64.

Residues of Polychlorinated Biphenyls and DDT in Water and Sediment of the St. Lucie Estuary, Florida, 1977[1]

Tsen C. Wang, Joseph P. Krivan, Jr., and Robert S. Johnson

ABSTRACT

DT residues in the St. Lucie River bottom sediments eased after Lake Okeechobee water was discharged ugh the St. Lucie Canal into the area. ΣDDT levels e highest in sediment samples from the Palm City area, ging from 1.8 ppb to 6.15 ppb. Sediment samples from A1A Highway Bridge area contained 1.6–6.8 ppb clor 1254. Levels of polychlorinated biphenyls (PCBs) ΣDDT in sediment samples from the junction of the Lucie and Indian Rivers were not detectable. Surface er samples from the estuary did not show any de- able DDT or PCB residues.

Introduction

St. Lucie Estuary is a tidewater at the junction of North and South Forks of the St. Lucie River near art, Martin County, Florida (Fig. 1). The main r empties into the Atlantic Ocean through the St. ie Inlet. The Indian River, a shallow lagoon, flows oss the St. Lucie River and also discharges into the Lucie Inlet. The St. Lucie Canal leaves Lake Okee- bee at Port Mayaca and extends to the South Fork the St. Lucie River at Stuart. Lake Okeechobee er released through the St. Lucie Canal carries fine d, shell fragments, and organic material into the Lucie Estuary (*3*). Runoff from the canal could oduce organochlorine and organophosphorus insec- ides into the estuary aquatic environment (*6, 7, 9*). purpose of this work was to survey polychlorinated henyls (PCBs) and ΣDDT in water and sediments he St. Lucie Estuary.

Sampling and Analysis

mples of surface water and sediment were collected at erent locations on the river as shown in Figure 1. mples were taken June 14, June 21, and July 8, 1977.

ab water samples were collected in one gallon glass ent bottles that had been cleaned with chromic acid, tone, and methylene chloride. Three liters of each sample was drained through a glass column containing 50 ml Amberlite XAD-2 resin (*4*) at 250 ml/minute. The column was eluted with 200 ml acetonitrile at full gravity flow, followed by 500 ml distilled water. The combined eluate was then extracted with hexane. The water extracts were cleaned on a Florisil microcolumn (*8*) before gas chromatographic analysis.

A copper core sampler was used to take the sediment samples. Three samples, collected from each station on the river, were composited and subsampled for analysis. The 100-g subsamples were extracted with isopropyl alcohol–hexane solvent. The sediment was extracted first in isopropyl alcohol and then in hexane to recover the isopropyl alcohol together with desorbed material. The extract was washed with distilled water, filtered through a sodium sulfate–Celite column, and concentrated to 1 ml before cleanup (*13*). The hexane extract was then passed through a Florisil column, and the first fraction was passed through a silicic acid column to separate PCBs from the chlorinated pesticides (*2*). Activated copper foil was added to the first fraction to remove any sulfur from the bottom sediment extracts before they were applied to the silicic acid column (*5, 12*). Residues in the samples were further treated with potassium hydroxide for confirmation and sample cleanup (*1, 14*).

Compounds were identified by electron-capture gas chromatography on dual columns packed with 1.5 percent OV-17 plus 1.95 percent QF-1 and 4 percent SE-30 plus 6 percent OV-210 solid support. Samples of sufficient size and concentration were confirmed by thin-layer chromatography (*11*). PCBs and ΣDDT were quantified by matching the unknown peaks on the chromatogram to the standard samples. Lower detection limits for PCBs and ΣDDT were 0.5 ppb and 0.01 ppb in water and 0.10 ppb and 1.0 ppb in bottom sediment, respectively. After water and sediment samples were collected from the St. Lucie River, duplicate residue analyses were performed. The arithmetic means of PCB and ΣDDT concentrations for each sediment sample are presented in Table 1.

bor Branch Foundation, Inc., Rural Route 1, Box 196, Fort e, Fla. 33450. Harbor Branch Contribution No. 148.

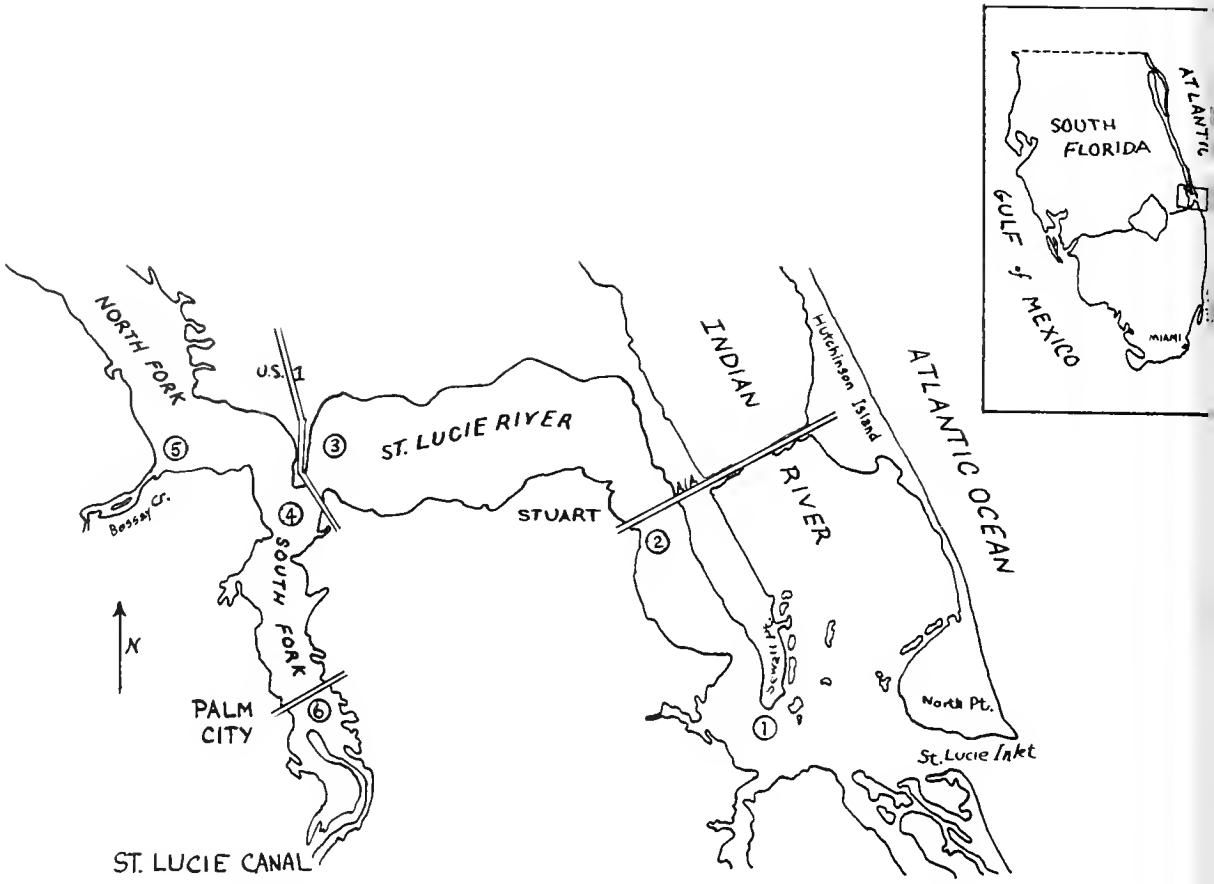


FIGURE 1. *Sampling stations on the St. Lucie Estuary, Florida, 1977 (See Table 1 for key identification.)*

Results and Discussion

Three sets of water and sediment samples collected on different dates were analyzed. The results are shown in Table 1. Sediment samples from Station 2, near Highway A1A bridge, contained 1.6–6.8 ppb Aroclor 1254. This area could be locally contaminated by any PCB-containing fluids or formulations such as hydraulic fluids, plasticizers, lubricants, heat exchanger electric transformers, insulators, paints, or sealing compounds (*10*). No PCBs were found at any of the other sampling stations.

As shown in Table 1, ΣDDT levels were higher in the second and third sets of samples than in the first set. On June 20, 1977, the St. Lucie Canal discharged water from Lake Okeechobee through the St. Lucie River at a rate of 1,000 ft^3/minute. The second set of samples was collected during the second day that the canal water was being discharged into the estuary. The th set of samples was collected during the last two days the discharging schedule. The higher concentration DDT compounds in the second and third sets of samp could be due to runoff from the canal.

Highest ΣDDT levels were 1.8–6.15 ppb in samp from Station 6, near the Palm City Bridge. Signific ΣDDT levels were found in sediment samples as lows: from the junction of Bessey Creek and No Fork, 0.2–1.69 ppb; from the junction of South F and North Fork, 0.85 ppb; near Highway US1, 0. 0.68 ppb; and near A1A Bridge, 0.6–1.09 ppb. samples from Station 1, about 15 miles from Palm C DDT and PCBs were not detectable.

Three sets of surface water samples were also collec and analyzed. PCBs and DDT were not found in water samples.

TABLE 1. *Residues of polychlorinated biphenyls and ΣDDT in sediment of the St. Lucie Estuary, Florida, 1977*

LE IFR	Sampling Station Area	Detectable Compounds	Arithmetic Mean Residues, ppb		
			June 14, 1977	June 21, 1977	July 8, 1977
	Junction of the St. Lucie and Indian Rivers		DDT & PCBs were not detected		
	Highway A1A Bridge	Aroclor 1254	6.8	1.6	4.6
		p,p'-TDE	0.6	0.25	0.89
		p,p'-DDE	ND	0.56	0.20
		ΣDDT	0.6	0.81	1.09
	Highway U.S. 1 Bridge	*o,p'*-DDE	ND	0.17	ND
		p,p'-DDE	0.09	0.29	0.31
		p,p'-TDE	ND	0.22	0.19
		ΣDDT	0.09	0.68	0.50
	Junction of South and North Forks	*o,p'*-DDE	—	0.53	ND
		p,p'-DDE	—	0.18	0.53
		p,p'-TDE	—	0.15	0.32
		ΣDDT	—	0.86	0.85
	Bessey Creek, North Fork	*o,p'*-DDE	ND	0.53	ND
		p,p'-DDE	0.2	0.73	0.16
		o,p'-TDE	ND	0.13	ND
		p,p'-TDE	ND	0.30	0.14
		ΣDDT	0.2	1.69	0.30
	Palm City Bridge, South Fork	*o,p'*-DDE	ND	0.92	0.52
		p,p'-DDE	ND	0.94	0.83
		o,p'-TDE	ND	0.24	0.30
		p,p'-TDE	1.8	0.75	1.10
		o,p'-DDT	ND	ND	1.10
		p,p'-DDT	ND	ND	2.30
		ΣDDT	1.8	2.85	6.15

3: ND = not detected.

LITERATURE CITED

Ahnoff, M., and B. Josefsson. 1975. Cleanup procedures for PCB analysis on river water extracts. Bull. Environ. Contam. Toxicol. 13(2):159–166.

Armour, J. A., and J. A. Burke. 1970. Method for separating polychlorinated biphenyls from DDT and its analogs. J. Assoc. Off. Anal. Chem. 53(4):761–768.

Gulf Research Reports. 1963. St. Lucie Estuary. Ocean Springs, Miss. 1(5):192–194.

Harvey, G. R. 1972. Absorption of chlorinated hydrocarbons from seawater by a crosslinked polymer. Tech. Rept. Woods Hole Oceanographic Institution, Woods Hole, Mass. pp. 1–17.

Johnsen, R. E., and L. Y. Munsell. 1977. Facile elimination of sulfur interference in pesticide analysis by gas chromatography. Bull. Environ. Contam. Toxicol. 17(5):573–576.

Johnson, D. W. 1968. Pesticide and fishes: a review of selected literature. Trans. Am. Fish. Soc. 97(4):398–424.

Lauer, G. J., H. P. Nicholson, W. S. Cox, and J. I. Teasley. 1966. Pesticide contamination of surface waters by sugarcane farming in Louisiana. Trans. Am. Fish. Soc. 95(3):310–316.

Law, L. M., and D. F. Goerlitz. 1970. Microcolumn chromatographic cleanup for the analysis of pesticides in water. *J. Assoc. Off. Anal. Chem.* 53(6):1276–1286.

(9) *Nicholson, H. P., and D. W. Hill. 1970.* Pesticide contamination of water and mud and their environmental impact. Proc. Cornell University Conf. Waste Management, Ithaca, N.Y. pp. 178–179.

(10) *Nisbet, I. C. T., and A. F. Sarofim. 1972.* Rates and routes of transport of PCBs in the environment. Environ. Health Perspect. 1(1):21.

(11) *Oliver, B. M. 1972.* TLC systems for identification of pesticides, Paper TSD–1, Chemical and Biological Investigation Branch, U.S. Environmental Protection Agency, Washington, D.C. pp. 1–5.

(12) *Thompson, J. F. (ed.). 1974.* Manual of Analytical Methods for the Analysis of Pesticide Residues in Human and Environmental Samples, U.S. Environmental Protection Agency, Washington, D.C. Section 9C, pp. 1–9.

(13) *U.S. Environmental Protection Agency. 1972.* Laboratory Manual, National Monitoring Laboratory, Bay St. Louis, Miss. pp. 18–19.

(14) *Young, S. J. V., and J. A. Burke. 1972.* Micro scale alkali treatment for use in pesticide residue confirmation of sample cleanup. Bull. Environ. Contam. Toxicol. 7(2):160–167.

SOILS

Dicofol Residues in United States Soils Having a Known History of Its Use as a Miticide, 19

William R. Lyman [1] and Rollin J. Anderson [2]

ABSTRACT

Soil samples were collected from a total of 21 sites in California, Washington, Florida, Pennsylvania, and Michigan. Dicofol (Kelthane) miticide had been applied at various times over a 5-year period to 17 of the sites; four sites had received no applications. Samples were collected at 0–75-mm and 75–150-mm depths, and submitted to gas-liquid chromatographic analysis. Samples from only four of the 17 treated sites contained mean residues equal to or exceeding 2.00 ppm. Residues in all cases were only a small fraction of the total amount applied. Apparently, a mechanism for the dissipation of dicofol exists, but it is unidentified at this time.

Introduction

Dicofol is marketed as a miticide under the trade name Kelthane. In laboratory studies, dicofol has shown little tendency toward microbial degradation or migration in soil through leaching (Rohm and Haas Co., unpublished data: 1978). It is subject to some photolytic degradation and, under alkaline conditions, breaks down readily to yield chloroform and 4,4′-dichlorobenzophenone. Studies have shown that dicofol residues are low compared to residues of DDT and other organochlorine insecticides (*2–6, 8–10*). Harris and Sans confirmed that residues tend to remain near the surface (*3*). In general, however, no information was given on the amounts applied. When such information was provided, the amounts applied were relatively low. This paper reports the results of analyses of soil samples collected during 1974 from sites where the history of dicofol usage was known. Sites represented widely separated geographical locations within the United States and five different categories of use history. A range of soil types resulted incidentally.

Sample Collection

Through Rohm and Haas Company field sales representatives and their contacts with growers, distributors, and spray applicators, growers were sought who had records of the amounts and timing of dicofol applications to their crops or orchards over a period of years. In this way a total of 17 sites in California, Washington, F ida, Pennsylvania, and Michigan were selected. S were chosen in five use history categories as follo dicofol applied for five or more successive years inc ing 1973; dicofol applied for several successive y including 1972, but not in 1973; dicofol applied several successive years but not later than 1971; dic applied in 1973, but not previously; no known us dicofol.

Most sites selected were 10–20-ha. apple or ci orchards. Soil was taken with a core sampler at de of 0–75 mm and 75–150 mm from ten or more domly selected spots within each site. The core samp were 19 mm (¾ inch) in diameter except in Flo sand where a 12-mm (½ inch) sampler was used. 0–75-mm segments from the various cores were c posited as were the 75–150-mm segments. Samples v shipped to the laboratory where they were stored fr until analysis.

Analyses

A 50-g representative subsample, free of stones, added to 10 ml water in a one-pint Waring Blendo and allowed to stand 30 minutes. The subsample blended with 50 ml isopropanol for 2 minutes at speed. Then 100 ml benzene was added, and the mix was blended for 3 minutes. The mixture was filt with suction; transfer and rinse were accomplished a 1:2 mixture of isopropanol–benzene, bringing the volume to 200 ml. Forty ml of extract, equivalen 10 g soil, was dried in a rotary vacuum evaporator, the residue was dissolved in petroleum ether. Flo was activated by heating overnight for 16 hours ir oven at 100°C, then deactivated by the addition percent water. The adsorbent was packed into a 1- diameter column to a depth of 10 cm, and topped 2 cm anhydrous sodium sulfate. The petroleum e solution was poured onto the column. The flask rinsed with 10 ml petroleum ether and the column washed with 20 ml petroleum ether; all effluents discarded. Dicofol was eluted with 25 ml of 2 per ethyl ether in petroleum ether. The eluate was ev rated to dryness and dissolved in 1 ml *n*-hexane; 0 anhydrous sodium sulfate was added to absorb moist

[1] Agricultural Products Research, Rohm and Haas Co., Spring House, Penn. 19477.
[2] Tracor, Inc., 6500 Tracor Lane, Austin, Tex. 78721.

μl aliquot of the solution was injected into the gas matograph.

ysis was performed on a Tracor Model 550 gas matograph equipped with a ^{63}Ni electron-capture ctor. Instrument parameters and operating condi- follow:

olumn:	Pyrex, 1.83 m long x 6.4 mm OD, packed with 10 percent SE-30 on 80–100-mesh Gas-Chrom Q	
emperatures:	column	210°C
	injector	275°C
	detector	305°C
arrier gas:	nitrogen flowing at 60 ml/minute	
etention time:	4.25 minutes	

er the conditions of analysis described above, di- l is decomposed quantitatively to 4,4′-dichlorobenzo- ione which is the peak measured. During extraction cleanup, 4,4′-dichlorobenzophenone, if present, is eparated. Thus, the residue measured is the sum of fol and dichlorobenzophenone. Each day that analy- vere run, known amounts of dicofol standard were ted until the response was stable. Further standard tions were interspersed with injections of samples.

alibration curve was drawn, plotting peak height is the amount of standard injected. Dicofol in sam- injections was determined from the calibration e. Recovery throughout the analytical process was sured by fortifications to soil before blending. All are corrected for recovery which was generally 00 percent. Sensitivity was 0.01 ppm.

firmatory analyses were not run on the samples. Be- e residue levels were low, confirmation was less rtant. Compared to many chlorinated pesticides h might interfere, dicofol (measured as dicholoro- ophenone) has a relatively short retention time on a mn such as SE-30 which separates materials mainly rding to vapor pressure. This is shown in data of bein (*1*).

Results and Discussion

on application, sampling, and analyses are reported able 1. Not every sample precisely fits the category hich it is assigned. In about half the cases, three or replicate samples were provided. In these cases, average residue is given, along with the range of es among the replicate samples. In one case only, no ples were provided from the 3–6 inch soil depth.

samples represent a wide range of dicofol usage, less than 1 kg/ha. applied during 1 year to over g/ha. applied over 8 years.

weight of a medium density soil (loam) to a depth inches over an area of 1 acre has been stated to be oximately 2 million pounds (*7*). Thus, in metric s, the weight of soil to a depth of 75 mm (3 inches) 1 ha. is 9.6×10^5 kg. Thus, 1 kg of pesticide applied to 1 ha. should result in an average concentration in soil of 1.04 ppm if distributed to a depth of 75 mm. Plowing and cultivation to a greater depth would proportionately lessen the residue concentration. Table 1 shows the maximum residue concentration to be expected if all of the dicofol applied reached the soil and remained in the top 75 mm. In the last column is given the ratio of the average concentration found to the maximum possible concentration calculated.

No dicofol was detected in soil samples from the four sites which had no history of its use. Samples from only four of the 17 treated sites contained mean residues in the top 75 mm of soil equaling or exceeding 2.00 ppm. In nearly all cases, the amount of dicofol remaining in soil was only a small fraction of the total applied.

The data in Table 1 suggest that the amount of dicofol residue remaining in soil bears no obvious relation to the total amount applied or to the interval between the last application and sampling. However, dicofol may be more persistent in sand than in other soil types.

Conclusions

Although the mechanisms by which dicofol residues are dissipated are not known, it is clear that such mechanisms must exist. The levels of residue found in soils from various locations of known usage history are in line with those reported by other workers in more general and extensive pesticide monitoring studies. These data also confirm that dicofol residues tend to remain near the soil surface.

Acknowledgments

We are grateful to W. R. Comegys, M. Fleischfresser, T. J. Neidlinger, E. E. Sieckert, H. L. Vincent, and J. P. Hartnett for collecting soil samples and to R. W. Bell for technical assistance in the analyses.

LITERATURE CITED

(*1*) *Fishbein, L. 1974.* Chromatographic and biological aspects of DDT and its metabolites. J. Chromatogr. 98(1):t77–25t.

(*2*) *Frank, R., H. E. Braun, K. Ishida, and P. Suda. 1976.* Persistent organic and inorganic pesticide residues in orchard soils and vineyards of southern Ontario. Can. J. Soil Sci. 56(4):463–484.

(*3*) *Harris, C. R., and W. W. Sans. 1969.* Vertical distribution of residues of organochlorine insecticides in soils collected from six farms in southwestern Ontario. Proc. Entomol. Soc. Ontario 100:156–164.

(*4*) *Harris, C. R., and W. W. Sans. 1971.* Insecticide residues in soils on 16 farms in southwestern Ontario—1964, 1966, and 1969. Pestic. Monit. J. 5(3):259–267.

(*5*) *Harris, C. R., R. A. Chapman, and J. R. W. Miles. 1977.* Insecticide residues in soils on fifteen farms in southwestern Ontario. J. Environ. Sci. Health B12(3): 163–177.

(*6*) *Kiigemagi, U., and L. C. Terriere. 1972.* Persistence of DDT in orchard soils. Bull. Environ. Contam. Toxicol. 7(6):348–352.

TABLE 1. *Dicofol residues in United States soils having a known history of its use, 1974*

Sample Code	State	Soil Type	Total Dicofol, Kg/Ha	Years Applied	TSI[1], Days	Sample Depth, mm	Residue, ppm		No. of Reps	Maximum Residue, ppm	Ra Fou M
							Average	Range			
DICOFOL APPLIED FOR SEVERAL YEARS, INCLUDING 1973											
74–023	Calif.	Sandy loam	53.8	66–68, 70–73	414	0–75	1.08	0.28–2.86	6	56.0	0.0
74–027	Wash.	Clay loam	5.6	69–73	276	0–75	0.98		1	5.8	0.1
						75–150	0.26		1		
74–066	Penn.	Clay	23.5	71–73	314	0–75	2.0	1.84–2.30	3	24.0	0.0
						75–150	0.43	0.22–0.64	3		
74–181	Fla.	Sand	15.0	66–71, 73	554	0–75	3.48	2.91–4.04	3	16.0	0.2
						75–150	0.84	0.21–1.90	3		
DICOFOL APPLIED FOR SEVERAL YEARS, BUT NOT IN 1973											
74–014	Calif.	Clay loam	7.0	67–72	665	0–75	0.09	0.00–0.14	3	7.4	0.0
						75–150	0.00	0.00–0.00	3		
74–026	Wash.	Clay loam	5.6	68–72	639	0–75	0.00		1	5.8	0.0
						75–150	0.00		1		
74–067	Penn.	Silt loam	16.8	71–72	679	0–75	0.34	0.22–0.42	3	17.0	0.0
						75–150	0.26	0.11–0.44	3		
74–154	Fla.	Sand	11.2	66–72	719	0–75	0.28	0.18–0.38	3	12.0	0.0
						75–150	0.00	0.00–0.00	3		
DICOFOL APPLIED FOR SEVERAL YEARS, BUT NOT FOR 3 YEARS OR MORE BEFORE SAMPLING IN 1974											
74–029	Wash.	Silt loam	5.6	66–70	1384	0–75	0.28		1	5.8	0.0
						75–150	0.06		1		
74–056	Mich.	Clay loam	50.4	60–69	1804	0–75	0.06	0.00–0.19	3	53.0	0.0
						75–150	0.00	0.00–0.00	3		
74–068	Penn.	Silt loam	—[2]	pre-1969	1825	0–75	1.02	0.79–1.16	3	—	-
						75–1-50	0.60	0.29–1.10	3		
74–153	Fla.	Sand	6.55	65–69, 71	1003	0–75	3.25	1.87–4.14	3	6.8	0.4
						75–150	1.13	0.23–1.65	3		
DICOFOL APPLIED IN 1973 ONLY (NONE BEFORE THEN)											
74–015	Calif.	Clay loam	1.3	1973	300	0–75	0.00	0.00–0.00	3	1.4	0.0
						75–1-50	0.00	0.00–0.00	3		
74–030	Wash.	Silt loam	0.9	1973	259	0–75	0.12		1	0.09	0.1
						75–150	0.00		1		
74–057	Mich.	Sand	3.4	1973	333	0–75	0.00		1	3.5	0.0
						75–150	0.00		1		
74–147	Fla.	Sand	4.5	1973	314	0–75	0.46	0.08–0.75	3	4.7	0.1
						75–150	0.00	0.00–0.00	3		
74–148	Fla.	Sand	13.4	73–74	175	0–75	2.58	0.65–4.6	3	14.0	0.1
						75–150	0.63	0.20–0.94	3		
NO KNOWN USE OF DICOFOL											
74–013	Calif.	Clay loam	0.0	—	—	0–75	0.00		5		
						75–150	0.00		3		
74–028	Wash.	Silt loam	0.0	—	—	0–75	0.00		1		
						75–150	0.00		1		
74–058	Mich.	—[3]	0.0	—	—	0–75	0.00		1		
						75–150	0.00		1		
74–162	Fla.	Sand	0.0	—	—	0–75	0.00		3		
						75–150	0.00		3		

[1] TSI = Treatment until Sampling Interval.
[2] Records of use not available. Dicofol known to have been used prior to 1969.
[3] Information not provided.

(7) *Klingman, G. C., and F. M. Ashton. 1975.* Weed Science, Principles and Practice. John Wiley and Sons, New York, N.Y. Appendix, p. 415.

(8) *Kuhr, R. J., A. C. Davis, and J. B. Bourke. 1974.* DDT residues in soil, water, and fauna from New York apple orchards. Pestic. Monit. J. 7(3/4):200–204.

(9) *Mullins, D. E., R. E. Johnsen, and R. I. Starr.* Persistence of organochlorine insecticide residues agricultural soils of Colorado. Pestic. Monit. J. 5(268–275.

(10) *Wiersma, G. B., H. Tai, and P. F. Sand. 1972.* cide residue levels in soils, FY 1969—National Monitoring Program. Pestic. Monit. J. 6(3):194–

CALL FOR PAPERS

Abstracts due December 1, 1979

for conference

Application of Appropriate Technology

to Chemical Dose and Chemical Residue Monitoring

May 28–30, 1980

U.S. Environmental Protection Agency

Office of Research and Development

Washington, D.C.

CONFERENCE TOPICS

Environmental Monitoring Requirements

Types of Chemicals Monitored

Environmental Monitoring Procedures and Techniques

Review of Analysis Costs and Procedures

Sampling Methodology

Epidemiological Considerations

Techniques Designed to Simplify Analytic Procedures

Approaches Designed to Simplify or Decrease Monitoring

ress correspondence to:

ıonse F. Forziati, Ph.D.
Environmental Protection Agency
e of Research and Development (RD-683)
M Street, S.W.
hington, D.C. 20460
) 426-2317

APPENDIX

Chemical Names of Compounds Discussed in This Issue

ALDRIN	Hexachlorohexahydro-*endo*, *exo*-dimethanonaphthalene 95% and related compounds 5%
AROCLOR 1254	PCB, approximately 54% chlorine
AROCLOR 1260	PCB, approximately 60% chlorine
BHC (Benzene Hexachloride)	1,2,3,4,5,6-Hexachlorocyclohexane (mixture of isomers)
CHLORDANE	1,2,3,4,5,6,7,8,8-Octachloro-2,3,3a,4,7,7a-hexahydro-4,7-methanoindene. The technical product is a mixtu several compounds including heptachlor, chlordene, and two isomeric forms of chlordane.
CHLORDENE	4,5,6,7,8,8-Hexachloro-3a,4,7,7a-tetrahydro-4,7-methano-1*H*-indene
CIODRIN	Dimethyl phosphate of α-methylbenzyl 3-hydroxy-*cis*-crotonate
DDE	Dichlorophenyl dichloro-ethylene (degradation product of DDT); *p,p'*-DDE: 1,1-Dichloro-2,2-bis(*p*-c phenyl) 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 possibl some are present in the commercial product. *o,p'*-DDT: [1,1,1-Trichloro-2-(*o*-chlorophenyl)-2-(*p*-chloroph ethane]
DIAZINON	*O,O*-Diethyl *O*-(2-isopropyl-6-methyl-4-pyrimidinyl) phosphorothioate
DICOFOL	1,1-Bis(chlorophenyl)-2,2,2-trichloroethanol
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-di anonaphthalene
DURSBAN	*O,O*-Diethyl *O*-(3,5,6-trichloro-2-pyridyl) phosphorothioate
ENDOSULFAN	Hexachlorohexahydromethano-2,4,3-benzodioxathiepin 3-oxide
ENDRIN	Hexachloroepoxyoctahydro-*endo,endo*-dimethanonaphthalene
EPN	*O*-Ethyl *O*-(*p*-nitrophenyl) phenylphosphonothioate
ETHION	*O,O,O',O'*-Tetraethyl *S,S'*-methylene bisphosphorodithioate
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-methanoindene
KELTHANE®	See Dicofol
LEPTOPHOS	*O*-(4-Bromo-2,5-dichlorophenyl) *O*-methyl phenylphosphonothioate
LINDANE	*Gamma* isomer of 1,2,3,4,5,6-hexachlorocyclohexane
MALATHION	*O,O*-Dimethyl dithiophosphate of diethyl mercaptosuccinate
METHOXYCHLOR	2,2-Bis(*p*-methoxyphenyl)-1,1,1-trichloroethane 88% and related compounds 12%

(Continued next page)

APPENDIX (*continued*)

HYL PARATHION	*O,O*-Dimethyl *O*-*p*-nitrophenyl phosphorothioate
X	1,1a,2,2,3,3a,4,5,5,5a,5b,6-Dodecachlorooctahydro-1,3,4-metheno-1*H*-cyclobuta[cd]pentalene
ACHLOR	1,2,3,4,5,6,7,8-Nonachlor-3a,4,7,7a-tetrahydro-4,7-methanoindan
CHLORDANE	2,3,4,5,6,6a,7,7-Octachloro-1a,1b,5,5a,6,6a-hexahydro-2,5-methano-2*H*-indeno(1,2-β)oxirene
ATHION	*O,O*-Diethyl *O*-*p*-nitrophenyl phosphorothioate
(Polybrominated henyls)	Mixtures of brominated biphenyl compounds having various percentages of bromine
(Polychlorinated henyls)	Mixtures of chlorinated biphenyl compounds having various percentages of chlorine
	Pentachloronitrobenzene
HANE	1,1-Bis(ethylphenyl)-2,2-dichloroethane
RATE	*O,O*-Diethyl *S*-[(ethylthio)methyl] phosphorodithioate
	Pentachlorobenzene
	1,2,4,5-Tetrachloro-3-nitrobenzene
	2,2-Bis(*p*-chlorophenyl)-1,1-dichloroethane (including isomers and dehydrochlorination products)
DAN I	See Endosulfan
APHENE	Chlorinated camphene (67–69% chlorine). Product is a mixture of polychlor bicyclic terpenes with chlorinated camphenes predominating.

ERRATUM

Pesticides Monitoring Journal, Volume 13, Number 1, page 1. The abstract of the article "Polychlorinated Biphenyl and Other Organic Chemical Residues in Fish from Major Watersheds of the United States, 1976" contains two erroneous statements.

". . . 53 percent of the [composite fish] samples contained more than 5 ppm PCBs, whole fish basis, which is the current tolerance level set by the Food and Drug Administration, U.S. Department of Health, Education, and Welfare." *Correction:* The FDA tolerance level for PCBs in fish is based on the edible portion only. Whole fish is likely to contain higher levels of PCBs than the edible portion is.

"Only 14 percent of the samples contained less than the proposed action level of 2 ppm PCBs." *Correction:* Again, the proposed FDA tolerance (not action) level for PCBs in fish applies to the edible portion only. Because it is not technically accurate to mathematically convert PCB residue levels in whole fish to those present in the edible portion, the data reported above and elsewhere in the article cannot be compared to either current or proposed tolerance levels for PCB residues in fish.

e *Pesticides Monitoring Journal* welcomes from all ırces qualified data and interpretative information on ticide monitoring. The publication is distributed ncipally to scientists, technicians, and administrators ociated with pesticide monitoring, research, and er programs concerned with pesticides in the environnt. Other subscribers work in agriculture, chemical nufacturing, food processing, medicine, public health, l conservation.

icles are grouped under seven headings. Five follow basic environmental components of the National ticide Monitoring Program: Pesticide Residues in ple; Pesticide Residues in Water; Pesticide Residues Soil; Pesticide Residues in Food and Feed; and ticide Residues in Fish, Wildlife, and Estuaries. The h is a general heading; the seventh encompasses fs.

nitoring is defined here as the repeated sampling and lysis of environmental components to obtain reliable mates of levels of pesticide residues and related npounds in these components and the changes in se levels with time. It can include the recording of dues at a given time and place, or the comparison of dues in different geographic areas. The Journal will lish results of such investigations and data on levels pesticide residues in all portions of the environment sufficient detail to permit interpretations and consions by author and reader alike. Such investigations uld be specifically designed and planned for monig purposes. The Journal does not generally publish ginal research investigations on subjects such as ticide analytical methods, pesticide metabolism, or d trials (studies in which pesticides are experimenly applied to a plot or field and pesticide residue deion rates and movement within the treated plot or d are observed).

thors are responsible for the accuracy and validity heir data and interpretations, including tables, charts. references. Pesticides ordinarily should be identiby common or generic names approved by national international scientific societies. Trade names are eptable for compounds which have no common nes. Structural chemical formulas should be used n appropriate. Accuracy, reliability, and limitations sampling and analytical methods employed must be cribed thoroughly, indicating procedures and cons used, such as recovery experiments at appropriate ls, confirmatory tests, and application of internal dards and interlaboratory checks. The procedure loyed should be described in detail. If reference is le to procedures in another paper, crucial points or lifications should be noted. Sensitivity of the method limits of detection should be given, particularly when very low levels of pesticide residues are being reported. Specific note should be made regarding correction of data for percent recoveries. Numerical data, plot dimensions, and instrument measurements should be reported in metric units.

PREPARATION OF MANUSCRIPTS

——Prepare manuscripts in accord with the *CBE Style Manual*, third edition, Council of Biological Editors, Committee on Form and Style, American Institute of Biological Sciences, Washington, D.C., and/or the *U.S. Government Printing Office Style Manual*. For further enrichment in language and style, consult Strunk and White's *Elements of Style*, second edition, MacMillan Publishing Co., New York, N.Y., and *A Manual of Style*, twelfth edition, University of Chicago Press, Chicago, Ill.

——On the title page include authors' full names with affiliations and addresses footnoted; the senior author's name should appear first. Authors are those individuals who have actually written or made essential contributions to the manuscript and bear ultimate responsibility for its content. Use the Acknowledgment section at the end of the paper for crediting secondary contributors

——Preface each manuscript with an informative abstract not to exceed 200 words. Construct this piece as an entity separate from the paper itself; it is potential material for domestic and foreign secondary publications concerned with the topic of study. Choose language that is succinct but not detailed, summarizing reasons for and results of the study, and mentioning significant trends. Bear in mind the literature searcher and his/her need for key words in scanning abstracts.

——Forward original manuscript and three copies by first-class mail in flat form: do not fold or roll.

——Type manuscripts on 8½-by-11-inch paper with generous margins on all sides, and end each page with a completed paragraph. Recycled paper is acceptable if it does not degrade the quality of reproduction. Double-space all copy, including tables and references, and number each page.

——Place tables, charts, and illustrations, properly titled, at the end of the article with notations in the text to show where they should be inserted. *Treat original artwork as irreplaceable material.* Lightly print author's name and illustration number with a ballpoint pen on the back of each figure. Wrap in cardboard to prevent mutilation; do not use paperclips or staples.

——Letter charts distinctly so that numbers and words will be legible when reduced. Execute drawings in

black ink on plain white paper. Submit original drawings or sharp glossy photographs; no copies will be accepted.

——Number literature citations in alphabetical order according to author. For journal article include, respectively, author, year, title, journal name as abbreviated in *Chemical Abstracts Service Source Index*, and volume, issue, and page numbers. For book references cite, respectively, author, year, chapter title, pages, and editor if pertinent, book title, and name and city of publisher. For Government manuals list originating agency and relevant subgroup, year, chapter title and editor if pertinent, manual title, and relevant volume, chapter, and/or page numbers. Do not list private communications among Literature Cited. Insert them parenthetically within the text, including author, date, and professional or university affiliation indicating author's area of expertise.

The Journal welcomes brief papers reporting monitoring data of a preliminary nature or studies of limited scope. A section entitled Briefs will be included as necessary to provide space for short papers which present timely and informative data. These papers must be limited to two published pages (850 words) and should conform to the format for regular papers accepted by the Journal.

Manuscripts require approval by the Editorial Advisory Board. When approved, the paper will be edited for clarity and style. Editors will make the minimum changes required to meet the needs of the gene Journal audience, including international subscrib for whom English is a second language. Authors accepted manuscripts will receive edited typescripts approval before type is set. After publication, ser authors will receive 100 reprints.

Manuscripts are received and reviewed with the unc standing that they have not been accepted previou for publication elsewhere. If a paper has been gi or is intended for presentation at a meeting, or i significant portion of its contents has been publis or submitted for publication elsewhere, notations such should be provided. Upon acceptance, the orig manuscript and artwork become the property of *Pesticides Monitoring Journal.*

Every volume of the Journal is available on microf Requests for microfilm and correspondence on edito matters should be addressed to:

Paul Fuschini (TS-793)
Editorial Manager
Pesticides Monitoring Journal
U.S. Environmental Protection Agency
Washington, D.C. 20460

For questions concerning GPO subscriptions and b issues write:

Superintendent of Documents
U.S. Government Printing Office
Washington, D.C. 20402

The Administrator of the U.S. Environmental Protection Agency has determined that the publication of this periodical is necessary in the transaction of public business required by law of this Agency. Use of funds for printing this publication approved by the Director of the Office of Management and Budget, May 19, 1976.

ORDER BLANK
FOR PMJ

To: Superintendent of Documents
Government Printing Office
Washington, D.C. 20402

Please enter my Subscription for Pesticides Monitoring Journal. I am enclosing Money Order ☐ Check ☐ for this subscription. ($7.90 a year; $2.00 additional for foreign mailing)

Please address the PMJ as follows: _____

_____

_____

UNITED STATES GOVERNMENT PRINTING OFFICE, WASHINGTON, D. C. 1967

For sale by the Superintendent of Documents, U.S. Government Printing Office, Washington, D. C. 20402. Subscription price $7.90 a year, $2.00 additional for foreign mailing. Price for a single copy of this issue is $2.00.

United States
Environmental Protection
Agency
(TS-793)
Washington DC 20460

Official Business
Penalty for Private Use
$300

Fourth-Class Mail
Postage and Fees Paid
EPA
Permit No. G-35

FEDERAL WORKING GROUP ON PEST MANAGEMENT
(RESPONSIBLE TO THE COUNCIL ON ENVIRONMENTAL QUALITY)

If you do not desire to continue receiving this publication, please CHECK HERE ☐; cut off this label and return it to the above address. Your name will be removed from the mailing list.

PESTICIDES MONITORING JOURNAL

DECEMBER 1979

VOLUME 13 NUMBER 3

PEMJAA (13) 81–135 (1979)

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

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

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

The *Pesticides Monitoring Journal* is published by the Chemical Information Division, Office for Program Integration and Information, Office of Pesticides and Toxic Substances, U.S. Environmental Protection Agency.

Pesticide monitoring activities of the Federal Government, particularly in those agencies represented on the Monitoring Panel which participate in operation of the national pesticides monitoring network, are expected to be the principal sources of data and articles. However, pertinent data in summarized form, together with discussions, are invited from both Federal and non-Federal sources, including those associated with State and community monitoring programs, universities, hospitals, and nongovernmental research institutions, both domestic and foreign. Results of studies in which monitoring data play a major or minor role or serve as support for research investigation also are welcome; however, the Journal is not intended as a primary medium for the publication of basic research. Publication of scientific data, general information, trade names, and commercial sources in the *Pesticides Monitoring Journal* does not represent endorsement by any Federal agency.

Manuscripts received for publication are reviewed by an Editorial Advisory Board established by the Monitoring Panel. Authors are given the benefit of review comments prior to publication. For further information on Journal scope and manuscript preparation, see Information for Contributors at the back of this issue.

Address correspondence to:

Paul Fuschini (TS-793)
Editorial Manager
Pesticides Monitoring Journal
U. S. Environmental Protection Agency
Washington, D.C. 20460

CONTENTS

Volume 13 December 1979 Numbe

HUMANS

Sources of Parathion Exposures for Israeli Aerial Spray Workers, 1977

Bension Cohen,[1] Eliahu Richter,[2] Eliahu Weisenberg,[3] Judith Schoenberg,[3] and Menachem Luria [1,4]

ABSTRACT

osure of Israeli agricultural spray pilots and ground ws to parathion was studied. Measurements were made personal samplers containing wet midget impingers; ples were analyzed by gas chromatography.

kpit air exposure levels during 11–21-minute sampling ods for 12 flights ranged from nearly 0 to 430 μg/m³. ing sampling periods of 30 minutes to 4 hours the shold limit valuc (TLV) of 100 μg/m³ was exceeded in f 19 instances. In seven measurements of ground crew osures, TLV was not exceeded. Air washing with par- on resulted in airborne contamination of the ground l area at more than three times the TLV. Skin exposure suggested that this route of exposure was significant for nd crew workers but not for pilots. Calculations based the present data and standard absorption formula sug- ed that total daily intake for ground crew, but not for ts, exceeded the Accepted Daily Intake (ADI) of 5 μg/kg y weight. Sources of exposure and contamination for nd crew and pilots were identified. Recommended en- nmental control measures for parathion exposure should ude cockpit air filtration, modification in flight patterns, ng landing areas, installation of hosing and drainage,)H neutralization point, and separate loading and un- ling sites. Personal control measures were suggested as pplement.

Introduction

agricultural use of pesticides in Israel is very inten- relative to other countries. Among the most com- ly used pesticides is parathion, mainly applied in km² of cotton fields (*1*). During the last five years, thion consumption has increased from 216 tons 973 to 830 tons in 1977 (*1*), all of which is applied ng two to three summer months. The increased of parathion for agricultural applications is related s low cost and high efficiency against crop pests.

partment of Human Environmental Sciences, School of Applied ce and Technology, The Hebrew University of Jerusalem, Israel.
partment of Medical Ecology, Hadassah Medical School, The ew University of Jerusalem, Israel.
istry of Health, The Government of Israel.
whom all correspondence should be addressed.

Highly toxic, parathion causes cholinesterase (ChE) inhibition in humans at low exposure levels. The threshold limit value (TLV) for parathion exposures is 100 $\mu g/m^3$ over 8 hours or 300 $\mu g/m^3$ for short-term limit exposures (STL) (*12*) provided no dermal absorption occurs. Besides the well known acute effects, repeated low exposures may cause slower nerve conductivity and abnormalities in muscle action potential (*8*), possibly at levels below those affecting ChE.

Parathion exposures of pilot and ground workers have been studied in terms of ambient concentration, respiratory and skin exposures, the decrease of ChE concentration in blood, and, more recently, parathion metabolites in urine. Wolfe et al. (*4, 15*) measured respiratory and skin exposures of various spray workers to several pesticides. Their results showed that for pilots, respiratory parathion doses averaged 0.02 mg/hour and skin exposure averaged 13 mg/hour. Although only a fraction of the parathion to which the skin is exposed penetrates the body, Wolfe et al. concluded that skin exposure is potentially more dangerous.

Higher skin and respiratory exposures were found among flag carriers and plane loaders. Medical examinations of air and ground crews of an aerial spray company by Davies et al. (*3*) revealed that ChE blood levels in one third of the workers had decreased significantly. The ChE decreases were correlated with increased amounts of *p*-nitrophenol (PNP) in the urine. Ware and Morgan (*14*) measured parathion concentrations in air as well as skin exposure of cotton field workers at various intervals after aerial spray. Parathion concentrations were not high enough to affect the common ChE test. However, PNP was detected in urine, and parathion was found in the serum.

The present research was performed among workers of an aerial spray company which employs about 50 pilots, 60 loaders, and 100 mechanics. The company sprays about 50 percent of the pesticides in Israel. During peak season, the company's pilots experience

a heavy work burden which starts at 4 A.M. and includes 4–5 hours of spraying flights, 15–25 takeoffs and landings, several hundred hairpin turns, and frequent passes under power lines. During the spraying flights, the pilots were exposed to high temperatures, high g forces, noise vibration and various pesticides. Medical examinations since 1973 have shown a gradual increase in the number of workers with some decrease in ChE blood level. In 1976, 40 percent of the pilots' tests showed decreases of $\geqq$ 10 percent. Decreases of $\geqq$ 30 percent were found in 40 percent of mechanics' and 30 percent of loaders' tests. In view of the pilots' working conditions and the ground crews' medical data and accident rates, authors wanted to estimate ambient levels of parathion in the environment of aerial spraying workers, in order to identify and evaluate the sources of exposure and to propose means for control.

Sampling and Analysis

LABORATORY STUDY OF SAMPLERS

The present research required a sampler for field applications which could efficiently collect parathion aerosols and vapors. Several methods have been used for pesticide sampling from air (*13*). Two methods were examined for appropriateness to the present study: wet midget impingers, which are most commonly used in pesticide monitoring (*2, 14*), and packed absorption columns. In both cases, ethylene glycol was the absorption liquid and a Cassella personal sampler was used for the controlled air drawing.

For safety reasons, authors substituted malathion for parathion in most of the laboratory studies. Malathion is an organophosphorus insecticide with chemical structure and physical properties similar to those of parathion, but with a toxicity lower by a facter of $\sim$ 100. Malathion vapors and aerosols were generated inside a double-walled 200 $\times$ 80 $\times$ 60-cm inhalation chamber. Large sized particles, $>$20 microns in diameter, and small sized particles, $<$2 microns in diameter, were generated separately by two different atomizers. Va were created by evaporating known amounts of m thion or parathion in a closed glass dish. Samples v taken at periods ranging from 30 minutes to 4 ho after which the collectors were taken for extraction analysis. The extraction was performed according the guidelines of the U.S. Environmental Protec Agency (*11*). Following extraction, the collected m thion or parathion was dissolved in 1 ml of pure hex

Analysis was performed on a Packard Model 807 chromatograph with the following instrument par eters and operating conditions:

Detector:	flame photometric
Column:	6-ft long $\times$ ¼-inch OD glass, packed wi percent OV-210 on Chromosorb W (AW)
Temperature:	column 225°C
Carrier gas:	nitrogen flowing at 40 ml/minute
Sensitivity:	1 ng malathion 1.6 ng parathion

Before and after every series of measurements, a st ard sample of parathion or malathion was injected.

Results of the laboratory survey of samplers are s marized in Table 1. The results indicate that the r efficient method was the wet midget impinger. M over, resistance to air flow limited the amount of v which could be used in the glass wool experime Therefore, the impingers with a collection efficienc 82 $\pm$ 10 percent were chosen for the field study.

FIELD STUDY

Personal samplers were placed on the instrument pa in the cockpits for the study of pilot exposures. Gro crew exposures were determined by placing sin samplers on the chest pockets of the workers. W site exposures were monitored by sampling the air fixed location at 1.5 m aboveground. After expos the ethylene glycol from the impinger was introdu into a bottle containing 60 ml distilled water. The

TABLE 1. *Laboratory survey of samples for the collection of parathion aerosols and vapors*

Collector	No. of Experiments	Pesticide	% Efficiency $<$2-μ particles	% Efficiency $>$20-μ particles	V
Glass bead column: 50 mm long $\times$ 20 mm ID glass column filled with ethylene glycol-coated 3-mm-diameter glass beads. Efficiency was studied by using 2 collectors in series.	1 2	malathion malathion	75	58–71	
Glass wool column: 20 mm ID tube, containing 0.3 g ethylene glycol–coated glass wool. 2–3 columns in series for the efficiency test.	3 2	malathion malathion	70–92	78–93	
Wet midget impinger: Impinger contains 15 ml ethylene glycol; 2nd and 3rd traps contained ethylene glycol–coated glass wool.	2 1 2	malathion malathion malathion	78–87	82	3
Wet midget impinger: 2 in series for efficiency determination.	1 1	parathion parathion			8 0

: was carefully flushed with 10 ml hexane which then added to the extraction bottle. The bottle was ›rously shaken for 60 seconds and was stored in a l place until analysis. The stability of parathion in ane under similar conditions has been tested and degradation has been detected. Skin exposure of t and ground crews was estimated by the attach- ıt of Whatman filter paper No. 1 dipped in ethylene :ol. Parathion was extracted from the filter paper ›rding to the method described above. Parathion tamination of pilots' and ground crews' hands was luated by having them wash their hands with hexane, extracting the parathion as described above.

ıples were taken during August and September 1977 ween 5 A.M. and 9 A.M. at ambient temperatures 18–30°C and relative humidity of 60–80 percent. ›ts and ground crews were informed of all exposure a.

Results

athion measurements in cockpits were divided into groups. In the first, 12 samples were taken during a single flight of parathion spraying which lasted 11–21 minutes. The data are shown in Table 2. Parathion concentrations ranged from 0 to 440 mg/m³. In seven samples the TLV was exceeded, and in one sample, parathion exceeded the STL. Results of the longer sampling periods are summarized in Table 3. In this category, sampling duration ranged from 35 to 260 minutes in which the TLV was exceeded in two of 18 cases; STL was exceeded in one of the two. Sample 1 in Table 3 was taken during the application of azodrin and can be considered as a control.

Table 4 describes seven personal samplings of aircraft loaders. In Table 5, the data of nine samples taken at the aircraft loading area are presented. In both cases parathion concentrations were below TLV. Parathion concentrations measured at other work sites are summarized in Table 6. Subthreshold ambient concentrations of parathion were found in the pesticide storage hut in Ashkelon. Concentrations exceeding STL were found in the two samples taken at the aircraft washing area. At the neighboring sites, high concentrations of parathion were found when the wind came from the direction of the washing area.

TABLE 2. *Ambient parathion concentrations sampled during 11–21-minute periods in cockpits of Israeli agricultural spray planes*

MPLE NO.	DATE	STARTING HOUR	SAMPLING DURATION, MIN.	CONCENTRATION OF PARATHION, μG/M³ ± 10%	STATUS OF AIR SHUTTLE OPENING	DETECTION BY PILOT'S SENSE OF SMELL	AIRCRAFT MODEL
1	Aug. 24	05:25	11	430	open	Detected	Snow
2	Aug. 16	07:50	12	9	open	Not Determined	Snow
3	Aug. 16	05:30	13	12	open	Not Determined	Pawnee Brave
4	Aug. 28	07:00	14	270	open	Slightly Detected	Snow
5	Aug. 17	06:30	15	ND	open	ND	Snow
6	Aug. 17	07:00	17	ND	open	ND	Snow
7	Aug. 24	07:45	17	190	open	Slightly Detected	Snow
8	Aug. 23	07:25	18	250	open	Not Determined	Snow
9	Aug. 24	06:10	18	160	open	ND	Snow
0	Aug. 24	06:30	18	250	open	ND	Snow
1	Aug. 18	05:35	20	92	closed	ND	Snow
2	Aug. 18	05:10	21	130	closed	ND	Snow

TE: ND = not detected.

TABLE 3. *Ambient parathion concentrations sampled during 35–260-minute periods in cockpits of Israeli agricultural spray planes*

MPLE NO.	DATE	STARTING HOUR	SAMPLING DURATION, MIN.	CONCENTRATION OF PARATHION, μG/M³ ± 10%	STATUS OF AIR SHUTTLE OPENING	DETECTION BY PILOT'S SENSE OF SMELL	AIRCRAFT MODEL
1[1]	Aug. 16	06:00	35	ND	—	Not Determined	Pawnee Brave
2	Aug. 31	05:40	35	35	open	ND	Snow
3	Aug. 24	05:15	38	43	—	Not Determined	Snow
4	Aug. 30	05:45	39	85	open	ND	Snow
5	Aug. 23	06:15	43	ND	open	Not Determined	Snow
6	Aug. 23	07:45	43	120	—	Not Determined	Snow
7	Aug. 29	05:20	44	22	open	ND	Snow
8	Aug. 23	05:50	45	18	open	Not Determined	Snow
9	Aug. 23	05:50	45	14	open	Not Determined	Snow
0	Aug. 17	05:10	54	2	partly open	Slightly Detected	Pawnee Brave
1	Aug. 31	07:20	63	14	closed	ND	Helicopter
2	Sept. 9	07:00	71	410	closed	Detected	Turbo Snow
3	Aug. 18	05:20	78	12	closed	ND	Pawnee Brave
4	Sept. 1	06:15	97	8	open	Not Determined	Snow
5	Sept. 1	05:45	111	18	closed	Slightly Detected	Snow
6	Sept. 9	05:15	114	11	open	ND	Snow
7	Aug. 30	06:20	190	23	open	ND	Snow
8	Sept. 9	05:00	191	8	—	Not Determined	Snow
9	Aug. 25	05:15	260	6	—	Not Determined	Snow

TE: ND = not detected.
nple taken during application of azodrin and can be considered a control.

TABLE 4. *Exposures of aircraft loaders to parathion, Ashkelon and Bee'ry Airfields, Israel*

Sample No.	Date	Place	Sampling Starting Hour	Sampling Duration, Min.	Concentration, μg/m³ ± 10%
1	Sept. 9	Ashkelon	05:00	35	67
2	Sept. 6	Bee'ry	05:25	100	15
3	Sept. 9	Ashkelon	05:00	107	23
4	Sept. 2	Ashkelon	04:30	112	39
5	Sept. 2	Ashkelon	04:15	147	40
6	Sept. 8	Ashkelon	05:00	155	14
7	Sept. 8	Ashkelon	05:00	175	11

Discussion

PILOT EXPOSURE

Pilots are exposed to pesticides in ambient air during two stages of their work: at the loading site and in flight. Pilots spend 20–40 minutes/day at the loading site where they are exposed to pesticide-contaminated dust, mist, and vapors. In-flight exposure results from flying back into clouds of pesticide aerosols and vapors which remain dispersed after spraying.

If the breathing rate of spray pilots is similar to that of battle pilots, approximately 25 liters/minute (*10*), then there is complete absorption of inhaled parathion (*4, 9, 15*). The values for respiratory parathion intake for the samples of longer duration of Table 3 can be calculated and are shown on Table 7.

Apart from sample No. 12, calculated values in present report are similar to the 0.02 μg/hour repo by Wolfe et al. (*4, 15*) for pilots' respiratory expo and are far below the Accepted Daily Intake (AI In sample No. 12, however, which was taken i Turbo Snow aircraft, ADI probably was exceeded w in less than one hour. More samples would have b needed to determine whether to attribute this leve cockpit sealing defects or to temperature and wind c ditions prevailing in the region.

For some of the short-term samples, wind speed direction were also measured. These values were examined in relation to two categories: wind dire 45–135° to spray line (type 1); and wind either par to spray line or nearly absent (type 2).

The present data show that high cockpit concentrat were measured only when type 2 wind conditions vailed. Type 1 wind conditions were associated low concentrations. The present findings confirm influence of wind conditions on cockpit exposure reported previously (*4, 15*). Also, they may exp the wide concentration range found mainly in the sh time samples. These concentrations may be the ave of several instant peaks, which pilots smell (Tables 2

Pilots tend to leave the aeration shuttle open w releasing the spray load. In sample No. 12, Tabl despite the ventilation shuttle always being kept cl

TABLE 5. *Air sampling for parathion at aircraft loading areas, Ashkelon and Plugot Airfields, Israel*

Sample No.	Date	Place	Starting Hour	Sampling Duration, Min.	Concentration of Parathion, μg/m³ ± 10%	Samp Meth
1	Aug. 16	Ashkelon	05:45	150	6	impi
2	Aug. 25	Ashkelon	04:50	154	20	impi
3	Aug. 25	Ashkelon	05:00	106	13	cyclo
4	Aug. 29	Plugot	05:30	218	36	impi
5	Aug. 29	Ashkelon	05:45	32	15	impi
6	Sept. 1	Ashkelon	05:45	200	4	impi
7	Sept. 1	Ashkelon	06:40	91	4	impi
8	Sept. 11	Ashkelon	04:35	60	60	impi
9	Sept. 11	Ashkelon	06:00	60	63	cyclo

TABLE 6. *Ambient concentrations of parathion at various worksites, Ashkelon and Herzelia Airfields, Israel*

Sample No.	Location	Date	Site	Starting Hour	Sampling Duration, Min.	Concentration of Parathion, μg/m³ ± 10%	Remarks
1	Ashkelon	Sept. 7	Pesticide	07:00	170	1	
2	Ashkelon	Aug. 17	storage	03:20	287	2	
3	Ashkelon	Aug. 24	hut	04:10	218	25	Extremely hot day (>35°C) puddles of water and pesticides on the floor
4	Ashkelon	Aug. 25		04:10	230	2	Cooler day, clean floor
5	Ashkelon	Aug. 17	Office	07:00	221	3	
6	Herzelia	Sept. 20	Mechanical workshop	12:00	100	19	
7	Herzelia	Sept. 21	Aircraft	11:00	85	290	Wind blows from
8	Herzelia	Sept. 23	washing area	11:00	108	350	washing area towards
9	Herzelia	Sept. 23	Offices front	11:00	97	43	garage and offices
10	Herzelia	Sept. 23	Aircraft	11:00	110	97	
11	Herzelia	Sept. 26	garage	11:00	107	12	Wind blows in opposite direction from garage and offices.

TABLE 7. *Respiratory intakes of parathion by pilots of Israeli agriculture spray service*

ıPLE NO. M TABLE 3	DURATION, MIN.	AMBIENT PARATHION CONCENTRATION, μG/M³	TOTAL PARATHION INHALED, μG	μG PARATHION INHALED/HOUR
12	71	410	730	620
13	78	12	23	18
14	79	8	16	12
15	111	18	50	27
16	144	11	40	17
17	190	23	110	35
18	191	8	38	12
19	260	6	36	9

pilot smelled parathion during the flight. This case gested the possibility of routes of penetration into cockpit other than via the shuttle. Authors did not erve an association between parathion concentration aircraft type.

o possible explanations offered for the lower para- n concentration measured with the longer sampling ods are time dilution of the instant peak, and the aying of pesticides other than parathion during pling.

UND CREW EXPOSURE

ual observation indicated that crews are exposed to athion and other pesticides by contaminated dust wn and dispersed from the unpaved ground when aircraft takes off and from vapor from puddles and taminated equipment.

respiratory parathion intake can be calculated from results of the ground crew personal sampling (Table If the ventilation rate is 25 liters/minute, and there complete absorption of inhaled parathion, then res- atory intake alone is in the range of 46–176 μg; DI is ~ 400 μg. Parathion concentration measured he ambient air at the fixed loading area sites (Table were in the range of concentration measured with sonal samplers attached to workers' pockets.

eral ground crew workers became nauseated when elling the pesticides and experienced headaches and laise while working at the pesticide storage hut near nkelon. Measurement at the site (Table 6) sug- ted that ambient parathion concentration remained when the hut was kept clean. However, a com- ation of hot days and puddles containing pesticides the hut floor might result in tenfold higher concen- tion (Table 6). The 25 μg/m³ level found, although l below TLV, is probably one ingredient in a cock- of vapors of pesticides stored in the poorly ven- ted hut.

rzelia airport serves as the company's central airport ere its offices and maintenance and repair shop are ated. During summers, episodes of acute poisoning e reported among administrative personnel. As shown Table 6, aircraft washers seem to have the closest ıtact with pesticides. They experience parathion concentrations which apparently exceeded STL for several hours a day. They are exposed mainly to aerosols including those produced during washing or when the aircraft is taxiing. Ground crew use of protective equipment, such as boots, rubber aprons, gloves, and masks probably prevents more frequent, and more serious episodes. Authors feel that the washing area, which is at the center of the airport complex, is a major source of exposure for workers in the workshop, offices, and garage, which are all within 20–40 m of it. The sample taken at the entrance of the neighboring workshop hut was collected 1–2 hours after plane washing. This value may be considered as the background parathion concentration.

SKIN EXPOSURE

Despite the well known difficulties associated with measuring skin exposure and estimating the absorption, most authorities are convinced that skin exposure exceeds respiratory exposure. Total dermal absorption is a function of exposed skin area, anatomic region (*7*), and ambient temperature (*6*). Pilots and ground crews usually wear freshly cleaned long-sleeved overalls. This reduces average exposed skin area to approximately 2000 cm² (*5*). At the same time, high temperature, sweating, exposure lasting several hours, and delays before showering all seem to enhance skin penetration.

Eight studies showed that pilots are exposed to 5–200 μg/hour dermally; ground crews' skin exposure is 40–5000 μg/hour. Calculations based on an absorption ratio of 10 percent (*7*) suggest that total absorption for pilots is up to 20 μg/hour and for ground crews as much as 500 μg/hour. For pilots, dermal absorption seemed to be in the same range as respiratory exposure. However, for ground crews, parathion absorption via skin exposure alone could exceed the ADI.

Direct hand contact provided a further opportunity for parathion penetration. In six hexane hand wash measurements, it was shown that as much as 4000 μg can be washed off. Opportunities for ground crew hand contact exposure included preparing and loading the pesticide, holding loading pipes, and cleaning cockpit windshields. Gloves were seldom used.

Our flight exposure data (Tables 2, 3) specifically indicated that sense of smell could not be relied upon in all instances to detect possibly hazardous parathion air exposures.

Conclusion

Recommended environmental control measures for parathion exposure included paving of the landing area, drainage, NaOH neutralization points, separate loading and unloading sites, and hosing arrangements. Recommended personal control measures included wearing impermeable uniforms, boots, and gloves, and proper mask use, storage, and maintenance.

Control of airborne exposure to the pilot in the cockpit via both inhalation and skin absorption would require absolute filters to prevent aerosol penetration to the cockpit along with air ventilation and cooling to decrease pilot discomfort. In addition, modification of flight patterns, in certain settings, might reduce aircraft exposure to the sprayed aerosol plume.

Personal air and skin sampling is helpful in assessing and tracing sources of air and skin exposure and contamination by parathion in the context of a comprehensive surveillance and control program for agricultural spray pilots and ground crews.

LITERATURE CITED

(1) *Cotton Production and Marketing Board, Ltd. 1976.* Management report and private information. Tel Aviv, Israel.

(2) *Culver, D., P. Caplan, and G. S. Batchelor. 1956.* Studies of human exposure during aerosol application of malathion and chlorthion. AMA Arch. Ind. Health 13(1):37–50.

(3) *Davies, J. E., M. T. Shafik, A. Barquet, C. Morgade, and J. X. Danauskas. 1976.* Worker reentry safety: a medical overview of reentry periods and the use of urinary alkylphosphates in human pesticide monitoring. Residue Rev. 62:45–47.

(4) *Durham, W. F., and H. R. Wolfe. 1963.* An additional note regarding measurements of the exposure of workers to pesticides. Bull. World Health Org. 29(2):279–281.

(5) *Gunther, F. A., Y. Iwata, G. E. Carman, and C. A. Smith. 1977.* The citrus reentry problem: research on its cause and effects and approaches to its mini tion. Residue Rev. 67:1–132.

(6) *Hayes, G. R., A. J. Funchas, and W. V. Har 1964.* Dermal exposure of human volunteers t rathion. Arch. Environ. Health 8:829–833.

(7) *Maibach, H. I., R. J. Feldman, T. H. Milby, ar F. Serat. 1971.* Regional variation in percuta penetration in man. Arch. Environ. Health 2 208–211.

(8) *Roberts, D. V. 1976.* EMG voltage and motor conduction velocity in OP pesticide factory wo Int. Arch. Occup. Environ. Health 36(4):267–27

(9) *Simpson, G. R., and A. Beck. 1965.* Exposu parathion: dermal and inhalation exposure t rathion while spraying tomato bushes with a kna mister. Arch. Environ. Health 11(12):784–786.

(10) *U.S. Air Force. 1953.* Medical Service: physiolo flight. AFP 160–10(4):16.

(11) *U.S. Environmental Protection Agency. 1977.* M of analytical methods for the analysis of pes residues in human and environmental samples. tion 8/A.

(12) *U.S. National Institute for Occupational Safety Health.* Criteria for a recommended standard c cupational exposure to parathion.

(13) *Van Dyk, L. P., and K. Visweswariah. 1975.* cides in air: sampling methods. Residue Rev. 5 134.

(14) *Ware, G. W., and D. P. Morgan. 1976.* Worke entry safety: Techniques of determining safe re intervals for organophosphate-treated cotton Residue Rev. 62:79–100.

(15) *Wolfe, H. R., W. F. Durham, and J. F. Armst 1967.* Exposure of workers to pesticides. Environ. Health 14(4):622–633.

FOOD AND FEED

Pesticides and Other Chemical Residues in Infant and Toddler Total Diet Samples—(I)—August 1974–July 1975 [1]

Roger D. Johnson, Dennis D. Manske, Dallas H. New, and David S. Podrebarac

ABSTRACT

e 1964, the Food and Drug Administration, U.S. De-nent of Health, Education and Welfare, has reported lues of pesticides and other chemicals present in the age diet of the young adult male. The present report is first in a series of market baskets whose purpose is to itor the average diet of infants and toddlers for the residues. Ten market baskets were collected in 10 which ranged in population from less than 50,000 to 0,000 or more. Averages and ranges of residues found reported by food class. Results of recovery studies of vn residues and chemicals within various food classes lso presented.

Introduction

e 1964, the Food and Drug Administration (FDA), Department of Health, Education and Welfare, rted residues of pesticides and other chemicals in-d in the average diet of the United States' largest , the young adult male (*1, 10*). Although changes been made in sampling frequency, areas sampled, ytical methods, and types of residues sought, the ram has continued essentially in the same form the present. During this, the eleventh year of the y, the program has been broadened in scope by ıcing 10 of the original 30 adult market baskets 10 infant and toddler market baskets represent-ı basic 14-day diet for infants and for toddlers. The 's Office of Nutrition and Consumer Services, au of Foods, has used available 1965 U.S. Depart-t of Agriculture survey data to calculate the average consumption of particular foods and food groups 6-month-old infants and 2-year-old toddlers from geographic regions of the United States, i.e., South, heast, North Central, and West.

The foods were prepared by a dietitian in the manner in which a consumer would prepare and serve them at home. Food items were separated into 11 commodity classes as listed in Table 1. Each class was then composited into a slurry and analyzed for organochlorine and organophosphorus pesticides, carbaryl, herbicides, metals including selenium, zinc, cadmium, mercury, lead, and arsenic; and industrial chemicals including polychlorinated biphenyls (PCBs) and pentachlorobenzene. Methodology included atomic absorption spec-

TABLE 1. *Commodity classes of infant and toddler foods analyzed for pesticides and other chemical residues, August 1974—July 1975*

KEY	FOOD CLASS
I	Drinking water[1]
II	Whole milk, fresh[1]
III	Other dairy and substitutions, infant
	Other dairy and substitutions, toddler
IV	Meat, fish, and poultry, infant
	Meat, fish, and poultry, toddler
V	Grain and cereal products, infant
	Grain and cereal products, toddler
VI	Potatoes[1,2]
VII	Vegetables, infant
	Vegetables, toddler
VIII	Fruit and fruit juice, infant
	Fruit and fruit juice, toddler
IX	Oils and fats[1,3]
X	Sugar and adjuncts, infant
	Sugar and adjuncts, toddler
XI	Beverages[1,4]

NOTE: Use key with Table 3.

[1] Due to similarity in diet between infants and toddlers for certain classes of foods, single determinations are made and reported for both.

[2] No infant composite for western region.

[3] No infant composite for the north central, western, and southern regions.

[4] No infant composite from north central region.

ıas City District Office Laboratory, Food and Drug Administra-U.S. Department of Health, Education and Welfare, Kansas Mo. 64106.

troscopy, fluorometry, gas chromatography, thin-layer chromatography, mass spectroscopy, and established extraction and cleanup techniques (*2–9, 11*). Conditions, techniques, and limits of quantitation were described in the adult market baskets series, with the exception of the water composite.

The water composite was extracted with methylene chloride, and the extracts were dried by passage through sodium sulfate and were evaporated to a small volume (*12*). The equivalent of 1000 mg water was injected into a gas chromatograph. The limit of detection was set at 0.0002 ppm heptachlor epoxide.

Results

In the infant market basket, authors found 306 residues of 28 different compounds; 121 residues were at the trace level. In the toddler market basket, authors found 468 residues of 30 different compounds; 179 were at the trace level. The 32 different residues found are listed in decreasing order of frequency in Table 2. Methoxychlor and parathion were found only in infant food composites; ronnel, endosulfan, TCNB, and leptophos were found only in toddler food composites. Table 3 shows the frequency of occurrences of residues by food class, and Table 4 shows the levels of chemical residues found within each food class. The average stated in Table 4 is based on the total number of composites examined for that food class. No trace residues have been included in calculating the average.

The most common residues and their maximum levels are discussed below for each of the 11 food classes. No findings have been corrected for recoveries.

DRINKING WATER

Tap water composites were collected from the same areas as the market baskets, and single determinations were made and reported for both infant and toddler classes. The tap water was used throughout the market basket study in the preparation of other items requiring dilution or addition of water. Six of the 10 water samples contained zinc, ranging from 0.1 ppm to 0.7 ppm and averaging 0.2 ppm. Cadmium was also found in one of the market baskets at the trace level.

WHOLE MILK, FRESH

This composite was common to both infant and toddler classes. Zinc was reported most frequently, in all 10 market baskets, ranging from 2.5 ppm to 5.2 ppm and averaging 3.7 ppm. Dieldrin was found in four market baskets, ranging from 0.001 ppm to 0.002 ppm and averaging a trace for all baskets. Half the market baskets showed DDE residues in the range 0.001–0.005 ppm with an average of 0.001 ppm. Other repor residues included benzene hexachloride (BHC), h chlor epoxide, selenium, and HCB.

TABLE 2. *Chemical residues found in infant and tod food composites from 10 United States cities— August 1974–July 1975*

Chemical Found	No. of Composites With Residues	No. of Positive Composites With Residues Reported as Trace [1]	Range,
INFANT			
Zinc	92	0	0.10–
Cadmium	41	35	0.05–
Selenium	32	15	0.10–
Lead	28	17	0.10–
Dieldrin	20	9	0.001–
DDE	15	3	0.001–
Mercury	1	1	T
BHC	14	9	T–
Malathion	13	1	0.006–
Diazinon	7	7	T
HCB	7	4	0.001–
Heptachlor epoxide	6	4	(
Lindane	3	1	0.008–
Toxaphene	3	0	0.16–
Botran	3	0	0.001–
p,p'-TDE	2	2	T
Carbaryl	2	2	T
PCNB	2	1	(
PCA	2	0	0.003–
Arsenic	5	5	T
DDT	1	1	T
Methoxychlor	1	1	T
Parathion	1	1	T
CIPC	1	0	(
PCB	1	1	T
PCP	1	0	(
Octachlor epoxide	1	1	T
Pentachlorobenzene	1	0	(
TODDLER			
Zinc	105	0	0.10–
Cadmium	61	50	0.05–
Selenium	44	24	0.14–
Dieldrin	34	8	0.001–
Lead	31	18	0.10–
BHC	31	14	T–
DDE	24	4	0.001–
Lindane	20	8	0.001–
Malathion	18	1	0.004–
Heptachlor epoxide	17	14	0.001–
Diazinon	12	7	0.001–
HCB	12	7	0.001–
Arsenic	9	4	0.100–
Mercury	8	7	
TDE	6	5	
CIPC	6	0	0.011–
Botran	6	0	0.001–
DDT	5	4	
PCA	5	1	0.003–
Toxaphene	4	1	0.100–
PCNB	4	1	0.004–
Pentachlorobenzene	4	2	
Carbaryl	2	1	
Aroclor 1254	2	2	T
Ronnel	1	1	T
Endosulfan	1	0	
TCNB	1	1	T
PCP	1	0	
Octachlor epoxide	1	1	T
Phosvel	1	0	

[1] Chemicals capable of being detected by the specific analytical odology may be confirmed quantitatively but are not quantifiable they are present at concentrations below the limit of quanti Limit of quantitation varies with residues and food classes.

OTHER DAIRY AND SUBSTITUTIONS

Infant.—Variations in infants' and toddlers' diet evident in this composite. The infant food comp

3LE 3. *Frequency of occurrence of chemical residues, ood class, in infant and toddler food composites from 10 United States cities—August 1974–July 1975*

EMICAL	Food Class[1]										
	I	II	III	IV	V	VI	VII	VIII	IX	X	XI
NUMBER OF OCCURRENCES IN INFANT FOODS											
	6	10	10	10	10	7	10	10	3	8	8
ium	1	—	1	6	10	7	10	1	3	1	1
ium	—	3	3	10	10	—	2	—	2	2	—
	—	—	2	4	5	1	6	6	—	1	3
lrin	—	4	4	7	1	2	—	—	2	—	—
	—	5	4	4	—	—	2	—	—	—	—
ıic	—	—	—	1	—	—	1	2	—	1	—
	—	6	5	3	—	—	—	—	—	—	—
thion	—	—	—	—	10	—	—	—	3	—	—
non	—	—	—	—	4	1	1	—	—	1	—
	—	2	1	3	—	—	—	—	1	—	—
achlor epoxide	—	2	1	3	—	—	—	—	—	—	—
ane	—	—	—	—	2	1	—	—	—	—	—
phene	—	—	—	—	—	—	—	—	3	—	—
n®	—	—	—	—	—	—	—	3	—	—	—
TDE	—	—	—	1	—	—	1	—	—	—	—
aryl	—	—	—	—	—	—	—	1	—	1	—
B	—	—	—	—	—	—	—	—	2	—	—
	—	—	—	—	—	—	1	—	1	—	—
ury	—	—	—	1	—	—	—	—	—	—	—
DDT	—	—	—	1	—	—	—	—	—	—	—
oxychlor	—	—	1	—	—	—	—	—	—	—	—
hion	—	—	—	—	—	—	1	—	—	—	—
	—	—	—	—	—	1	—	—	—	—	—
	—	—	—	—	—	—	1	—	—	—	—
	—	—	—	1	—	—	—	—	—	—	—
chlor epoxide	—	—	—	1	—	—	—	—	—	—	—
chlorobenzene	—	—	—	—	—	—	—	—	1	—	—
NUMBER OF OCCURRENCES IN TODDLER FOODS											
	6	10	10	10	10	10	10	10	10	10	9
ium	1	—	3	5	10	10	10	2	10	8	2
rin	—	4	9	10	1	4	2	—	4	—	—
ium	—	3	5	10	10	1	1	—	8	6	—
	—	—	1	3	4	3	10	4	—	3	3
	—	6	10	7	—	—	3	—	—	5	—
	—	5	8	9	—	—	1	—	—	1	—
ane	—	—	1	2	—	1	7	—	—	9	—
thion	—	—	—	—	9	—	—	—	6	3	—
achlor epoxide	—	2	8	7	—	—	—	—	—	—	—
non	—	—	1	1	5	1	1	1	—	2	—
	—	2	3	3	—	—	—	—	4	—	—
ic	—	—	1	5	—	—	—	2	—	1	—
	—	—	1	4	—	—	—	—	—	1	—
	—	—	—	—	—	5	—	1	—	—	—
n®	—	—	—	—	—	—	—	4	—	2	—
	—	—	1	4	—	—	—	—	—	—	—
	—	—	—	—	—	—	—	—	5	—	—
phene	—	—	—	—	—	—	—	—	4	—	—
3	—	—	—	—	—	—	—	—	4	—	—
chlorobenzene	—	—	—	—	—	—	—	—	4	—	—
ıryl	—	—	—	—	—	—	1	1	—	—	—
el	—	—	1	—	—	—	—	—	—	—	—
ulfan	—	—	—	—	—	—	—	1	—	—	—
3	—	—	—	—	1	—	—	—	—	—	—
	—	—	—	—	—	—	—	—	—	1	—
hlor epoxide	—	—	—	1	—	—	—	—	—	—	—
el	—	—	—	—	—	—	1	—	—	—	—
ıry	—	—	—	8	—	—	—	—	—	—	—
or 1254	—	—	—	1	—	—	—	—	1	—	—
ulfan sulfate	—	—	—	—	—	—	—	1	—	—	—

Table 1 for key to food classes.

ıded evaporated milk and various formula prepa-ns. Zinc was found in all 10 market baskets, rang-from 0.9 ppm to 6.5 ppm, and averaging 4.5 ppm. averaged a trace in five market baskets; range 0.001–0.002 ppm. Three of the 10 baskets con-d trace to 0.12 ppm selenium; average was 0.01 selenium. Residues of heptachlor epoxide, HCB, ıoxychlor, lead, and cadmium were also found.

ıler.—The toddlers' food composite included ice cream, chocolate milk, skim milk, cheese, and lesser amounts of other products such as half and half, fudgesicles, and puddings. Zinc and BHC were found in all 10 baskets at 2.2–7.8 ppm (average 5.6 ppm) and 0.001–0.003 ppm (average 0.002 ppm), respectively. Dieldrin was reported for nine market baskets, ranging from 0.002 ppm to 0.007 ppm and averaging 0.004 ppm; DDE and heptachlor epoxide were found in eight market baskets at 0.003 to 0.012 ppm, average 0.004 ppm) and trace to 0.002 ppm (average trace), respectively. Selenium was found in five market baskets at the trace level. Authors also found residues of HCB, cadmium, lindane, diazinon, ronnel, arsenic, DDT, TDE, and lead.

MEAT, FISH, AND POULTRY

Infant.—This composite contained the greatest number of residues, eight organochlorines, six metals, and one industrial chemical. Some regions limited the infant diet to commercially prepared meat-vegetable products, whereas others included fresh meat and eggs. Food composites from all 10 market baskets contained selenium, ranging from 0.10 ppm to 0.19 ppm and averaging 0.08 ppm, and zinc, ranging from 8.2 ppm to 41.8 ppm and averaging 19.1 ppm. Dieldrin levels of 0.001–0.003 ppm, average 0.001 ppm, were found in seven market baskets. DDE residues were found in four of the 10 market baskets, ranging from 0.005 ppm to 0.024 ppm and averaging 0.004 ppm. Other pesticide and metal residues reported near the trace level included BHC, heptachlor epoxide, HCB, DDT, TDE, octachlor epoxide, mercury, arsenic, lead, and cadmium. PCBs were found at trace level in the composite of one market basket.

Toddler.—Food composites in this category likewise contained the greatest number of residues: nine organochlorines, six metals, one organophosphate, and one industrial chemical. Fresh meats, fish, and poultry products, similar to the adult market basket, were composited. Three residues were found in all 10 market baskets: dieldrin, 0.002–0.004 ppm, average 0.002 ppm; selenium, 0.15–0.34 ppm, average 0.23 ppm; and zinc, 23.2–41.4 ppm, average 31.7 ppm. DDE was reported for nine market baskets ranging from 0.002 ppm to 0.064 ppm and averaging 0.012 ppm. Mercury was reported in eight market baskets at trace to 0.02 ppm levels, and averaging trace. Arsenic residues averaged 0.06 ppm in five market baskets; range was 0.10–0.18 ppm. Lead was found in three meat composites of the 10 analyzed, with results of 0.10 ppm, 0.11 ppm, and trace, averaging 0.02 ppm. Other reportable residues included BHC, cadmium, heptachlor epoxide, lindane, DDT, TDE, HCB, diazinon, octachlor epoxide, and PCBs.

GRAIN AND CEREAL PRODUCTS

Infant.—The predominant ingredients in the composites were dry cereals and flour, corn, or bread. Residues

TABLE 4. *Levels of chemical residues, by food class, of infant and toddler food composites from 10 United States cities—August 1974–July 1975*

Chemical	Residue, ppm		Chemical	Residue, ppm	
	Infant	Toddler		Infant	Toddler
I. DRINKING WATER					
ZINC			CADMIUM		
Average	0.2	0.2	Average	T	T
Positive composites			Positive Composites		
Total number	6	6	Total number	1	1
Number reported as trace	0	0	Number reported as trace	1	1
Range	0.1–0.7	0.1–0.7	Range	T	T
II. WHOLE MILK, FRESH					
ZINC			BHC		
Average	3.7	3.7	Average	0.0002	0.0002
Positive composites			Positive composites		
Total number	10	10	Total number	6	0
Number reported as trace	0	0	Number reported as trace	3	3
Range	2.5–5.2	2.5–5.2	Range	0.0004–0.001	0.0004–(
DIELDRIN			HEPTACHLOR EPOXIDE		
Average	T	T	Average	T	T
Positive composites			Positive composites		
Total number	4	4	Total number	2	2
Number reported as trace	2	2	Number reported as trace	1	1
Range	0.001–0.002	0.001–0.002	Range	T–0.001	T–0.001
DDE			SELENIUM		
Average	0.001	0.001	Average	T	T
Positive composites			Positive composites		
Total number	5	5	Total number	3	3
Number reported as trace	1	1	Number reported as trace	3	3
Range	0.001–0.005	0.001–0.005	Range	T	T
HCB					
Average	T	T			
Positive composites					
Total number	2	2			
Number reported as trace	2	2			
Range	T	T			
III. OTHER DAIRY AND SUBSTITUTIONS					
ZINC			LINDANE		
Average	4.5	5.6	Average		T
Positive composites			Positive composites		
Total number	10	10	Total number		1
Number reported as trace	0	0	Number reported as trace		1
Range	0.9–6.5	2.20–7.80	Range		T
DIELDRIN			ARSENIC		
Average	T	0.004	Average		T
Positive composites			Positive composites		
Total number	4	9	Total number		1
Number reported as trace	3	0	Number reported as trace		1
Range	T–0.002	0.002–0.007	Range		T
DDE			BHC		
Average	T	0.004	Average	T	0.002
Positive composites			Positive composites		
Total number	4	8	Total number	5	10
Number reported as trace	2	2	Number reported as trace	3	2
Range	0.002–0.003	0.003–0.012	Range	0.001–0.002	0.001–0
TDE			HEPTACHLOR EPOXIDE		
Average		T	Average	T	T
Positive composites			Positive composites		
Total number		1	Total number	1	8
Number reported as trace		1	Number reported as trace	0	6
Range		T	Range	0.001	T–0.002
SELENIUM			DDT		
Average	0.01	T	Average		T
Positive composites			Positive composites		
Total number	3	5	Total number		1
Number reported as trace	2	5	Number reported as trace		1
Range	T–0.12	T	Range		T
CADMIUM			LEAD		
Average	T	0.01	Average	T	T
Positive composites			Positive composites		
Total number	1	3	Total number	2	1
Number reported as trace	1	2	Number reported as trace	2	1
Range	T	T–0.07	Range	T	T

(Continued next page)

TABLE 4. (Cont'd). *Levels of residues, by food class, of infant and toddler food composites from 10 United States cities—August 1974–July 1975*

Chemical	Residue, ppm		Chemical	Residue, ppm	
	Infant	Toddler		Infant	Toddler
III. OTHER DAIRY AND SUBSTITUTIONS *(Cont'd)*					
NNEL			HCB		
verage		T	Average	T	T
sitive composites			Positive composites		
Total number		1	Total number	1	3
Number reported as trace		1	Number reported as trace	1	2
Range		T	Range	T	T–0.001
ZINON			METHOXYCHLOR		
verage		T	Average	T	
sitive composites			Positive composites		
Total number		1	Total number	1	
Number reported as trace		0	Number reported as trace	1	
Range		0.002	Range	T	
IV. MEAT, FISH, AND POULTRY					
C			DDT		
verage	19.1	31.7	Average	T	0.001
sitive composites			Positive composites		
Total number	10	10	Total number	1	4
Number reported as trace	0	0	Number reported as trace	1	3
Range	8.2–41.8	23.2–41.4	Range	T	T–0.007
RCURY			TDE		
erage	T	T	Average	T	T
sitive composites			Positive composites		
Total number	1	8	Total number	1	4
Number reported as trace	1	7	Number reported as trace	1	3
Range	T	T–0.02	Range	T	T–0.004
ENIC			LEAD		
erage	T	0.06	Average	0.01	0.02
sitive composites			Positive composites		
Total number	1	5	Total number	4	3
Number reported as trace	1	1	Number reported as trace	3	1
Range	T	0.10–0.18	Range	T–0.10	0.10–0.11
			PCB		
erage	T	T	Average	T	T
sitive composites			Positive composites		
Total number	3	7	Total number	1	1
Number reported as trace	3	5	Number reported as trace	1	1
Range	T	T–0.001	Range	T	T
DANE			OCTACHLOR EPOXIDE		
erage		T	Average	T	T
sitive composites			Positive composites		
Total number		2	Total number	1	1
Number reported as trace		2	Number reported as trace	1	1
Range		T	Range	T	T
ENIUM			DDE		
erage	0.8	0.23	Average	0.004	0.012
sitive composites			Positive composites		
Total number	10	10	Total number	4	9
Number reported as trace	4	0	Number reported as trace	0	0
Range	0.10–0.19	0.15–0.34	Range	0.005–0.024	0.002–0.064
MIUM			HCB		
erage	T	T	Average	T	T
sitive composites			Positive composites		
Total number	6	5	Total number	3	3
Number reported as trace	6	5	Number reported as trace	1	1
Range	T	T	Range	0.001–0.004	T–0.003
LDRIN			DIAZINON		
erage	0.001	0.002	Average		T
sitive composites			Positive composites		
Total number	7	10	Total number		1
Number reported as trace	2	1	Number reported as trace		1
Range	0.001–0.003	0.002–0.004	Range		T
TACHLOR EPOXIDE					
erage	T	T			
sitive composites					
Total number	3	7			
Number reported as trace	3	7			
Range	T	T			

inued next page)

TABLE 4. (Cont'd). *Levels of residues, by food class, of infant and toddler food composites from 10 United States cities—August 1974–July 1975*

Chemical	Residue, ppm		Chemical	Residue, ppm	
	Infant	Toddler		Infant	Toddler
V. GRAIN AND CEREAL PRODUCTS					
ZINC			SELENIUM		
Average	13.9	8.0	Average	0.23	0.22
Positive composites			Positive composites		
Total number	10	10	Total number	10	10
Number reported as trace	0	0	Number reported as trace	0	0
Range	9.1–18.4	5.4–9.9	Range	0.20–0.30	0.14–0.3(
LEAD			CADMIUM		
Average	0.073	0.03	Average	T	T
Positive composites			Positive composites		
Total number	5	4	Total number	10	10
Number reported as trace	2	2	Number reported as trace	10	10
Range	0.20–0.31	0.10–0.16	Range	T	T
MALATHION			DIAZINON		
Average	0.017	0.009	Average	T	T
Positive composites			Positive composites		
Total number	10	9	Total number	4	5
Number reported as trace	1	0	Number reported as trace	4	3
Range	0.006–0.039	0.004–0.018	Range	T	0.002–0.(
TCNB			LINDANE		
Average		T	Average	0.002	
Positive composites			Positive composites		
Total number		1	Total number	2	
Number reported as trace		1	Number reported as trace	0	
Range		T	Range	0.008–0.012	
			DIELDRIN		
			Average	T	T
			Positive composites		
			Total number	1	1
			Number reported as trace	1	0
			Range	T	0.003
VI. POTATOES					
ZINC			CADMIUM		
Average	3.8	3.7	Average	0.01	0.03
Positive composites			Positive composites		
Total number	7	10	Total number	7	10
Number reported as trace	0	0	Number reported as trace	5	4
Range	2.1–6.8	2.5–6.8	Range	T–0.05	0.05–0.0
DIELDRIN			LINDANE		
Average	0.001	0.001	Average	T	T
Positive composites			Positive composites		
Total number	2	4	Total number	1	1
Number reported as trace	0	1	Number reported as trace	1	1
Range	0.004–0.005	0.002–0.005	Range	T	T
CIPC			LEAD		
Average	0.007	0.015	Average	T	T
Positive composites			Positive composites		
Total number	1	5	Total number	1	3
Number reported as trace	0	0	Number reported as trace	1	3
Range	0.051	0.011–0.052	Range	T	T
DIAZINON			SELENIUM		
Average	T	T	Average		T
Positive composites			Positive composites		
Total number	1	1	Total number		1
Number reported as trace	1	1	Number reported as trace		1
Range	T	T	Range		T
VII. VEGETABLES					
ZINC			CARBARYL		
Average	4.6	4.4	Average		T
Positive composites			Positive composites		
Total number	10	10	Total number		1
Number reported as trace	0	0	Number reported as trace		0
Range	3.0–7.9	3.4–6.4	Range		0.01
CADMIUM			DIAZINON		
Average	0.01	T	Average	T	T
Positive composites			Positive composites		
Total number	10	10	Total number	1	1
Number reported as trace	9	10	Number reported as trace	1	0
Range	T–0.08	T	Range	T	0.001

(Continued next page)

TABLE 4. (Cont'd). *Levels of residues, by food class, of infant and toddler food composites from 10 United States cities—August 1974–July 1975*

Chemical	Residue, ppm		Chemical	Residue, ppm	
	Infant	Toddler		Infant	Toddler
VII. VEGETABLES *(Cont'd)*					
E			BHC		
verage	0.001	T	Average		T
ositive composites			Positive composites		
Total number	2	1	Total number		3
Number reported as trace	0	0	Number reported as trace		0
Range	0.002–0.011	0.002	Range		0.001–0.002
ENIUM			DIELDRIN		
verage	T	T	Average		T
ositive composites			Positive composites		
Total number	2	1	Total number		2
Number reported as trace	2	1	Number reported as trace		1
Range	T	T	Range		T–0.001
E			LEPTOPHOS		
verage	T		Average		T
ositive composites			Positive composites		
Total number	1		Total number		1
Number reported as trace	1		Number reported as trace		0
Range	T		Range		0.005
RATHION			PCA		
verage	T		Average	T	
ositive composites			Positive composites		
Total number	1		Total number	1	
Number reported as trace	1		Number reported as trace	0	
Range	T		Range	0.003	
AD			PCP		
verage	0.04	0.08	Average	T	
ositive composites			Positive composites		
Total number	6	10	Total number	1	
Number reported as trace	3	5	Number reported as trace	0	
Range	0.10–0.18	0.10–0.22	Range	0.01	
DANE			ARSENIC		
verage		T	Average	T	
ositive composites			Positive composites		
Total number		7	Total number	1	
Number reported as trace		4	Number reported as trace	1	
Range		0.001–0.002	Range	T	
VIII. FRUIT AND FRUIT JUICES					
C			DIAZINON		
verage	1.1	1.6	Average		T
ositive composites			Positive composites		
Total number	10	10	Total number		1
Number reported as trace	0	0	Number reported as trace		0
Range	0.6–1.8	0.7–3.1	Range		0.001
TRAN			CIPC		
verage	0.002	0.004	Average		0.012
ositive composites			Positive composites		
Total number	3	4	Total number		1
Number reported as trace	0	0	Number reported as trace		0
Range	0.001–0.013	0.003–0.024	Range		0.120
SENIC			CADMIUM		
verage	T	T	Average	T	T
ositive composites			Positive composites		
Total number	2	2	Total number	1	2
Number reported as trace	2	2	Number reported as trace	1	2
Range	T	T	Range	T	T
AD			CARBARYL		
verage	0.04	0.02	Average	T	T
ositive composites			Positive composites		
Total number	6	4	Total number	1	1
Number reported as trace	3	2	Number reported as trace	1	1
Range	0.10–0.24	T–0.12	Range	T	T
OSULFAN					
verage		T			
ositive composites					
Total number		1			
Number reported as trace		0			
Range		0.006			

ntinued next page)

TABLE 4. (Cont'd). *Levels of residues, by food class, of infant and toddler food composites from 10 United States cities—August 1974–July 1975*

Chemical	Residue, ppm		Chemical	Residue, ppm	
	Infant	Toddler		Infant	Toddler
IX. OILS AND FATS					
ZINC			SELENIUM		
Average	22.4	14.3	Average	T	T
Positive composites			Positive composites		
Total number	3	10	Total number	2	8
Number reported as trace	0	0	Number reported as trace	2	8
Range	20.9–25.3	9.6–18.3	Range	T	T
CADMIUM			DIELDRIN		
Average	0.08	0.02	Average	0.002	T
Positive composites			Positive composites		
Total number	3	10	Total number	2	4
Number reported as trace	0	6	Number reported as trace	1	3
Range	0.07–0.10	0.05–0.08	Range	T–0.006	T–0.003
TOXAPHENE			PCNB		
Average	0.35	0.061	Average	0.01	0.003
Positive composites			Positive composites		
Total number	3	4	Total number	2	4
Number reported as trace	0	1	Number reported as trace	1	1
Range	0.16–0.51	0.10–0.26	Range	T–0.03	0.004–0.0
MALATHION			PCA		
Average	0.12	0.048	Average	0.003	0.006
Positive composites			Positive composites		
Total number	3	6	Total number	1	5
Number reported as trace	0	0	Number reported as trace	0	1
Range	0.09–0.17	0.043–0.125	Range	0.008	0.003–0.0
HCB			PENTACHLOROBENZENE		
Average	0.001	0.001	Average	0.001	0.001
Positive composites			Positive composites		
Total number	1	4	Total number	1	4
Number reported as trace	0	2	Number reported as trace	0	2
Range	0.002	0.006–0.008	Range	0.002	T–0.006
PCB					
Average		T			
Positive composites					
Total number		1			
Number reported as trace		1			
Range		T			
X. SUGAR AND ADJUNCTS					
ZINC			ARSENIC		
Average	1.1	3.9	Average	T	0.02
Positive composites			Positive composites		
Total number	8	10	Total number	1	1
Number reported as trace	0	0	Number reported as trace	1	0
Range	0.2–2.8	0.4–8.6	Range	T	0.16
BHC			LEAD		
Average		T	Average	T	0.02
Positive composites			Positive composites		
Total number		5	Total number	1	3
Number reported as trace		4	Number reported as trace	1	1
Range		T–0.002	Range	T	0.10–0.1
SELENIUM			LINDANE		
Average	T	T	Average		0.002
Positive composites			Positive composites		
Total number	2	6	Total number		9
Number reported as trace	2	6	Number reported as trace		0
Range	T	T	Range		0.001–0.
MALATHION			CADMIUM		
Average		0.003	Average	T	T
Positive composites			Positive composites		
Total number		3	Total number	1	8
Number reported as trace		1	Number reported as trace	1	8
Range		0.007–0.020	Range	T	T
TDE			DDE		
Average		T	Average		T
Positive composites			Positive composites		
Total number		1	Total number		1
Number reported as trace		1	Number reported as trace		1
Range		T	Range		T
PCP			DIAZINON		
Average		0.009	Average	T	T
Positive composites			Positive composites		
Total number		1	Total number	1	2
Number reported as trace		0	Number reported as trace	1	2
Range		0.09	Range	T	T

(*Continued next page*)

TABLE 4. (Cont'd). *Levels of residues, by food class, of infant and toddler food composites from 10 United States cities—August 1974–July 1975*

Chemical	Residue, ppm		Chemical	Residue, ppm	
	Infant	Toddler		Infant	Toddler
X. SUGAR AND ADJUNCTS *(Cont'd)*					
RAN			CARBARYL		
erage		0.001	Average	T	
sitive composites			Positive composites		
Total number		2	Total number	1	
Number reported as trace		0	Number reported as trace	1	
Range		0.001–0.007	Range	T	
XI. BEVERAGES					
:			LEAD		
erage	0.5	0.8	Average	0.02	T
sitive composites			Positive composites		
Total number	8	9	Total number	3	3
Number reported as trace	0	0	Number reported as trace	2	3
Range	0.1–1.6	0.1–2.1	Range	T–0.14	T
MIUM					
erage	T	T			
sitive composites					
Total number	1	2			
Number reported as trace	1	2			
Range	T	T			

E: Average residues are based upon the total number of composites examined, excluding all Trace reportings. It is quite possible that values ted as T can be well below the detection limits of the method for that composite.

id in all 10 market baskets included: zinc, 9.0–18.4 , average 13.9 ppm; selenium, 0.20–0.30 ppm, age 0.23 ppm; malathion, 0.006–0.039 ppm, average ppm; and cadmium, all trace levels. Lead was id in five market baskets, ranging from 0.20 ppm .31 ppm and averaging 0.073 ppm. Diazinon, diel- , and lindane residues were also found.

dler.—By contrast to the infant diet, this com- e included breads, cakes, cookies, macaroni, canned , and noodle soup. All 10 market baskets showed following residues: zinc, 5.4–9.9 ppm, average 8.0 ; selenium, 0.14–0.30 ppm, average 0.22 ppm; and ium, all trace levels. Malathion, found in nine et baskets, ranged from 0.004 ppm to 0.018 ppm averaged 0.009 ppm. Lead was reported in four et baskets, ranging from 0.10 ppm to 0.16 ppm averaging 0.03 ppm. Also found at low levels diazinon, 0.002–0.003 ppm, average trace; TCNB; dieldrin.

TOES

it.—This composite was included in only seven et baskets; no composites were obtained in the rn region. Residues reported in all baskets in- d zinc, 2.10–6.80 ppm, average 3.83 ppm; and ium, trace to 0.05 ppm, average 0.01 ppm. Other table residues were dieldrin, 0.004–0.005 ppm, ge 0.001 ppm; and CIPC, trace to 0.051 ppm, ge 0.007 ppm. Trace levels of diazinon, lindane, ead were also found.

ler.—This composite was included in all 10 market ts of the series. Composites in all 10 baskets contained residues of zinc, ranging from 2.5 ppm to 6.8 ppm and averaging 3.7 ppm, and cadmium ranging from 0.05 to 0.06 ppm and averaging 0.03 ppm. In addition, composites from five baskets contained CICP residues ranging from 0.011 ppm to 0.052 ppm and averaging 0.15 ppm, and dieldrin residues ranging from 0.002 ppm to 0.005 ppm and averaging 0.001 ppm. Lindane, lead, diazinon, and selenium were found only at trace levels.

VEGETABLES

Infant.—A variety of commercially prepared vegetables and vegetable-meat products were composited. Composites from all 10 baskets contained residues of zinc ranging from 3.0 ppm to 7.9 ppm and averaging 4.6 ppm and residues of cadmium ranging from trace to 0.08 ppm and averaging 0.01 ppm. Lead was found in six market baskets, ranging from 0.10 ppm to 0.18 ppm and averaging 0.04 ppm. PCP was found in the composite of one basket at the 0.01 ppm level but with an overall average of 0.001 ppm. DDE was found in composites of two market baskets of 0.002 ppm and 0.011 ppm and averaged 0.001 ppm. Trace amounts of PCA, TDE, diazinon, parathion, and selenium were also found.

Toddler.—Residues found in vegetable composites of all 10 baskets included: zinc, 3.4–6.4 ppm, average 4.4 ppm; lead, 0.10–0.22 ppm, average 0.08 ppm; and cadmium, trace levels. Lindane was found in seven baskets ranging from 0.001 ppm to 0.002 ppm and averaging a trace. Residues of carbaryl, BHC, diazinon, dieldrin, DDE, leptophos, and selenium were also found.

FRUITS AND FRUIT JUICES

Infant.—The infant diet of fruits and fruit juices was rather limited, including in most cases, raw bananas, commercially processed fruits, and a few selected fruit drinks. Zinc levels were highest, ranging from 0.6 ppm to 1.8 ppm and averaging 1.1 ppm in 10 market baskets. Lead, found in six market baskets, from 0.10 ppm to 0.24 ppm, and averaged 0.04 ppm. Other residues found at low levels included botran, average 0.002 ppm, carbaryl, arsenic, and cadmium.

Toddler.—The toddler diet included many fresh fruits and fruit juices. Zinc was found in all market baskets, ranging from 0.7 ppm to 3.1 ppm and averaging 1.6 ppm for the series. Lead was present in composites from four baskets, two at the trace level, 0.10 ppm, and 0.12 ppm, and averaging 0.02 ppm. Botran was found in four baskets ranging from 0.003 ppm to 0.024 ppm and averaging 0.004 ppm. Other residues included arsenic, cadmium, CIPC, diazinon, endosulfan, and carbaryl.

OILS AND FATS

Infant.—Only the northeast region distinguished the infant and toddler diets for this composite, and it differs only in the peanut butter content. The results represent three market baskets, all of which contained residues of the following: zinc, 20.9–25.3 ppm, average 22.4 ppm; toxaphene, 0.16–0.51 ppm, average 0.35 ppm; malathion, 0.09–0.17 ppm, average 0.12 ppm; and cadmium, 0.07–0.10 ppm, average 0.08 ppm. PCNB was found in composites from two market baskets ranging from trace to 0.03 ppm and averaging 0.01 ppm. Selenium was reported at trace levels for two market baskets. Other residues included dieldrin, HCB, PCA, and pentachlorobenzene.

Toddler.—All 10 market baskets contained zinc residues, ranging from 9.6 ppm to 18.3 ppm and averaging 14.3 ppm; and cadmium residues ranging from 0.05 ppm to 0.08 ppm and averaging 0.02 ppm. Trace levels of selenium were found in eight market baskets. Malathion was found in six market baskets, ranging from 0.043 ppm to 0.12 ppm and averaging 0.048 ppm; toxaphene averaged 0.06 ppm in four market baskets, 0.10–0.26 ppm. Five of the 10 baskets exhibited PCA residues ranging from 0.003 ppm to 0.030 ppm and averaging 0.006 ppm. The remaining residues included HCB, dieldrin, and pentachlorobenzene. A trace of PCB was reported in one composite.

SUGAR AND ADJUNCTS

Infant.—Sugar and either syrup, fruit topping, or jelly were composited. Zinc was the only quantifiable residue, found in eight market baskets; residues ranged from 0.2 to 2.8 ppm, and averaged 1.1 ppm. Trace residues of arsenic, lead, selenium, cadmium, carbaryl, and diazinon were found.

Toddler.—In addition to items on the infant diet, t composite contained jello desserts and assorted cand including chocolate. Zinc was found in all 10 mar baskets, ranging from 0.4 ppm to 8.6 ppm, and aver ing 3.9 ppm; lindane was reported for nine mar baskets, ranging from 0.001 ppm to 0.007 ppm a averaging 0.002 ppm. A trace of cadmium was fou in eight composites and a trace of selenium was fou in six composites. One composite contained 0.16 p arsenic, and another contained 0.09 ppm PCP. L was found in three composites, with results of tra 0.10 ppm, 0.11 ppm, and averaging 0.02 ppm. Tr amounts of BHC, malathion, DDE, TDE, diazin and botran were found.

BEVERAGES

Infant.—A marked difference in the regional diet the infant resulted in an unusual combination of ite One region had no specific infant diet, another had same diet for infant and toddler, and of the other regions, one had cola and brewed tea, and the ot had fruit soda. Zinc was reported in eight of the market baskets, ranging from 0.1 ppm to 1.6 p and averaging 0.5 ppm. The only other residue ported was lead, in three market baskets, ranging fr trace to 0.14 ppm and averaging 0.02 ppm. A trace cadmium was found in one composite.

Toddler.—Residues were the same as those repo for infant food composites.

Discussion

Table 5 provides a general overview of the results the survey. It identifies the classes of residues and number of compounds within the class that were fo in each food category.

TABLE 5. *Types and number of residues, by food c found in infant and toddler total diet samples from United States cities—August 1974–July 1975*

Type of Residue	Food Class [1]										
	1	II	III	IV	V	VI	VII	VIII	IX	X	XI T
INFANT											
Metals	2	2	4	6	4	3	5	4	3	5	3
Pesticides	—	5	6	8	4	3	4	2	4	2	—
Fungicides	—	—	—	—	—	1	I	—	2	—	—
Industrial chemicals	—	—	—	1	—	—	—	—	1	—	—
Herbicides	—	—	—	—	—	—	I	—	—	—	—
Total	2	7	10	15	8	7	11	6	10	7	3
TODDLER											
Metals	2	2	5	6	4	4	4	4	3	5	3
Pesticides	—	5	10	10	3	3	7	5	4	7	—
Fungicides	—	—	—	—	1	1	—	1	2	—	—
Industrial chemicals	—	—	—	1	—	—	—	—	2	—	—
Herbicides	—	—	—	—	—	—	—	—	—	1	—
Total	2	7	15	17	8	8	11	10	11	13	3

[1] See key in table 1.

ANT

otal of 306 residues was found in the infant food
iposites of the 10 market baskets. The compounds,
gorized by predominant usage, were as follows:
or 65 percent were heavy metals, 99 or 32.3 per-
t were pesticides, and 2.7 percent included five
gicides, one herbicide, and 2 industrial chemicals.

heavy metals included zinc, cadmium, selenium,
, mercury, and arsenic. The most prevalent of these
zinc which ranged from 0.1 ppm to 41.8 ppm in
composites. Cadmium, the second most frequently
orted heavy metal residue, was found in 41 com-
tes, predominantly in grain and cereal products,
itoes, vegetables, and the meat, fish, and poultry
posites. Selenium was found in all meat and all
n composites, and in two or three of each of the
le milk, dairy, vegetables, oils and fats, and sugar
posites; none was found in the water, potato, fruit,
everage composites. Lead was found mostly in the
etable, fruit, grain composites, and to a lesser ex-
in the dairy, meat, sugar, and beverage composites;
esidue were reported in the water, whole milk, and
composites. The only positive report for mercury
in the meat composite. Arsenic was found in two
composites and in only one composite each of
t, vegetables, and sugar. Tables 2 and 4 show the
ls and distributions of the residues.

99 pesticide residues can be separated into three
s: organochlorines, 76 residues; organophosphates,
esidues; and two carbaryl residues. Of the organo-
rine residues, dieldrin was reported in 20 com-
tes, ranging from 0.001 ppm to 0.006 ppm, but
phene was reported in three oil and fat composites
much higher levels, ranging from 0.16 ppm to 0.51
. The organophosphate malathion was found in all
grain composites and in three infant oil and fat
posites ranging from 0.006 ppm to 0.17 ppm.
baryl, the only carbamate screened, was found only
e: once in the fruit composite and once in the
r composite, both at the trace level.

fungicide residues were found: PCNB was found
vo oil and fat composites, and its metabolite PCA
found in one vegetable composite. The fungicide
lues ranged from trace to 0.03 ppm. CIPC was
d in one potato composite at 0.051 ppm.

herbicide PCP was found in one vegetable com-
e at a level of 0.01 ppm.

industrial chemicals were reported. A trace of
was reported in one meat, fish, and poultry com-
e, and 0.002 ppm pentachlorobenzene was reported
ie oil and fat composite.

DLER

tal of 477 residues was found in the toddler food
posites of the 10 market baskets as follows: 258
or 54.1 percent were heavy metal residues; 196 or 41 percent were pesticide residues; 16 or 3.3 percent were fungicide residues, and 1.6 percent included six industrial chemical residues and one herbicide residue.

The heavy metals included zinc, cadmium, selenium, lead, arsenic, and mercury. Zinc accounted for 105 residues ranging from 0.1 ppm to 41.4 ppm and was found in almost all composites of every market basket. Cadmium was found in 61 composites, 50 of which were at the trace level, ranging from 0.05 ppm to 0.08 ppm; no cadmium was found in milk composites. Selenium was found in 44 composites, ranging from 0.14 ppm to 0.34 ppm; none was found in water, fruit and fruit juices, or the beverage composites.

Lead residues ranging from 0.10 ppm to 0.22 ppm were found in 31 composites; none was found in water, milk, or oil and fat composites. Arsenic, reported in five of the meat composites, two of the fruit, one of the dairy, and one of the sugar composites, ranged from 0.10 ppm to 0.18 ppm. Mercury was found in eight meat composites: seven at trace, one at 0.020 ppm.

Separation of the types of pesticide residues shows 162 organochlorine residues, 32 organophosphate residues, and 2 carbaryl residues. Just as in the infant composites, dieldrin was the most frequently reported organochlorine, with 34 positive findings at levels between 0.001 ppm and 0.007 ppm, whereas toxaphene was reported in four oil and fat composites, with one at trace level and the other three between 0.100 ppm and 0.26 ppm. Malathion was the organophosphate most frequently reported and at the highest level in 18 composites at levels of 0.004–0.025 ppm. Carbaryl was reported in two composites, one vegetable and one fruit, once at trace and once at the 0.001 ppm level.

The finding of 16 fungicide residues in the toddler diet is significant. Three chlorinated fungicides accounted for most of the residues: CIPC was found in five potato composites and one fruit composite ranging from 0.011 ppm to 0.120 ppm; PCNB was found in four oil and fat composites at levels of 0.004–0.016 ppm.

No chlorophenoxy acid herbicides were reported except PCP, found in one sugar composite at 0.09 ppm.

Two industrial chemicals were detected: pentachlorobenzene was found in four oil and fat composites at levels of trace to 0.006 ppm, and a PCB, Aroclor 1254, was found in one meat, fish, and poultry composite and in one oil and fat composite, both at trace levels.

Recovery studies were performed with each market basket, wherein composites were fortified with known compounds within each class of residue and, after corrections were made based on the unfortified composite contribution, calculations were made to determine the percentage of recovery. These results are included in Table 6.

TABLE 6. *Recovery data on residues, found in infant and toddler total diet samples from 10 United States cities—August 1974–July 1975*

Residue	Type of Food Composite	Spike Level, ppm	Range of Blank Level, ppm [1]	Range of Total Found, ppm [1]	No. of Recovery Studies
HCB	Fatty	0.001	0.000	0.0007	1
	Nonfatty	0.001	0.000	0.0004–0.0005	2
Mirex	Fatty	0.05	0.000	0.017	1
	Nonfatty	0.05	0.000	0.01–0.035	2
Leptophos	Fatty	0.05	0.000	0.044	1
	Nonfatty	0.05	0.000	0.024–0.041	2
Carbaryl	Nonfatty	0.20	0.00	0.15–0.20 (0.19)	16
Orthophenyl-phenol	Nonfatty	0.40	0.00	0.20–0.40 (0.32)	17
MCP	Fatty	0.02	0.00	0.0–0.015 (0.0055)	4
	Nonfatty	0.02	0.00	0.014–0.024 (0.018)	8
2,4-DB	Fatty	0.02	0.00	0–0.023 (0.009)	4
	Nonfatty	0.02	0.00	0.004–0.027 (0.017)	4
2,4,5-T	Fatty	0.02	0–0.002 (0.0007)	0.009–0.020 (0.013)	3
	Nonfatty	0.02	0.000	0.003–0.019 (0.016)	5
2,4-D	Fatty	0.02	0.000	0.011–0.014 (0.013)	2
	Fatty	0.04	0.000	0.010–0.020 (0.015)	2
	Nonfatty	0.02	0.000	0.008–0.018 (0.014)	4
	Nonfatty	0.04	0.000	0.004–0.042 (0.023)	4
PCP	Fatty	0.02	0	0.007	1
	Nonfatty	0.02	0–0.002 (0.0005)	0.014–0.020 (0.016)	4
2,4,5-TP	Fatty	0.04	0.000	0.022–0.074 (0.048)	2
	Nonfatty	0.04	0.000	0.013–0.039 (0.030)	4
BBHC	Fatty	0.02	0.000	0.010–0.019 (0.015)	2
	Nonfatty	0.02	0.000	0.017–0.018 (0.018)	4
ClPC	Nonfatty	0.05	0	0.036–0.070 (0.048)	3
Dieldrin	Fatty	0.01	0.0010–0.0068 (0.0029)	0.0105–0.0176 (0.0129)	3
	Nonfatty	0.005	0	0.004–0.0071 (0.0057)	6
Methyl parathion	Nonfatty	0.005	0	0.0023–0.0057 (0.0038)	5
Ronnel	Fatty	0.005	0	0.0030–0.0035 (0.0032)	2
	Nonfatty	0.005	0	0.0032–0.0052 (0.0045)	4
Oxychlordane	Fatty	0.005	0	0.0020–0.0021	2
	Nonfatty	0.003	0	0.0019–0.0034 (0.0027)	4
Parathion	Fatty	0.005	0	0.0041–0.0053	2
	Nonfatty	0.005	0	0.0044–0.0049 (0.0046)	4
Endrin	Fatty	0.01	0	0.0086–0.011	2
	Nonfatty	0.01	0	0.0082–0.0104 (0.0094)	4
Arsenic	Fatty	0.30	0.01–0.066 (0.0160)	0.205–0.340 (0.294)	10
	Nonfatty	0.30	0.005–0.065 (0.017)	0.205–0.415 (0.327)	20
Cadmium	Fatty	0.10	0.001–0.068 (0.020)	0.099–0.155 (0.052)	2
	Nonfatty	0.10	0.001–0.081 (0.019)	0.092–0.174 (0.118)	2
Lead	Fatty	0.20	0.000–0.056 (0.012)	0.113–0.296 (0.204)	1
	Nonfatty	0.20	0.000–0.160 (0.058)	0.108–0.381 (0.245)	2
Mercury	Fatty	0.06	0.000–0.013 (0.002)	0.051–0.073 (0.057)	
	Nonfatty	0.06	0.000–0.002 (0.0006)	0.056–0.071 (0.061)	
	Nonfatty	0.03	0.000	0.024–0.031 (0.028)	
Selenium	Fatty	0.20	0.01–0.17 (0.05)	0.07–0.31 (0.21)	1
	Nonfatty	0.20	0.00–0.28 (0.045)	0.09–0.63 (0.22)	1
Zinc	Fatty	5.0	3.0–4.9 (4.19)	7.7–12.5 (9.94)	
	Fatty	25.0	2.5–23.2 (14.7)	26.0–45.0 (37.9)	
	Nonfatty	5.0	0.0–6.40 (2.52)	3.40–14.0 (7.38)	1

[1] Numbers in parentheses represent average residue levels.

(*Continued*)

LITERATURE CITED

(*1*) *Association of Official Analytical Chemists. 1* Official Methods of Analysis, 12th ed., Washing D.C. Sections 25.026–25.030.

(*2*) *Association of Official Analytical Chemists. 1* Official Methods of Analysis, 12th ed., Washing D.C. Sections 25.0065–25.070.

(*3*) *Association of Official Analytical Chemists. 1* Official Methods of Analysis, 12th ed., Washing D.C. Sections 25.103–25.105.

(*4*) *Association of Official Analytical Chemists. 1* Official Methods of Analysis, 12th ed., Washing D.C. Sections 25.117–25.120.

(*5*) *Association of Official Analytical Chemists. 1* Official Methods of Analysis, 12th ed., Washing D.C. Sections 25.143–25.147.

(*6*) *Finocchiaro, J. M., and W. R. Benson. 1965.* T layer chromatographic determination of carb (Sevin) in some foods. J. Assoc. Off. Agric. C 48(4):736–738.

(*7*) *Food and Drug Administration. 1971.* Pesticide lytical Manual, Vol. I and II. U.S. Departmen Health, Education, and Welfare, Washington, D.C

(*8*) *Food and Drug Administration. 1976.* Compli Program Guidance Manual. Section 7305.002, IV, B, 4, a, 2(a).

(*9*) *Hundley, H. K., and J. C. Underwood. 1970.* D mination of total arsenic in total diet sample Assoc. Off. Anal. Chem. 53(6):1176–1178.

(*10*) *Johnson, R. D., and D.D. Manske. 1975.* Pest residues in total diet samples (IX). Pestic. Mon 9(4):157–169.

(*11*) *Johnson, R. D., and D. D. Manske. 1977.* Pest and other chemical residues in total diet san (XI). Pestic. Monit. J. 11(3):116–131.

(*12*) *Porter, M. L., R. J. Gajan, and J. A. Burke.* Acetonitrile extraction and determination of carb in fruits and vegetables. J. Assoc. Off. Anal. C 52(1):177–181.

FISH, WILDLIFE, and ESTUARIES

Organochlorine Pesticide Residues in Animals of Tasmania, Australia—1975–77

Harry Bloom,[1] Walter Taylor,[2] Walter R. Bloom,[3] and Geoffrey M. Ayling[4]

ABSTRACT

nals taken in Tasmania including duck (Anas super-sa), *eel* (Anguilla australis), *English perch* (Perca flu-*lis*), *white-faced heron* (Ardea pacifica), *brown trout* mo trutta), *European starling* (Sturnus vulgaris), *cat* is cattus), *cormorant* (Phalacrocorax *sp.*), *mutton bird* ffinus tenuirostris), *Tasmanian devil* (Sarcophilus har-), *rainbow trout* (Salmo gairdnerii), *Tasmanian raven* rvus mellori), *tench* (Tinca tinca), *and quail* (Coturnix *were sampled for* p,p'-*DDE*, p,p'-*TDE*, p,p'-*DDT*, *lin-*, *dieldrin, and hexachlorobenzene. Pesticide residue ls exceeded 0.1 ppm in at least one animal from each and in the majority of animals sampled from all areas. icide sources could not be determined, partly because atory species such as ducks, mutton birds, cormorants, eels may have ingested pesticides outside of Tasmania.*

Introduction

anochlorine pesticides have been used widely in nania, Australia to control agricultural pests. In icular, dieldrin has been used to mothproof woolens ufactured in northern Tasmania. Restrictions on nissible levels of pesticide residues in agricultural lucts exported to Europe and the United States have lted in a considerable decrease in pesticide use. vever, pesticides are still available for nonagricul-l and other domestic purposes.

a preliminary study in this program, analyses of tissues of several animals from Macquarie Island r Antarctica) showed surprising concentrations of following organochlorines:

Species	Residues, ppm HCB	Lindane	Dieldrin	ΣDDT
Gentoo penguin (*Pygoseelis papua*)	0.44	0.03	0.03	3.4
Royal penguin (*Eudyptes schlegeli*) (1)	0.08	0.01	0.02	0.47
(2)	0.16	0.01	0.02	0.41
Rockhopper penguin (*Eudyptes chrysocomi*) (1)	0.11	—	0.01	0.54
(2)	0.14	0.01	0.04	0.43
Weka (*Gallirallus australis*)	0.08	0.01	—	0.66
Macquarie Island cormorant (*Phalacrocorax albiventer*)	0.12	0.01	0.01	0.76
King penguin (*Aptenodytes patagonica*)	0.03	0.01	0.01	0.15

Researchers in other countries have studied the bioconcentration of DDT in the environment (*1*); the movement of ΣDDT into the atmosphere (*7*), which appears to be an important mode of transport of residues; pesticide residues in the Canadian Great Lakes region (*5*); the role of marine phytoplankton as a transport medium (*3*); the effects of DDT on reproduction of higher animals (*9*); and the physiological and biological effects of pesticides on poultry (*4*).

Because there had been no previous survey of pesticide residues in Tasmanian wildlife, the need existed for a study to determine whether pesticide concentrations in Tasmania were similar to those throughout the world.

Sample Collection

Animals were taken during 1975–77 throughout Tasmania, Australia (Fig. 1) by officers of the Tasmanian National Parks and Wildlife Service, Tasmanian Inland Fisheries Commission, and the Victoria Museum, Launceston, Tasmania. Although a sampling program was initially established, problems of logistics, manpower, the distribution of the various species, and weather made it necessary in the long term to sample animals which were readily accessible at the particular time and locality. Thus the initial aim of collecting animals high in the food chain was not entirely

mistry Department, The University of Tasmania, Hobart, Tas-a, Australia.
ernment Analyst's Laboratory, Campbell St., Hobart, Tasmania, alia.
ool of Mathematical and Physical Sciences, Murdoch University, , Western Australia.
e Department of the Environment, Hobart, Tasmania, Australia.

FIGURE 1. *World map showing location of Tasmania, Australia*

achieved. For similar reasons, all species could not be collected from all areas of Tasmania.

Locations from which animals were taken are shown in Figure 2. Species are listed in Table 1.

Analytical Procedures

SAMPLE PREPARATION

The sampled species, although differing widely in type, did not present any unusual problems in cleanup of residue for analysis.

Fat was extracted from the adipose tissue of ducks, Tasmanian devils, and cats by solution in hexane, and the solution was filtered through anhydrous sodium sulfate. The solvent was removed on a warm water bath. The extracted fat was cleaned on an alumina minicolumn (*6*).

Fish were macerated and extracted with a mixture of hexane–acetone–diethyl ether. The extracted fat was cleaned on an alumina minicolumn.

Birds were dissected, and the liver and breast tissue were analyzed separately following initial acetonitrile extraction of the homogenate. The extract was filtered through cotton wool and extracted by reverse-phase partition chromatography into hexane. The hexane extract was in turn concentrated and cleaned on an alumina minicolumn.

GAS-LIQUID CHROMATOGRAPHY (GLC)

Analyses were performed on a Tracor Model MT 220 gas chromatograph equipped with a Ni^{63} electron-capture detector. Instrument parameters and opera conditions follow:

Columns:	glass 6 ft long × ¼ inch OD, packed with a m of 2 percent OV–101 and 3 percent QF–1, or 3 pe OV–101, on 100–120-mesh Gas-Chrom Q
Temperatures:	injection port 225°C column oven 200°C detector 275°C
Carrier gas:	nitrogen flowing at 60 ml/minute
Purge gas:	nitrogen flowing at 20 ml/minute

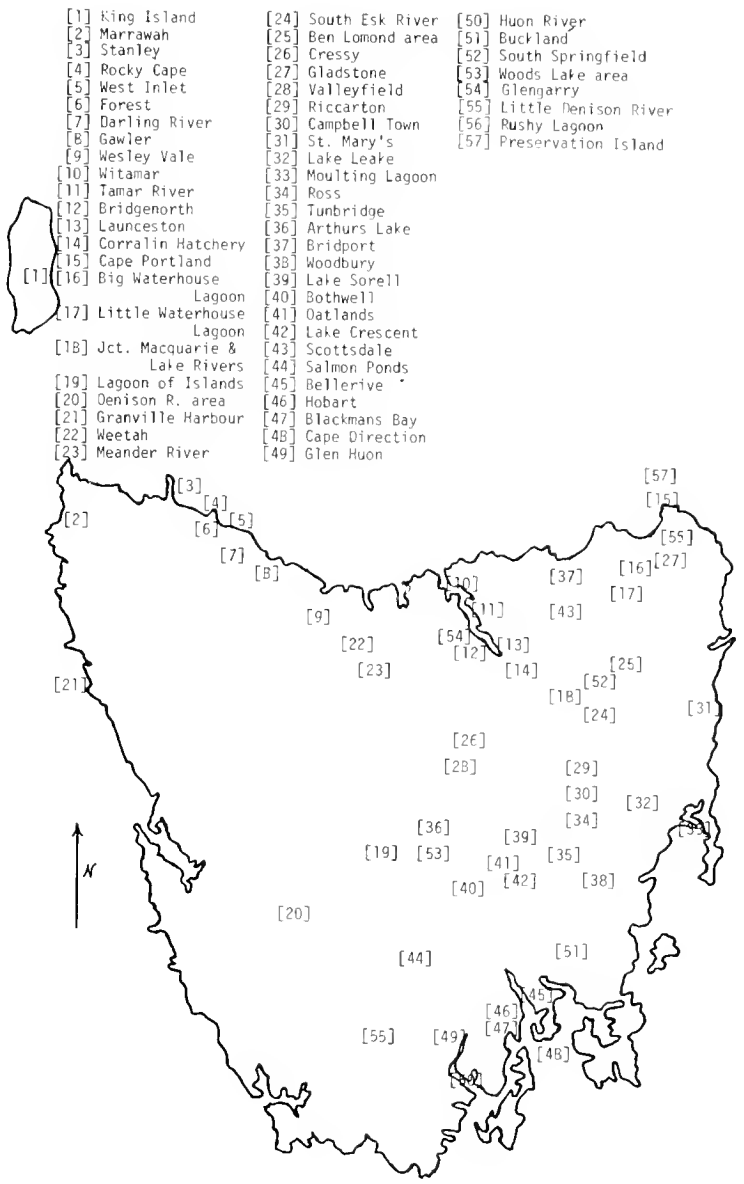
Quantitation was based on comparison with peak hei obtained by injecting known amounts of pestic Pesticide identity was confirmed by comparisor p-values (*2*) for several solvent systems. GLC re tion values on two columns of differing polarity, derivative formation.

All samples were analyzed for hexachloroben (HCB), lindane, dieldrin, *p,p′*-DDE, *p,p′*-TDE, *p,p′*-DDT.

Organochlorine pesticide standards of greater tha percent purity were obtained from various sou Recovery rates were 90–100 percent but were us close to 100 percent, hence correction for recovery not necessary.

Results and Discussion

In every area at least one animal contained a pest residue level exceeding 0.1 ppm, and for most a this was true for the majority of animals sam Pesticide sources could not be determined, partly cause migratory species such as ducks, mutton b cormorants, and eels may have ingested pesticides side of Tasmania.



URE 2. *Locations in Tasmania, Australia, where various animals were obtained for organochlorine pesticide residue analysis, 1975–77*

LE 1. *Species collected in Tasmania, Australia, for organochlorine pesticide residue analyses, 1975–77*

Common Name	Scientific Name
	Anas superciliosa
	Anguilla australis
sh perch	*Perca fluviatilis*
-faced heron	*Ardea pacifica*
n trout	*Salmo trutta*
ean starling	*Sturnus vulgaris*
	Felis cattus
orant	*Phalacrocorax sp.*
n bird	*Puffinus tenuirostris*
anian devil	*Sarcophilus harrisii*
ow trout	*Salmo gairdnerii*
anian raven	*Corvus mellori*
	Tinca tinca
	Coturnix sp.

To isolate any one area as having a significantly higher level of pesticide than other areas it would be desirable to have readings for several of the 14 animals, both in the area and elsewhere. The difficulty in obtaining samples in all areas precluded such a plan; in most cases only one species was sampled in any single area. Also, there is a large variety of sample sizes: from one Tasmanian devil in Granville Harbour to 37 ducks in Ross.

Wide fluctuations in the results for most species made the use of means and standard deviations of little value, e.g., for ducks from Cressy (area 26) the mean level

of ΣDDT was 32.07 ppm, and the standard deviation was 74.49 ppm.

The data here are characteristic of similar experiments. Many readings are clustered in a small range, here 0.0–0.2 ppm with a few outlying points as high as 321.0 ppm. When more than seven animals of the same species were sampled from the same area, the data in Table 2 were summarized as maximum, upper quartile, median, lower quartile, or minimum. When fewer than seven animals were sampled, all data

TABLE 2. *Summary of data on organochlorine pesticide residues in animals of Tasmania, Australia—1975–77*[1]

Area	Species	Range	Residues, ppm							Samples
			HCB	Lindane	DDE	Dieldrin	TDE	DDT	ΣDDT	
[1]	Cat									
		MAX.	0.50	0.40	9.80	3.90	1.40	5.40	15.20	20
		U.Q.	0.10	0.01	5.55	0.50	0.50	2.45	8.00	
		MED.	0.01	0.00	4.55	0.30	0.35	2.00	6.45	
		L.Q.	0.00	0.00	2.45	0.05	0.10	1.50	4.90	
		MIN.	0.00	0.00	0.30	0.00	0.00	0.40	0.80	
[2]	Duck		0.00	0.50	0.10	0.10	0.00	0.00	0.10	1
[3]	Duck		0.00	0.10	0.20	0.10	0.00	0.00	0.20	
			0.00	0.20	1.70	0.20	0.00	0.30	2.00	
			0.00	0.10	1.20	0.00	0.00	0.20	1.40	6
			0.00	0.01	1.00	0.90	2.00	2.60	5.60	
			0.00	0.10	0.01	0.10	0.00	0.00	0.01	
			0.00	0.00	0.60	0.01	0.10	0.01	0.70	
[4]	Duck		0.00	0.01	0.90	0.00	0.00	0.20	1.10	1
[5]	Duck		0.00	0.01	1.30	0.20	0.00	0.20	1.50	1
[6]	Duck		0.00	0.01	8.10	0.00	0.00	2.20	10.30	3
			0.00	0.01	1.20	0.01	0.00	0.30	1.50	
			0.00	0.01	0.60	0.10	0.00	0.40	1.00	
[7]	Brown trout	MAX.	0.00	0.20	0.90	0.50	1.20	1.60	3.60	23
		U.Q.	0.00	0.10	0.70	0.10	0.20	0.10	0.95	
		MED.	0.00	0.10	0.40	0.10	0.20	0.00	0.60	
		L.Q.	0.00	0.01	0.40	0.01	0.10	0.00	0.50	
		MIN.	0.00	0.00	0.01	0.00	0.00	0.00	0.01	
[8]	English perch	MAX.	0.20	0.50	8.40	1.50	5.50	1.50	14.10	30
		U.Q.	0.10	0.30	3.00	0.90	3.80	0.80	7.00	
		MED.	0.01	0.20	2.10	0.75	2.80	0.50	5.75	
		L.Q.	0.00	0.20	1.60	0.70	2.30	0.40	4.70	
		MIN.	0.00	0.10	0.90	0.50	1.30	0.10	2.80	
[9]	Eel	MAX.	0.00	0.60	8.20	6.00	6.20	18.30	32.70	29
		U.Q.	0.00	0.10	1.90	0.70	1.00	1.20	3.80	
		MED.	0.00	0.01	1.10	0.60	0.70	0.80	2.90	
		L.Q.	0.00	0.01	0.80	0.40	0.50	0.60	2.10	
		MIN.	0.00	0.01	0.30	0.00	0.30	0.40	1.20	
[10]	Cat		0.00	0.00	1.80	0.01	0.00	0.00	1.80	2
			0.00	0.00	0.70	0.01	0.00	0.00	0.70	
[11]	Rainbow trout		0.00	0.00	2.70	3.70	0.00	0.90	3.60	4
			0.00	0.00	1.60	2.40	0.00	0.50	2.10	
			0.00	0.00	0.10	0.20	0.00	0.20	0.30	
			0.00	0.00	0.10	0.20	0.00	0.10	0.20	
[12]	Cat		0.00	0.00	0.80	0.20	0.10	0.20	1.10	1
[13]	Cat		0.00	0.00	1.90	4.30	0.01	0.50	2.40	1
[14]	Tench		0.01	0.01	0.10	1.70	0.00	0.00	0.10	2
			0.00	0.00	0.01	0.00	0.00	0.00	0.01	
[15]	Duck		0.00	0.00	9.60	0.00	4.20	24.00	37.80	1
[15]	Tasmanian raven		0.00	0.00	0.00	0.00	0.00	0.00	0.00	1
[16]	Duck	MAX.	0.10	0.00	3.60	0.70	0.01	0.80	4.40	9
		U.Q.	0.10	0.00	1.40	0.10	0.00	0.50	1.85	
		MED.	0.00	0.00	0.70	0.00	0.00	0.10	0.70	
		L.Q.	0.00	0.00	0.30	0.00	0.00	0.00	0.35	
		MIN.	0.00	0.00	0.10	0.00	0.00	0.00	0.10	
[16]	Eel		0.20	1.30	0.80	0.30	1.20	0.20	2.20	6
			0.10	0.60	0.70	0.30	0.60	0.20	1.50	
			0.00	0.10	0.60	0.01	0.40	0.20	1.20	
			0.00	0.10	0.40	0.00	6.40	0.00	6.80	
			0.00	0.10	0.60	0.00	0.80	0.20	1.60	
			0.00	0.00	0.70	0.00	0.50	0.10	1.30	

(Continued next page)

TABLE 2. (Cont'd.) *Summary of data on organochlorine pesticide residues in animals of Tasmania, Australia—1975–77*

Area	Species	Range	Residues, ppm							
			HCB	Lindane	DDE	Dieldrin	TDE	DDT	ΣDDT	Samples
[17]	Eel		0.00	0.00	0.10	0.00	0.00	0.00	0.10	5
			0.00	0.01	0.00	0.00	0.00	0.00	0.00	
			0.01	0.01	0.10	0.00	0.00	0.00	0.10	
			0.00	0.01	0.10	0.00	0.00	0.00	0.10	
			0.00	0.01	0.00	0.00	0.00	0.00	0.00	
[17]	Cormorant		0.01	0.01	0.10	0.00	0.00	0.00	0.10	1
[18]	Eel	MAX.	0.00	0.20	1.20	0.60	0.40	0.70	2.30	15
		U.Q.	0.00	0.10	0.25	0.35	0.10	0.10	0.40	
		MED.	0.00	0.10	0.20	0.30	0.10	0.10	0.40	
		L.Q.	0.00	0.10	0.20	0.25	0.00	0.10	0.40	
		MIN.	0.00	0.10	0.00	0.00	0.00	0.00	0.00	
[19]	Tasmanian devil		0.10	0.01	0.50	0.01	0.00	0.01	0.50	1
[20]	Tasmanian devil		0.01	0.01	0.01	0.01	0.01	0.01	0.01	2
			0.01	0.01	0.01	0.01	0.01	0.01	0.01	
[21]	10		0.10	0.01	0.10	0.10	0.10	0.10	0.30	1
[22]	8		0.00	0.01	0.01	0.00	0.00	0.00	0.01	3
			0.00	0.01	0.01	0.00	0.00	0.00	0.01	
			0.01	0.01	0.01	0.00	0.00	0.00	0.01	
[23]	Duck	MAX.	0.00	0.01	7.60	0.30	0.80	0.80	7.70	10
		U.Q.	0.00	0.01	0.80	0.10	0.00	0.10	1.60	
		MED.	0.00	0.01	0.55	0.01	0.00	0.10	0.60	
		L.Q.	0.00	0.00	0.20	0.00	0.00	0.00	0.30	
		MIN.	0.00	0.00	0.10	0.00	0.00	0.00	0.20	
[24]	Brown trout		0.00	0.10	0.20	0.10	0.10	0.10	0.40	5
			0.00	0.10	0.20	0.01	0.01	0.01	0.20	
			0.00	0.10	0.20	0.10	0.01	0.10	0.30	
			0.00	0.01	0.20	0.01	0.10	0.10	0.40	
			0.00	0.01	0.20	0.10	0.10	0.10	0.40	
[24]	Tench	MAX.	0.60	8.80	0.60	0.80	0.00	0.00	0.60	12
		U.Q.	0.10	2.75	0.30	0.60	0.00	0.00	0.30	
		MED.	0.10	2.05	0.20	0.20	0.00	0.00	0.20	
		L.Q.	0.00	1.75	0.20	0.20	0.00	0.00	0.20	
		MIN.	0.00	1.10	0.20	0.10	0.00	0.00	0.20	
[25]	Tasmanian devil		0.01	0.01	0.01	0.01	0.01	0.01	0.01	1
[26]	Duck		0.00	0.00	1.90	0.00	0.00	0.00	1.90	6
			0.00	0.00	0.30	0.00	0.00	0.00	0.30	
			0.00	0.00	0.20	0.00	0.00	0.10	0.30	
			5.20	2.60	57.30	18.30	56.60	70.20	184.10	
			0.00	0.00	2.60	0.10	0.00	0.30	2.90	
			0.00	0.00	0.80	0.00	0.10	2.00	2.90	
[26]	Tasmanian raven	MAX.	0.00	0.01	1.10	0.01	0.01	0.00	1.10	16
		U.Q.	0.00	0.01	0.30	0.00	0.00	0.00	0.30	
		MED.	0.00	0.00	0.10	0.00	0.00	0.00	0.10	
		L.Q.	0.00	0.00	0.01	0.00	0.00	0.00	0.01	
		MIN.	0.00	0.00	0.01	0.00	0.00	0.00	0.01	
[27]	Duck		0.00	0.00	0.01	0.00	0.00	0.00	0.01	3
			0.00	0.00	0.60	0.00	0.00	0.20	0.80	
			0.00	0.00	25.80	0.00	0.00	9.00	34.80	
[28]	Duck		0.00	0.00	0.10	0.00	0.00	0.00	0.10	2
			0.00	0.00	0.01	0.01	0.00	0.00	0.01	
[29]	Duck		0.00	0.00	0.10	0.00	0.00	0.00	0.10	1
[30]	Duck		0.00	0.01	0.00	0.00	0.00	0.00	0.00	4
			0.00	0.00	0.01	0.00	0.00	0.00	0.01	
			0.00	0.00	0.40	0.20	0.00	0.00	0.40	
			0.00	0.20	0.10	0.01	0.10	0.10	0.30	
[31]	Cat		0.00	0.00	1.00	0.00	0.00	0.10	1.10	1
[32]	Cormorant		0.00	0.01	0.20	0.00	0.00	0.00	0.20	2
			0.01	0.01	0.20	0.00	0.00	0.00	0.20	
[33]	Duck	MAX.	0.20	0.01	11.20	0.30	0.00	23.70	34.90	26
		U.Q.	0.00	0.00	0.60	0.00	0.00	0.20	1.70	
		MED.	0.00	0.00	0.35	0.00	0.00	0.00	0.40	
		L.Q.	0.00	0.00	0.20	0.00	0.00	0.00	0.20	
		MIN.	0.00	0.00	0.01	0.00	0.00	0.00	0.01	

(Continued next page)

TABLE 2. (Cont'd.) *Summary of data on organochlorine pesticide residues in animals of Tasmania, Australia—1975–77*

Area	Species	Range	Residues, ppm							Samples
			HCB	Lindane	DDE	Dieldrin	TDE	DDT	ΣDDT	
[34]	Duck	MAX.	0.00	0.10	7.00	1.60	0.20	2.60	7.30	37
		U.Q.	0.00	0.01	0.60	0.10	0.00	0.10	1.00	
		MED.	0.00	0.00	0.40	0.01	0.00	0.00	0.40	
		L.Q.	0.00	0.00	0.20	0.00	0.00	0.00	0.20	
		MIN.	0.00	0.00	0.10	0.00	0.00	0.00	0.10	
[34]	White-faced heron		All the readings are zero							5
[34]	Cat	MAX.	0.00	0.00	5.60	0.40	0.60	4.60	9.00	9
		U.Q.	0.00	0.00	4.00	0.30	0.20	3.00	7.55	
		MED.	0.00	0.00	1.50	0.20	0.10	1.70	3.60	
		L.Q.	0.00	0.00	1.00	0.10	0.00	0.80	1.90	
		MIN.	0.00	0.00	0.80	0.10	0.00	0.10	0.90	
[34]	Tasmanian raven	MAX.	0.00	0.00	0.30	0.10	0.01	0.01	0.30	23
		U.Q.	0.00	0.00	0.01	0.01	0.00	0.00	0.01	
		MED.	0.00	0.00	0.01	0.01	0.00	0.00	0.01	
		L.Q.	0.00	0.00	0.01	0.00	0.00	0.00	0.01	
		MIN.	0.00	0.00	0.00	0.00	0.00	0.00	0.00	
[35]	Duck		0.00	0.01	3.90	0.30	0.00	4.70	8.60	3
			0.00	0.00	0.20	0.00	0.00	0.10	0.30	
			0.00	0.00	5.10	0.30	0.00	4.10	9.20	
[36]	Duck		0.00	0.00	0.20	0.00	0.00	0.00	0.20	4
			0.00	0.00	0.10	0.00	0.00	0.01	0.10	
			0.00	0.00	0.10	0.00	0.00	0.00	0.10	
			0.00	0.00	1.70	0.00	0.00	0.00	1.70	
[37]	Eel	MAX.	0.00	0.00	0.70	0.00	0.00	0.00	0.70	12
		U.Q.	0.00	0.00	0.55	0.00	0.00	0.00	0.55	
		MED.	0.00	0.00	0.30	0.00	0.00	0.00	0.30	
		L.Q.	0.00	0.00	0.20	0.00	0.00	0.00	0.20	
		MIN.	0.00	0.00	0.10	0.00	0.00	0.00	0.10	
[37]	Cormorant		0.00	0.01	0.01	0.00	0.00	0.00	0.01	1
[38]	Duck		0.00	0.00	1.50	0.01	0.00	0.10	1.60	2
			0.00	0.01	0.90	0.00	0.00	0.00	0.90	
[39]	Duck	MAX.	0.00	0.10	127.00	0.01	0.60	133.00	260.00	20
		U.Q.	0.00	0.05	1.10	0.00	0.00	0.35	1.20	
		MED.	0.00	0.00	0.50	0.00	0.00	0.00	0.65	
		L.Q.	0.04	0.00	0.10	0.00	0.00	0.00	0.15	
		MIN.	0.00	0.00	0.01	0.00	0.00	0.00	0.01	
[39]	4		All the readings are zero							5
[39]	Tasmanian raven		0.00	0.00	0.00	0.00	0.00	0.00	0.00	1
[40]	White-faced heron		0.00	0.00	0.00	0.00	0.00	0.00	0.00	1
[40]	European starling									
		MAX.	0.00	0.01	0.10	0.01	0.00	0.00	0.10	13
		U.Q.	0.00	0.00	0.01	0.01	0.00	0.00	0.01	
		MED.	0.00	0.00	0.01	0.01	0.00	0.00	0.01	
		L.Q.	0.00	0.00	0.01	0.01	0.00	0.00	0.01	
		MIN.	0.00	0.00	0.01	0.00	0.00	0.00	0.01	
[40]	Tasmanian raven		0.00	0.00	0.01	0.01	0.00	0.00	0.01	3
			0.00	0.00	0.01	0.01	0.00	0.00	0.01	
			0.00	0.00	0.01	0.00	0.00	0.00	0.01	
[41]	White-faced heron		0.00	0.00	1.00	0.00	0.00	0.00	0.00	1
[41]	European starling	MAX.	0.00	0.00	0.60	0.01	0.00	0.00	0.60	7
		U.Q.	0.00	0.00	0.01	0.01	0.00	0.00	0.01	
		MED.	0.00	0.00	0.01	0.01	0.00	0.00	0.01	
		L.Q.	0.00	0.00	0.01	0.01	0.00	0.00	0.01	
		MIN.	0.00	0.00	0.01	0.01	0.00	0.00	0.01	
[42]	Duck	MAX.	0.00	0.10	6.70	9.60	0.00	1.30	7.90	19
		U.Q.	0.00	0.00	0.85	0.00	0.00	0.05	1.05	
		MED.	0.00	0.00	0.20	0.00	0.00	0.00	0.30	
		L.Q.	0.00	0.00	0.05	0.00	0.00	0.00	0.05	
		MIN.	0.00	0.00	0.00	0.00	0.00	0.00	0.00	.
[42]	White-faced heron		All the readings are zero							2

(Continued next page)

TABLE 2. (Cont'd.) *Summary of data on organochlorine pesticide residues in animals of Tasmania, Australia—1975–77*

Area	Species	Range	Residues, ppm							
			HCB	Lindane	DDE	Dieldrin	TDE	DDT	ΣDDT	Samples
[43]	White-faced heron		0.00	0.00	2.10	0.00	0.00	0.00	2.10	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	0.00	0.00	
[43]	Tasmanian raven		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	0.01	0.00	0.00	0.00	0.01	
			0.00	0.00	0.01	0.00	0.00	0.00	0.01	
[44]	Cormorant		0.01	0.01	0.20	0.00	0.00	0.00	0.20	1
[45]	European starling									
		MAX.	0.00	0.01	0.40	0.10	0.00	0.00	0.40	19
		U.Q.	0.00	0.00	0.10	0.05	0.00	0.00	0.10	
		MED.	0.00	0.00	0.10	0.01	0.00	0.00	0.10	
		L.Q.	0.00	0.00	0.01	0.01	0.00	0.00	0.01	
		MIN.	0.00	0.00	0.01	0.01	0.00	0.00	0.01	
[46]	White-faced heron		0.00	0.00	0.01	0.00	0.00	0.00	0.01	1
[47]	European starling		0.00	0.00	0.50	0.01	0.00	0.00	0.50	3
			0.00	0.00	0.30	0.10	0.00	0.00	0.30	
			0.00	0.00	0.01	0.01	0.00	0.00	0.01	
[48]	Mutton bird	MAX.	0.01	0.01	0.01	0.01	0.00	0.00	0.01	31
		U.Q.	0.00	0.01	0.01	0.00	0.00	0.00	0.01	
		MED.	0.00	0.01	0.00	0.00	0.00	0.00	0.00	
		L.Q.	0.00	0.01	0.00	0.00	0.00	0.00	0.00	
		MIN.	0.00	0.01	0.00	0.00	0.00	0.00	0.00	
[49]	European starling									
		MAX.	0.00	0.00	8.20	0.01	0.00	0.00	8.20	30
		U.Q.	0.00	0.00	2.20	0.00	0.00	0.00	2.20	
		MED.	0.00	0.00	1.10	0.00	0 00	0.00	1.10	
		L.Q.	0.00	0.00	0.60	0.00	0.00	0.00	0.60	
		MIN.	0.00	0.00	0.00	0.00	0.00	0.00	0.00	
[50]	Duck	MAX.	0.00	0.10	136.00	0.20	62.00	321.00	519.00	22
		U.Q.	0.00	0.01	8.00	0.00	0.10	2.20	8.00	
		MED.	0.00	0.00	2.35	0.00	0.00	0.30	3.85	
		L.Q.	0.00	0.00	0.60	0.00	0.00	0.01	0.80	
		MIN.	0.00	0.00	0.20	0.00	0.00	0.00	0.20	
[51]	Cormorant		0.00	0.01	0.10	0.00	0.00	0.00	0.10	3
			0.00	0.00	0.10	0.00	0.00	0.00	0.10	
			0.00	0.00	0.10	0.00	0.00	0.00	0.10	
[52]	Cormorant		0.00	0.01	0.10	0.00	0.00	0.00	0.10	4
			0.00	0.00	0.01	0.00	0.00	0.00	0.01	
			0.00	0.00	0.10	0.00	0.00	0.00	0.10	
			0.00	0.01	0.01	0.00	0.00	0.00	0.01	
[53]	Tasmanian devil		0.01	0.01	0.01	0.10	0.00	0.01	0.01	3
			0.01	0.01	0.01	0.01	0.01	0.01	0.01	
			0.01	0.01	0.01	0.01	0.00	0.01	0.01	
[54]	Tasmanian raven		0.00	0.00	0.00	0.00	0.00	0.00	0.00	1
[55]	Tasmanian devil		0.01	0.00	0.01	0.01	0.01	0.00	0.01	1
[56]	Tasmanian raven		0.00	0.00	0.00	0.00	0.00	0.00	0.00	1
[57]	Quail		0.00	0.01	0.01	0.00	0.00	0.00	0.01	6
			0.00	0.01	0.01	0.00	0.00	0.00	0.01	
			0.00	0.01	0.01	0.00	0.00	0.00	0.01	
			0.01	0.01	0.01	0.00	0.00	0.00	0.01	
			0.01	0.01	0.10	0.01	0.00	0.00	0.10	
			0.01	0.01	0.01	0.01	0.00	0.00	0.01	

NOTE: MAX. = maximum, U.Q. = upper quartile, MED. = median, L.Q. = lower quartile, MIN. = minimum.

[1] The complete set of data can be obtained from Professor H. Bloom, Chemistry Department, The University of Tasmania, G.P.O. Box 252C, Hobart, Tasmania, Australia, 7001. Where fewer than seven animals were sampled, all data are given.

given. Where duplicate analyses were performed, the lower of the two values was used to calculate the results.

As a comparison of the distribution of pesticide residues in Tasmanian wildlife, Figure 3 shows the median values of ΣDDT over the various areas sampled.

The following exploratory analysis of the data was carried out, in order to isolate areas in which pesticide levels could be considered abnormally high. Comparisons were made between pesticide levels in animals of a given species and given area, and all other pesticide occurrences in that species. Authors compared areas from which five or more animals of a given sp were sampled as shown in Table 3. No such com son was possible in Gawler, Cape Direction, or Pr vation Islant (8, 48, and 57 areas, respectively) bec the species sampled in these areas were not sam anywhere else in Tasmania.

Comparisons between five-point summaries can be by representing them as box and whisker plots For example, the five-point summaries of DDE in eels from Wesley Vale and eels from all other p

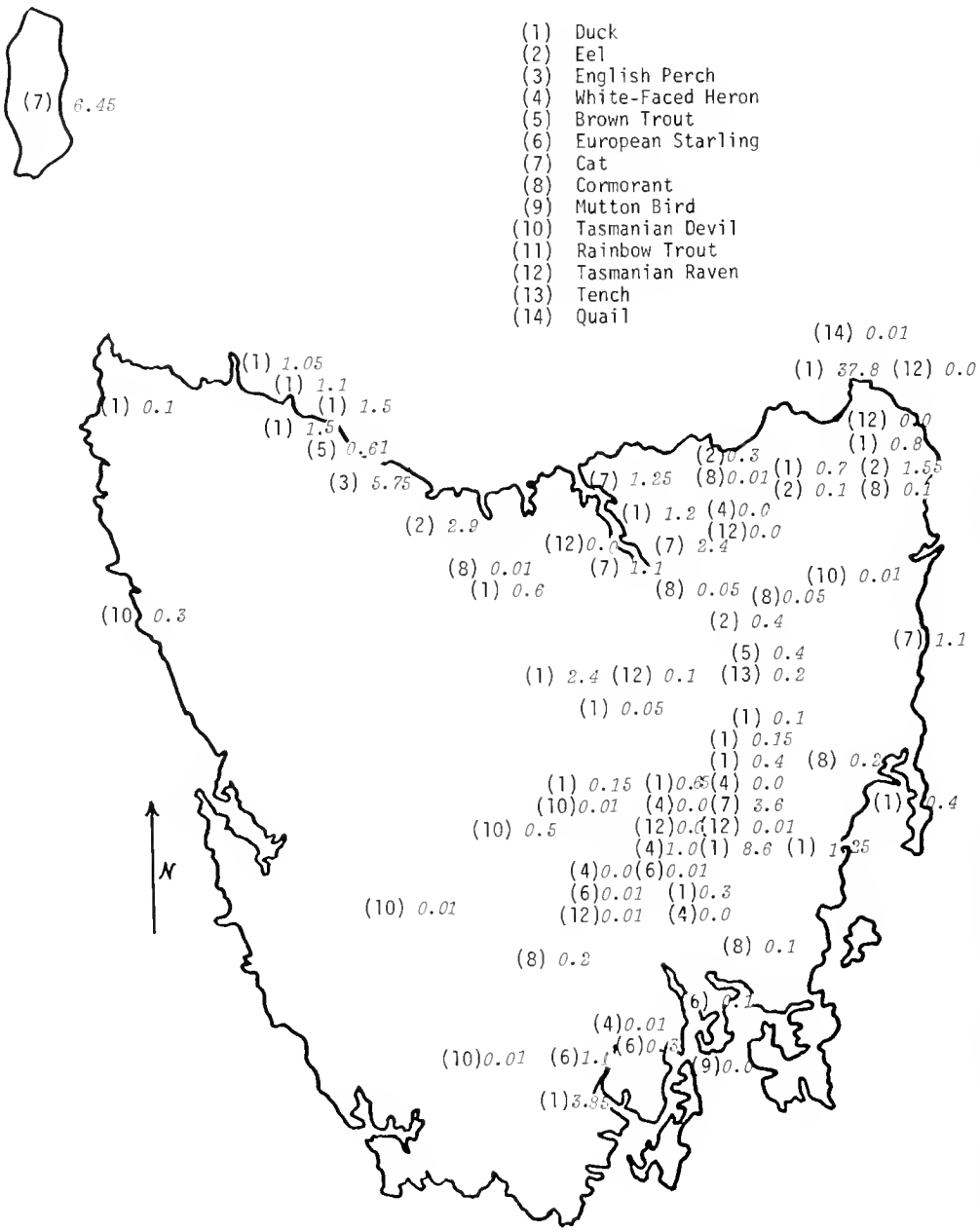


FIGURE 3. *Median values of ΣDDT, ppm, in animals from Tasmania, Australia—1975–77*

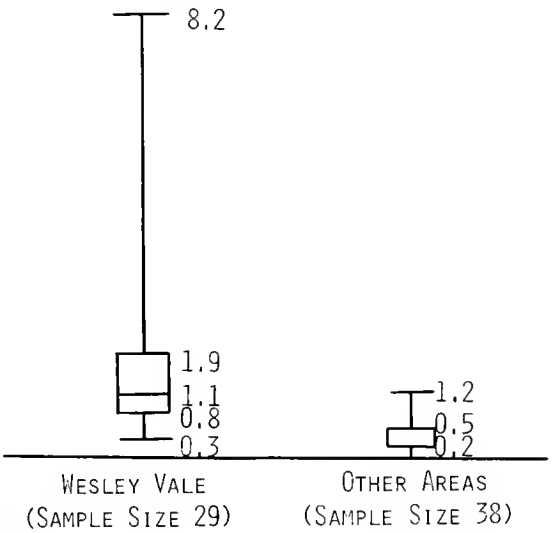
TABLE 3. *Areas from which five or more animals of a given species were sampled for organochlorine pesticide residue analyses, Tasmania, Australia—1975–77*

ı	1	3	7	8	9	16	16	17	18	23	24	24	26	26	33
es [2]	7	1	5	3	2	1	2	2	2	1	5	13	1	12	1
le size:															
en area	20	6	23	30	29	9	6	5	15	10	5	12	6	16	26
ıaining areas	14	179	5	0	38	176	61	62	52	175	23	0	179	34	159
ı	34	34	34	34	37	39	39	40	41	42	45	48	49	50	57
es [2]	1	4	7	12	2	1	4	6	6	1	6	9	6	1	14
le size:															
en area	37	5	9	23	12	20	5	13	7	19	19	31	30	22	6
ıaining areas	148	13	25	27	55	165	13	59	65	166	53	0	42	163	0

Figure 2 for key.
Figure 3 for key.

TABLE 4. *DDE levels in eels, Tasmania, Australia—1975–77*

Wesley Vale, Sample Size 29	Other Areas, Sample Size 38
Residue, ppm	
8.2	1.2
1.9	0.5
1.1	0.2
0.8	0.2
0.3	0.0



IGURE 4. *Box and whisker plot of the five-point summaries for ppm DDE in eels, Tasmania, Australia—1975–77*

given in Table 4; a box and whisker plot for each nary is shown in Figure 4. These are drawn to with key readings marked.

immediately apparent that DDE levels in eels from ey Vale are high compared to those eels from areas. In fact, about 90 percent of the Wesley readings are above 0.7 ppm, whereas about 84 ent of the remaining readings are below this level. result is interpreted as a location effect on the levels in eels.

above analysis was carried out for all of the areas species listed in Table 3, with the results given in

TABLE 5. *Location effects on organochlorine pesticide levels in five species of animals from Tasmania, Australia, 1975–77*

	Area	Species	n^1	n^2	Pesticide
1	(King Island)	cat	20	14	HCB, DDE, TDE, DDT
9	(Wesley Vale)	eel	29	38	DDE, dieldrin, TDE, DDT
		Tasmanian			
26	(Cressy)	raven	16	34	DDE
34	(Ross)	duck	37	148	Dieldrin
		European			
49	(Glen Huon)	starling	30	42	DDE
50	(Huon River)	duck	22	163	DDE, DDT

[1] Number of animals of the given species sampled in the given area.
[2] Number of animals of the given species sampled elsewhere.

Table 5. The final column in Table 5 lists the pesticides for a location effect of the area on the species shown.

A direct comparison of pesticide levels in different species was not as promising because there were very few areas where more than one species was sampled. However, the procedure outlined above was carried out for Big Waterhouse Lagoon, South Esk River, Cressy, Ross, and Lake Sorell (areas 16, 24, 26, 34, and 39, respectively) indicating that feral cats showed high levels of pesticide intake, followed in decreasing order by fish, ducks, and other birds. The results warrant further investigation.

Comparison with Other Studies

A comparison of the present study with similar studies elsewhere (*1, 3, 5, 7, 9,*) shows that neither Tasmania nor Macquarie Island can be regarded as biologically isolated. Highly efficient biological concentration and transportation mechanisms ensure that residues will reach such places from continental areas where relatively larger amounts of pesticides have been used.

Apparently, pesticide residue levels in Tasmanian wildlife are very similar to levels in other parts of the world where fairly strict controls have been implemented for several years. In the Canadian Great Lakes region, persistence and fate of DDT and aldrin/dieldrin in soils, streams, rivers, lakes, and the aquatic food chain has been intensively studied (*5*). It was found, as must be similarly concluded in Tasmania, that DDT and, to a lesser extent, dieldrin contamination is widespread, and that the major sources of contamination are from

recreational and urban uses rather than from agricultural uses of insecticides.

Acknowledgments

Authors thank D. Lynch, Tasmanian Inland Fisheries Commission; I. Eberhard and J. Burgess, Tasmanian National Parks and Wildlife Service; L. Woodhouse, Tasmanian Department of the Environment; E. Martyn and R. Hardy, Tasmanian Department of Agriculture; A. Richardson, Department of Zoology, University of Tasmania; F. Ellis, Victoria Museum; T. P. Speed, University of Western Australia; for helpful discussions on the handling of the data. Authors also thank R. F. Williams, Main Roads Department, Western Australia, for computing the results.

LITERATURE CITED

(1) *Bevenue, A. 1976.* The bioconcentration aspects of DDT in the environment. Residue Rev. 61:37–112.

(2) *Bowman, M. C., and M. Beroza. 1965.* Extractio values of pesticides and related compounds in si nary solvent systems. J. Assoc. Off. Agric. Chem (5):943–952.

(3) *Cox, J. L. 1972.* DDT residues in marine phytop ton. Residue Rev. 44:23–38.

(4) *Foster, T. S. 1974.* Physiological and biological e of pesticide residues in poultry. Residue Rev. 51 121.

(5) *Harris, C. R., and J. R. W. Miles. 1975.* Pesticide dues in the Great Lakes Region of Canada. Re Rev. 57:28–79.

(6) *Holden, A. V., and K. Marsden. 1969.* Single- clean-up of animal tissue extracts for organochl residue analysis. J. Chromatogr. 44(1969):481–492

(7) *Spencer, W. F. 1975.* Movement of DDT and its d atives into the atmosphere. Residue Rev. 59:91–117

(8) Turkey, J. W. *1976.* Exploratory Data Analysis. Add Wesley, Boston, Mass.

(9) *Ware, G. W. 1975.* Effects of DDT on reproducti higher animals. Residue Rev. 59:119–140.

DDT in Northern Pike (Esox lucius) *from the Richelieu River, Québec, Canada, 1974–75*

Serge Boileau,[1] M. Baril,[2] and J. G. Alary[1]

ABSTRACT

ıcentrations of DDT, TDE, DDE, and ΣDDT were de- ıined in homogenized whole fish samples of 129 north- pike (Esox lucius). *These fish were netted between June 4 and June 1975 in the first 10 km of the Richelieu er flowing in Canadian territory. Two years after the ning of DDT, ΣDDT levels ranged from 0.2 ppm fresh y weight in two-year-old specimens to 1.5 ppm in a ear-old pike. Residues increased greatly with age, and ificant seasonal variations in the ΣDDT levels were ıd in five- and six-year-old pike.*

Introduction

ch effort has been devoted to the qualitative and ntitative determination of organochlorine pesticide dues in North American wildlife. Attention has also ı given to determining pesticide residues in marine i.e., in the New Jersey salt marsh snail (*5*) and hannel catfish in the Des Moines River (*8*).

the present study, authors relate levels of DDT, Ξ, DDE, and ΣDDT in the northern pike (*Esox us*), to the period of capture and the age of the imens. The pike occupies the highest trophic level ıe Richelieu River.

Richelieu River is the outlet of Lake Champlain. latter is the sixth largest freshwater body in the ted States. Hydrologically, Lake Champlain is part he St. Lawrence Basin. It is both an interstate and nternational body of water, with 62 percent of its ace area in Vermont, 35 percent in New York, and rcent in Québec, Canada. Draining an 8,234-square- basin, through residential, industrial, and agri- ıral areas (*4*), the lake flows northward and dis- ges through the Richelieu River.

Sampling

in and Fournier found that, during its lifetime, : *lucius* inhabits an area with a radius of approxi- ly two miles (*6*). Therefore, all the specimens were captured in the first 10 km of the river flowing in Canadian territory.

A total of 149 fish were captured by gillnet as follows: 42 between June 1 and August 15, 1974 (period 1); 42 between August 16 and November 15, 1974 (period 2); and 45 between November 16, 1974, and June 1, 1975 (period 3). All fish appeared to be healthy at the time of collection.

Fresh weight was determined immediately. Scales and opercular bones were collected for the estimation of age (*7*), and the fish were wrapped in aluminum foil to prevent desiccation. The error in assigning age to pike is not known but it increases as the age increases. All fish were frozen at —30°C less than three hours after their capture.

Analytical Procedures

Residues were extracted by the method of Porter et al. (*11*) with few modifications. All solvents were pesticide grade quality. The sodium sulfate was conditioned at 650°C for 48 hours and was allowed to cool in an air-tight desiccator.

The Florisil was conditioned at 650°C for 72 hours, partially rehydrated with 2 percent water, and stored in a dark, air-tight glass container.

For each set of analyses, an entire frozen fish was cut into 20 cm^3 pieces. The fish cubes were thawed in 3 ml of 1:1 diethyl ether–petroleum ether/gram initial fresh weight before being homogenized for 3 minutes at 20,000 rpm in a 1-gallon stainless steel Waring blender. The homogenate was centrifuged at 3000 g for 15 minutes. The supernate was dehydrated on a 2.5-cm × 40-cm-long column of anhydrous sodium sulfate. The eluant was collected in a round-bottom flask and evaporated to near dryness in a flash evaporator. The last traces of ether were removed with a stream of nitrogen. and the remaining substance was assumed to be total fat. Five grams of fat was then dissolved in 40 ml of *n*-hexane, and the residue was partitioned between *n*-hexane and 50 ml acetonitrile-saturated *n*-hexane. This extraction was repeated four times.

ırtment des Sciences Biologiques, Universite du Quebec a Mon- C.P. 8888, Succ. A, Montreal, Quebec, Canada H3C 3P8.
ırtment d'Hygiene des Milieux, Universite de Montreal, C.P. Succ. A, Montreal, Quebec, Canada H3C 3P8.

The 200 ml of acetonitrile–*n*-hexane was collected in a 1-liter decantation flask to which was added 200 ml *n*-hexane, 10 ml dichloromethane, and 50 ml saturated sodium sulfate solution. The mixture was shaken for 2 minutes, 500 ml water was added, and then the mixture was shaken for an additional 2 minutes. The aqueous layer was decanted, the hexane phase was washed with three 150-ml portions of water, and finally dried on a 2.5-cm × 40-cm-long column of anhydrous sodium sulfate. The hexane solution was evaporated to approximately 3 ml. These last 3 ml were eluted through a 2.5-cm × 30-cm-long Florisil column with a mixture of 210 ml *n*-hexane and 90 ml dichloromethane. The column had previously been washed with 150 ml *n*-hexane.

The eluted solution was evaporated to approximately 1 ml, and the final volume was diluted to 10 ml with *n*-hexane.

A sample solution of 1 μl or less was injected into a Tracor Microtek Model 220 gas chromatograph equipped with a ^{63}Ni electron-capture linearizer detector. Instrument parameters and operating conditions follow:

Columns:	silanized borosilicate glass, 4.75 mm ID × 1.80 m long, packed with: (1) a mixture of 2 percent OV-17 and 2 percent OV-210 on 100–120-mesh Gas-Chrom Q (2) a mixture of 1 percent OV-17 and 3 percent OV-210 on 100–120-mesh Gas-Chrom Q
Temperatures:	detector 300°C injector 215°C columns 200°C
Carrier gas:	a mixture of 95 percent argon and 5 percent methane flowing at 70 ml/minute.

The area under the peak was measured with a printing disc integrator and the surface was used to quantitate the residues. Recoveries were 92 percent for DDT, 91 percent for DDE, and 89 percent for TDE. No corrections were made for recovery rates. The method precision has not been accounted for in the statistical treatment of the data.

Confirmatory tests consisted of rerunning the samples, on both columns, after they had been spiked with pure residues.

Lower limits of detection were 0.001 ppm fresh body weight for DDT, TDE, and DDE.

Results

Age of the pike varied from two to six years. Average fresh body weight ranged from 320 to 1700 g and the average percentage of fat varied from 1.1 to 1.9 (Table 1).

One-way variance analysis of the fresh body weight showed the following: Weights of the two-year-old pike were significantly higher ($P<0.05$) during period 3. Weights of three- and four-year-old pike were significantly lower ($P<0.05$) during period 1. Weights of five- and six-year-old specimens did not vary significantly with the period of capture. One-way vari analysis applied to percentage fat showed that level of fat did not fluctuate with the season of ture; and the two-year-old fish had a significantly l ($P<0.05$) lipid content that the other age groups, the lipid contents were not significantly different w the two-year-old group.

Variation due to sex could not be evaluated from t data because of the small number of females.

p,p'-DDT RESIDUES

Table 2 shows the average concentration, stan

TABLE 1. *Fresh body weight and percentage fat, by group and period of capture, of northern pike* (Esox lu *from the Richelieu River, Québec, Canada—1974–7*

Age, Years	Period of Capture[1]	*n*	Fresh Body Weight $\bar{x}$	S.D.	Range	Percentage $\bar{x}$	S.D.	R
2	1	12	250	70	120–380	1.1	0.35	0.
	2	10	230	40	230–330	0.95	0.35	0.
	3	12	420	100	240–630	1.3	0.50	0.
	A	34	320	100	120–630	1.1	0.42	0.
3	1	10	420	180	180–750	1.6	0.53	0.
	2	12	880	100	700–1000	1.5	0.55	0.
	3	13	920	160	750–1200	1.6	0.65	0.
	A	35	760	260	180–1200	1.6	0.59	0.
4	1	10	1100	150	720–1300	2.1	0.88	0.
	2	10	1100	140	770–1300	1.4	0.63	0.
	3	12	880	200	630–1200	1.5	0.63	0.
	A	32	1000	200	630–1300	1.7	0.77	0.
5	1	5	1300	280	990–1700	1.9	0.97	0.
	2	6	1600	310	1200–2100	1.9	0.85	0.
	3	4	1200	190	1000–1500	2.0	1.0	0.
	A	15	1400	300	990–2100	1.9	0.87	0.
6	1	5	1900	290	1600–2300	2.0	0.84	0.
	2	4	1700	220	1500–2000	1.2	0.45	0.
	3	4	1600	310	1400–2000	1.7	0.70	0.
	A	13	1700	290	1400–2300	1.6	0.73	0.

NOTE: A = values for the age group regardless of period of c
[1] Period 1: June 1–August 15, 1974; period 2: August 16–Nov 15, 1974; period 3: November 16, 1974–June 1, 1975.

TABLE 2. *p,p'-DDT residues, by age group and peri capture, in northern pike* (Esox lucius) *from the Ric River, Québec, Canada—1974–75*

Age, Years	Period of Capture[2]	*n*	Residues, ppm: Wet Weight[1] $\bar{x}$	S.D.	Range	Fat $\bar{x}$	S.D.	I
2	1	12	5.4	0.6	4.4–6.5	5.8	2.4	
	2	10	6.0	1.0	4.2–7.0	7.5	3.4	
	3	12	5.3	1.5	3.1–7.5	4.9	2.8	
	A	34	5.5	1.1	3.1–7.5	5.9	3.0	
3	1	10	12	2.7	7.3–15	7.8	3.5	
	2	12	9.5	1.0	8.4–11	7.6	4.0	
	3	13	11	1.9	7.8–14	8.9	6.3	
	A	35	11	2.1	7.3–15	8.1	4.8	
4	1	10	14	2.2	11–17	8.2	4.5	
	2	10	11	1.3	8.4–12	9.0	3.2	
	3	12	11	2.7	7.7–16	8.9	5.1	
	A	32	12	2.5	7.7–17	8.7	4.3	
5	1	5	20	4.4	15–26	14	8.7	
	2	6	14	2.5	10–17	9.5	6.2	
	3	4	21	3.1	17–24	14	9.1	
	A	15	18	4.4	10–26	12	7.6	
6	1	5	39	5.5	31–46	24	11	
	2	4	21	4.2	17–27	20	8.0	
	3	4	38	3.7	34–42	27	17	
	A	13	33	9.4	17–46	24	12	

NOTE: A = values for the age group regardless of period of c
[1] Values multiplied by 100.
[2] Period 1: June 1–August 15, 1974; period 2: August 16–No 15, 1974; period 3: November 16, 1974–June 1, 1975.

tion, and the range of values of *p,p'*-DDT in wet weight multiplied by 100 and in ppm fat.

n *p,p'*-DDT residues were expressed as ppm wet weight, one-way variance analysis showed the wing: There were no seasonal variations in *p,p'*- levels in the two- and three-year-old fish. *p,p'*- levels in the four-year-old pike caught during d 1 were significantly higher ($P<0.05$) than levels ur-year olds caught during the other two periods. DDT levels in five- and six-year-old pike caught ng period 2 were significantly lower ($P<0.05$) than s in five- and six-year olds caught during the other periods. When comparing the age groups, regardof the period of capture, authors found a signifiincrease ($P<0.05$) in residue levels with age pt between the three- and four-year-old groups.

the other hand, no seasonal variation could be cted when residues were expressed as ppm fat; the ease of residues with age was significant ($P<0.05$) pt between the three- and four-year-old fish and een the four- and five-year-old fish.

TDE RESIDUES

e 3 shows the average concentration, standard ation, and the range of values of *p,p'*-TDE in wet weight multiplied by 100 and in ppm fat. n the results were expressed as ppm wet body ht, one-way variance analysis showed the following:

e were no seasonal variations in *p,p'*-TDE levels ie two- and three-year-old fish. *p,p'*-TDE levels in -year-old pike caught during period 2 were signifiy lower ($P<0.05$) than levels in four-year-olds ht during the other two periods. *p,p'*-TDE levels in five-year-old pike caught during period 3 were significantly higher ($P<0.05$) than levels in five-year olds caught during the other two periods. *p,p'*-TDE levels in six-year-old pike caught during period 1 were significantly higher ($P<0.05$) than levels in six-year olds caught during period 2. *p,p'*-TDE levels increased significantly ($P<0.05$) between the three- and four-year-old fish and between the four- and five-year-old groups.

When the *p,p'*-TDE residues were expressed as ppm fat, authors found the following:

There were no seasonal variations in *p,p'*-TDE levels in the three-, five-, and six-year-old groups. *p,p'*-TDE levels in two-year-old pike were significantly lower ($P<0.05$) in fish caught during period 1 than levels in two-year olds caught during period 2, *p,p'*-TDE levels in four-year-old pike caught during period 2 were significantly lower ($P<0.05$) than levels in four-year olds caught during period 3, *p,p'*-TDE residue levels increased significantly ($P<0.05$) with age except between the three- and four-year-old groups and between the four- and five-year-old groups.

p,p'-DDE RESIDUES

Table 4 shows the average concentration, standard deviation, and range of values of *p,p'*-DDE as ppm wet weight multiplied by 100 and as ppm fat. When the residues were expressed as ppm wet weight, one-way variance analysis showed the following: There were no seasonal variations in *p,p'*-DDE levels in the 2- and 3-year-old fish. *p,p'*-DDE levels were significantly higher ($P<0.05$) in 4-, 5-, and 6-year-old pike caught during period 1 than levels in 4-, 5-, and 6-year olds

LE 3. p,p'-*TDE residues, by age group and period of ire, in northern pike* (Esox lucius) *from the Richelieu River, Quebec, Canada—1974–75*

Period of s Capture [2]	n	Residues, ppm: Wet Weight [1] $\bar{x}$	S.D.	Range	Fat $\bar{x}$	S.D.	Range
1	12	1.8	0.7	1.2–3.3	1.8	1.1	0.9–4.8
2	10	2.4	0.7	1.0–3.0	3.0	1.3	0.7–5.4
3	12	3.1	1.0	1.7–4.7	2.8	1.5	0.9–6.3
A	34	2.4	1.0	1.0–4.7	2.5	1.4	0.7–6.3
1	10	4.5	1.4	2.7–6.8	3.0	1.2	1.4–4.4
2	12	4.8	1.4	2.4–6.9	3.9	2.8	1.0–12
3	13	6.9	2.4	3.7–11	5.5	4.1	1.5–16
A	35	5.5	2.1	2.4–11	4.2	3.1	1.0–16
1	10	7.8	1.6	5.9–11	4.4	2.1	2.4–9.0
2	10	4.1	1.4	1.8–6.1	3.4	1.3	1.7–5.8
3	12	8.6	2.2	5.4–12	7.1	4.4	2.0–15
A	32	6.9	2.6	1.8–12	5.1	3.4	1.7–15
1	5	9.4	1.8	8.6–12	6.7	4.7	3.6–15
2	6	7.3	2.0	5.2–11	4.6	2.7	3.2–10
3	4	13	2.6	10–16	8.2	4.0	4.4–13
A	15	9.5	3.1	5.2–16	6.3	3.8	3.2–15
1	5	18	2.8	15–21	11	4.7	5.2–16
2	4	12	3.5	7.7–16	12	4.9	4.3–15
3	4	21	7.7	12–31	15	9.3	9.1–28
A	13	17	5.9	7.7–31	12	6.1	4.3–28

: A = values for the age group regardless of period of capture.
es multiplied by 100.
od 1: June 1–August 15, 1974; period 2: August 16–November 74; period 3: November 16, 1974–June 1, 1975.

TABLE 4. p,p'-*DDE residues, by age group and period of capture, in northern pike* (Esox lucius) *from the Richelieu River, Quebec, Canada—1974–75*

Age, Years	Period of Capture [2]	n	Residues, ppm: Wet Weight [1] $\bar{x}$	S.D.	Range	Fat $\bar{x}$	S.D.	Range
2	1	12	11	1.3	10–15	12	3.9	7.0–19
	2	10	12	1.3	9.0–13	15	8.9	8.7–35
	3	12	11	1.1	9.0–14	10	6.7	4.1–27
	A	34	11	1.5	9.0–15	12	6.7	4.1–35
3	1	10	21	4.3	16–27	14	6.4	5.7–28
	2	12	22	2.0	16–26	17	10	9.1–43
	3	13	18	1.6	16–20	14	6.6	5.7–29
	A	35	20	3.5	16–27	15	7.9	5.7–43
4	1	10	32	4.9	25–39	19	9.7	9.1–40
	2	10	24	3.1	18–27	21	11	7.8–46
	3	12	26	2.6	22–29	20	7.9	9.7–32
	A	32	27	4.7	18–39	20	9.2	7.8–46
5	1	5	69	3.8	62–72	51	40	19–120
	2	6	36	6.2	29–44	24	13	10–44
	3	4	37	4.2	33–41	26	18	11–51
	A	15	47	16	29–72	33	27	10–120
6	1	5	130	12	110–140	80	44	46–150
	2	4	44	4.2	39–48	41	15	27–58
	3	4	60	6.0	66–54	42	21	29–71
	A	13	81	40	39–140	56	35	27–150

NOTE: A = values for the age group regardless of period of capture.
[1] Values multiplied by 100.
[2] Period 1: June 1–August 15, 1974; period 2: August 16–November 15, 1974; period 3: November 16, 1974–June 1, 1975.

caught during periods 2 and 3. *p,p'*-DDE levels increased significantly ($P<0.05$) with age.

When the residues were expressed as ppm fat, authors found that there were no seasonal variations in *p,p'*-DDE levels in the 2-, 3-, and 4-year-old pike. *p,p'*-DDE levels in the 5- and 6-year-old pike caught during period 1 were significantly higher ($P<0.05$) than levels in 5- and 6-year olds caught during the other two periods. *p,p'*-DDE levels increased significantly ($P<0.05$) with age except between the 2- and 3-year-old groups.

ΣDDT RESIDUES

Table 5 shows average concentration, standard deviation, and range of values for ΣDDT as ppm wet weight multiplied by 100 and as ppm fat. When residues were expressed as ppm wet weight, one-way variance analysis showed the following: There were no seasonal variations in ΣDDT residues in the two- and three-year-old fish; ΣDDT levels in four-, five-, and six-year-old pike were significantly lower ($P<0.05$) during period 2 and significantly higher ($P<0.05$) during period 1 than levels in four-, five-, and six-year olds caught during the other two periods (Fig. 1). ΣDDT levels increased significantly ($P<0.01$) with age (Fig. 2).

When ΣDDT residues were expressed as ppm fat, authors found there were no significant seasonal variations in the ΣDDT levels (Fig. 3); and ΣDDT levels increased significantly ($P<0.05$) with age (Fig. 4).

The water level of Lake Champlain, recorded at Rouses Point between June 1974 and June 1975, is illustrated in Figure 5 as the mean, maximum, and minimum each month.

TABLE 5. *ΣDDT residue, by age group and period of capture, in northern pike* (Esox lucius) *from the Richelieu River, Quebec, Canada—1974–75*

Age, Years	Period of Capture [2]	n	Residues, ppm: Wet Weight [1] $\bar{x}$	S.D.	Range	Fat $\bar{x}$	S.D.	Range
2	1	12	19	1	16–22	20	7	11–33
	2	10	20	1	18–22	25	12	13–52
	3	12	20	3	14–26	18	10	10–34
	A	34	19	2	14–26	19	11	10–52
3	1	10	37	4	32–43	19	14	11–45
	2	12	36	3	32–40	29	16	15–72
	3	13	36	4	29–41	28	16	10–58
	A	35	36	3	29–43	26	14	10–72
4	1	10	53	4	48–60	31	16	15–63
	2	10	39	3	33–43	33	14	13–63
	3	12	46	2	42–48	36	16	16–64
	A	32	46	7	33–60	34	15	13–64
5	1	5	98	4	93–100	71	51	29–160
	2	6	57	4	54–62	38	21	19–76
	3	4	71	3	67–74	47	31	21–91
	A	15	74	18	54–100	50	38	19–160
6	1	5	190	8	170–190	110	57	61–200
	2	4	77	4	75–82	87	17	61–100
	3	4	120	4	110–120	83	46	53–150
	A	13	130	48	75–190	96	43	53–200

NOTE: A = values for the age group regardless of period of capture.
[1] Values multiplied by 100.
[2] Period 1: June 1–August 15, 1974; period 2: August 16–November 15, 1974; period 3: November 16, 1974–June 1, 1975.

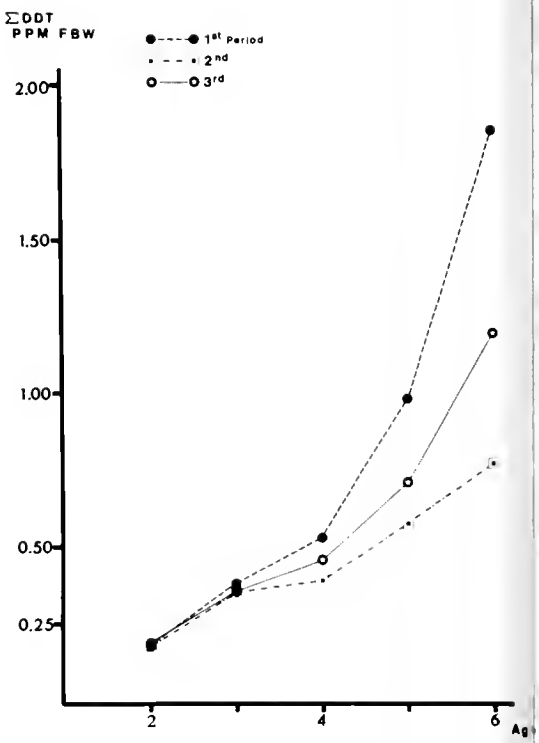


FIGURE 1. *Average ΣDDT levels, ppm wet weigh five age groups of northern pike* (Esox lucius) *during periods of capture, Richelieu River, Québec, Can 1974–75*

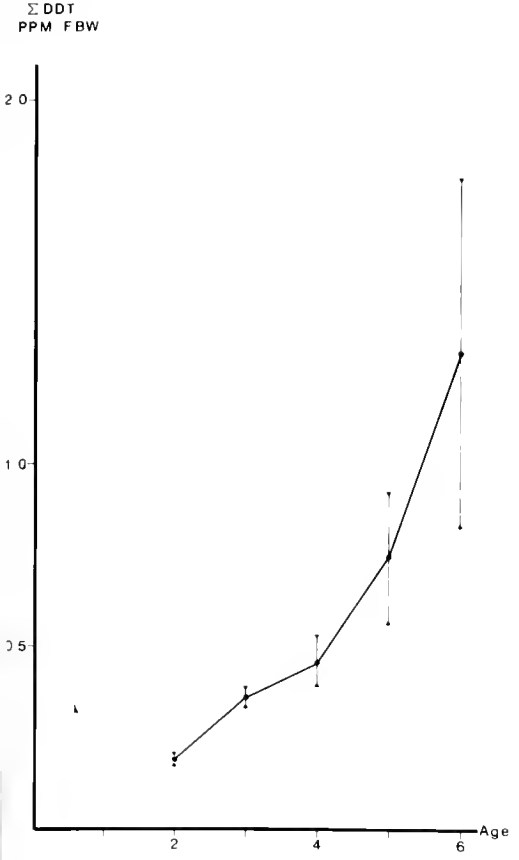
Discussion

Buhler et al. (*1, 2*) reported that whole-body residues increased with size for salmon. This corr well with the present data showing that residue creased significantly with age of the northern pike conclusion is even more explicit when results ar pressed on a fresh-body-weight basis compared lipid basis (Fig. 2 versus Fig. 4).

The extent to which DDT residues affected the ph ogy of pike was not determined, but authors feel a human population whose diet was based on thi would certainly be exposed to large amounts of resi

Seasonal variations in residue levels in fish have rec little attention. Kelso et al. (*9*) working with six ent species, found that residue levels peaked in No ber and were at a minimum during May and July; variations corresponded to the seasonal domestic agricultural use of pesticides in the watershed.

Simpson et al. (*12*) surveyed mercury content in and fish, including a wide range of freshwater fis specimens collected from Pickwick Reservoir in Te



JRE 2. *Average ΣDDT and standard deviation, ppm weight, for five age groups of northern pike* (Esox s) *from the Richelieu River, Québec, Canada—1974–75*

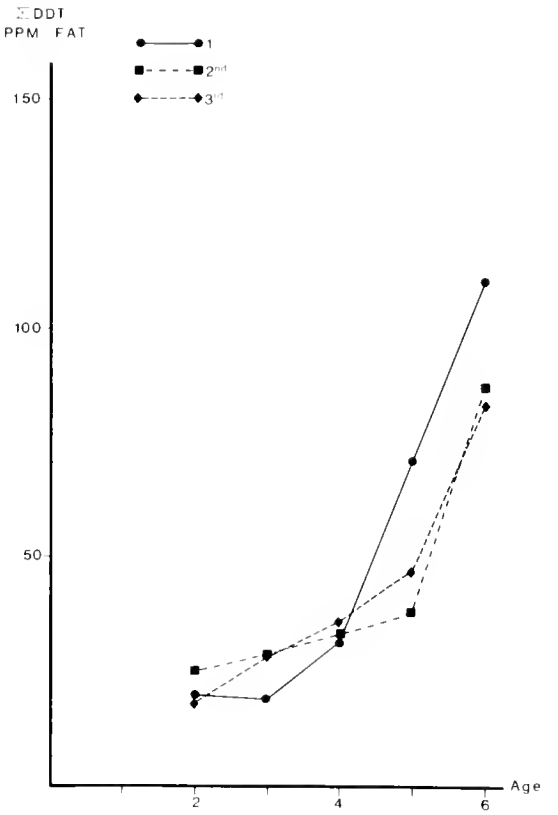


FIGURE 3. *Average ΣDDT levels, ppm fat, in five age groups of northern pike* (Esox lucius) *during three periods of capture, Richelieu River, Québec, Canada—1974–75*

they found maximum mercury concentrations be- n June and September 1970 and between April and 1971.

study of oysters from the Caloosahatchee River iage basin in Florida, Butler (*3*) observed that easonal fluctuation of pesticide residues indicated gricultural or at least a scheduled use of DDT. ound it significant that extensive acreage in this iage basin was devoted to the culture of sugarcane sweetcorn crops which would be maturing and ving fairly heavy pesticide applications during the residue periods.

gg and Bulkley (*8*) found a seasonal variation in rin concentrations in the muscle tissue of channel h (*Ictalurus punctatus*) that were 300–399-mm Three peaks were found, in April, July, and mber.

e present study, a significant seasonal variation of T occurred in the older fish groups where results xpressed as ppm fresh body weight, but this varia- is not significant when the data are expressed as fat. It was also impossible to detect a significant nal variation of lipid levels in these pike.

The seasonal variation in the present results could hardly be attributed to the agricultural use of DDT because the pesticide was banned in 1973.

Therefore, authors must hypothesize that there is a persistent input of DDT that contaminates the prey of pike. According to Woodwell et al. (*13*), although DDT has been banned in Canada and the United States, the aerial movement of DDT worldwide could account for a great deal of DDT input to aquatic fauna.

Fischer et al. (*4*) reported that the drainage basin of Lake Champlain includes 10,540 acres of apple orchards: 5,740 acres in New York and 4,800 acres in Vermont. Kuhr et al. (*10*) found up to 357 ppm DDT in the first six inches of soil in orchards that had not been sprayed with DDT for more than 15 years. Over 70 percent of the aged deposits were still in the form of unchanged DDT, the remainder being the metabolites DDE and TDE.

Authors can only speculate that rainfall is the major cause of DDT input to the aquatic system of Lake Champlain. Figure 5 shows that the lower water levels correspond to the second period of capture when minimum residues were found. One would expect a greater

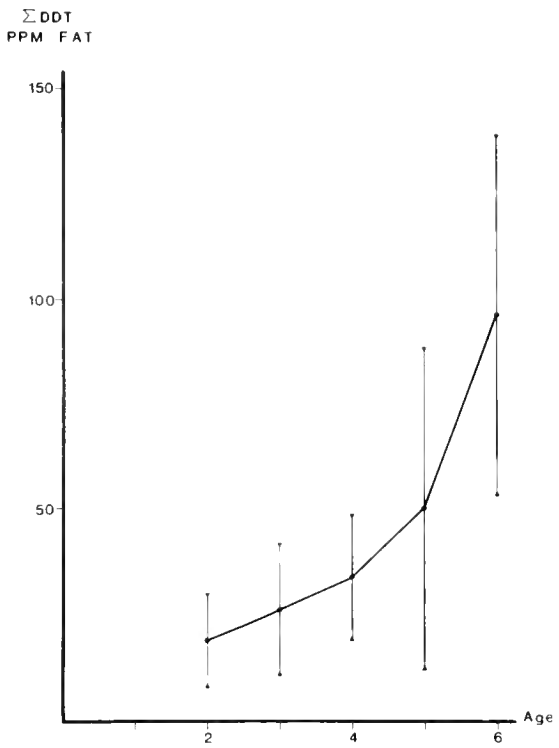


FIGURE 4. *Average ΣDDT and standard deviation, ppm fat, for five age groups of northern pike* (Esox lucius) *from the Richelieu River, Québec, Canada—1974–75*

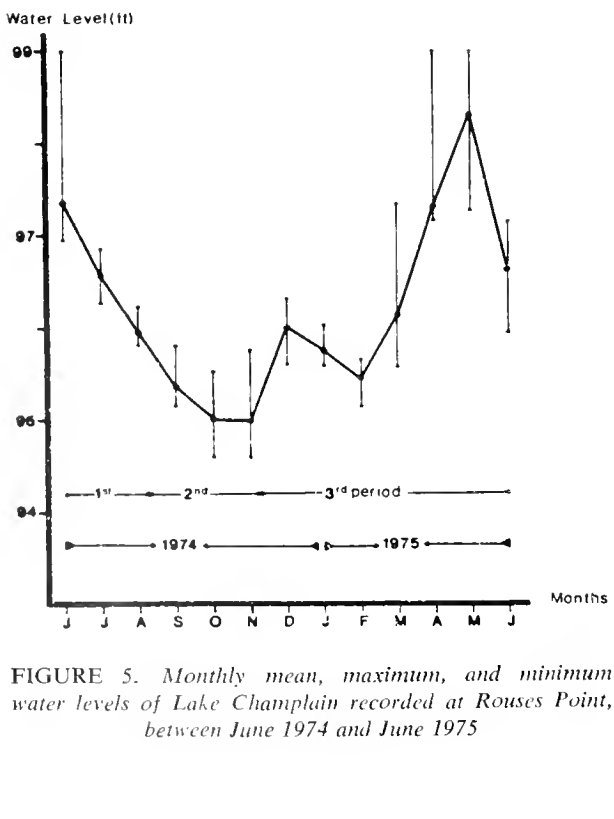


FIGURE 5. *Monthly mean, maximum, and minimum water levels of Lake Champlain recorded at Rouses Point, between June 1974 and June 1975*

lapse of time between minimum water levels and r
mum residues.

More data on water analysis are needed to deter
whether rainfall deposits the airborne DDT or wh
it leaches residues present in the upper soil layers.

LITERATURE CITED

(1) *Buhler, D. R., M. E. Rasmusson, and W. E. Sh
1969.* Chronic oral DDT toxicity in juvenile coh
chinook salmon. Toxicol. Appl. Pharmacol. 1
535–555.

(2) *Buhler, D. R., and W. E. Shanks. 1970.* Influen
body weight on chronic oral DDT toxicity in
salmon. J. Fish. Res. Board Can. 27(2):347–358.

(3) *Butler, P. A. 1973.* Organochlorine residues in
arine mollusks, 1965–72, National Pesticide Mo
ing Program. Pestic. Monit. J. 6(4):238–362.

(4) *Fischer, R. M., M. Zeller, and T. L. Davis. 1976.*
Champlain planning guide for water and related
resources. New England River Basins Commi
Boston, Mass. 12 pp.

(5) *Fitzpatrick, G., and D. J. Sutherland. 1976.* U
of the mosquito larvicide Temefos by the salt r
snail, New Jersey, 1973–74. Pestic. Monit. J. 1
4–6.

(6) *Fournier, H. 1979.* M.Sc. Thesis. Université du
bec á Montréal. 32 pp.

(7) *Frost, W., and C. Kipling. 1958.* The determinati
the age and growth of pike (*Esox lucius*) from
and opercular bones. J. Cons. Perm. l'Explor.
24(1):314–341.

(8) *Kellogg, R. L., and R. V. Bulkley. 1976.* Sea
concentrations of dieldrin in water, channel c
and catfish-food organisms, Des Moines River, Io
1971–73. Pestic. Monit. J. 9(4):186–194.

(9) *Kelso, J. R. M., H. R. Mac Crimmon, and
Ecobichon. 1970.* Seasonal insecticide residue ch
in tissues of fish from the Grand River, On
Trans. Am. Fish. Soc. 99(2):423–426.

(10) *Kuhr, R. J., A. C. Davis, and J. B. Bourke.*
N. Y. Food Life Sci. 10(3):18–20.

(11) *Porter, M. L., S. J. V. Young, and J. A. Burke.*
A method for the analysis of fish, animal, and
try tissue for chlorinated pesticide residues. J.
Off. Anal. Chem. 53(6):1300–1303.

(12) *Simpson, R. E., W. Horwitz, and C. A. Roy.*
Surveys of mercury levels in fish and other
Pestic. Monit. J. 7(3/4):127–138.

(13) *Woodwell, G. M., P. P. Craig, and H. A. Jol
1971.* DDT in the biosphere: where does it go
ence 174(4014):1101–1107.

Organochlorine Residues in Young Herons from the Upper Mississippi River—1976

Harry M. Ohlendorf,[1] James B. Elder,[2] Rey C. Stendell,[1,3] Gary L. Hensler,[1] and Richard W. Johnson[4]

ABSTRACT

ks of great blue herons (Ardea herodias) *from four ıries located near South St. Paul, Royalton, and Wa- ı, Minnesota, and La Crosse, Wisconsin, were analyzed ɔrganochlorines. Highest mean wet-weight concentra- , 6.43 ppm PCBs, 1.31 ppm DDE, and 1.90 ppm T, were found in the South St. Paul chicks. Among s from the other three heronries, most levels were ar, but were significantly lower than levels in South St. chicks. Lowest mean organochlorine levels, 0.37 ppm , 0.38 ppm ΣDDT, and 0.22 ppm PCBs, were found in s from Royalton. All birds from South St. Paul and rosse contained residues of DDT and TDE whereas one of the 10 birds from Royalton contained DDT and contained TDE residues. Five of the 12 birds from ısha contained DDT; eight contained TDE. Except for residues in La Crosse heron chicks, the rate of organo- ine residue accumulation in the birds was generally less the rate of dilution caused by growth.*

Introduction

lues of toxic chemicals in biological materials are il for determining the spatial distribution of en- mental contamination and for identifying sources ollution. Mayflies (*Hexagenia bilineata*), for ex- e, were used to determine geographic distribution sidues of polychlorinated biphenyls (PCBs) in the r Mississippi River (*5*), following the discovery evated levels in fish collected from certain seg- s of the river (*3, 4, 6*). Similarly, residues in heron indicated geographic and species differences in ntrations of organochlorine pesticides and PCBs *0*). In the present study, authors collected great heron (*Ardea herodias*) chicks at four locations the upper Mississippi River to determine geo- ıic variation in selected organochlorine residues.

ent Wildlife Research Center, Fish and Wildlife Service, U.S. ment of the Interior, Laurel, Md. 20811.
and Wildlife Service, U.S. Department of the Interior, Twin Minn. 55111.
nt address: Fish and Wildlife Service, U.S. Department of the r, Washington, D.C. 20240.
ch Scientific Services, Inc. (formerly WARF Institute, Inc.), ox 7545, Madison, Wis. 53707.

Methods

COLLECTION AND DISSECTION

Great blue heron chicks were collected June 2–8, 1976, at the following sites: 5 km west of Royalton, Minnesota; Pig's Eye Island, near South St. Paul, Minnesota; Upper Mississippi River Wild Life and Fish Refuge, near Wabasha, Minnesota; and Upper Mississippi River Wild Life and Fish Refuge, 3 km south of La Crosse, Wisconsin (Fig. 1). The birds were collected as near to fledging as possible, but before they were able to fly.

One young heron with a broken wing was found alive and alert on the ground in the Wabasha heronry. Although the bird was analyzed and included in Table 1, it was not included in comparisons of localities or nests because authors determined from its thin body

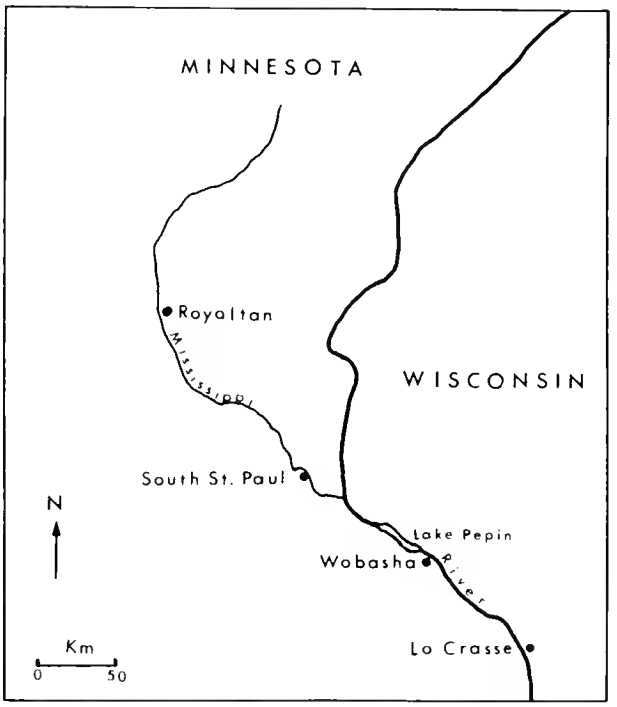


FIGURE 1. *Upper Mississippi River in Minnesota and Wisconsin, showing cities near which young great blue herons were collected in 1976*

TABLE 1. *Mean weight, percent lipid, and organochlorine residues in great blue herons, upper Mississippi River, 1976*[1]

Nest Number (Number of Birds)	Body Weight, g	Carcass Weight, g	Lipid Content, %	Residues, ppm Wet Weight			Residues, ppm Lipid Weight		
				DDE	ΣDDT	PCBs	DDE	ΣDDT	PCB
ROYALTON, MINN.; 10 SPECIMENS FROM 4 NESTS									
1 (2)	1120.5	525.0	5.2	0.80	0.80	0.32	15.4	15.4	6.
2 (1)	544.0	230.0	3.4	0.70	0.70	0.34	20.6	20.6	10.
3 (4)	1290.5	583.5	3.2	0.22	0.23	0.21	8.5	9.0	7.
4 (3)	1589.8	753.7	5.1	0.19	0.19	0.15	4.0	4.0	3.
Locality mean[2]	1271.6 A	587.5 B	4.2 B	0.37 B	0.38 B	0.22 C	9.7 A	9.9 B	6.
SOUTH ST. PAUL, MINN.; 10 SPECIMENS FROM 4 NESTS									
5 (3)	1481.2	752.7	6.5	1.33	1.92	7.21	20.1	28.9	109.
6 (2)	1810.6	961.0	10.0	1.62	2.31	5.56	16.1	23.0	55.
7 (2)	2032.5	1064.0	7.1	1.21	1.78	3.54	17.2	25.5	51.
8 (3)	1991.7	1086.0	9.3	1.16	1.69	8.14	12.5	18.2	87.
Locality mean[2]	1810.5 A	956.6 A	8.2 A	1.31 A	1.90 A	6.43 A	16.5 A	23.9 A	80.
WABASHA, MINN.; 11 SPECIMENS FROM 5 NESTS									
– (1)[3]	955.0	462.0	0.9	0.50	0.58	2.26	55.6	64.6	251.
9 (3)	1732.8	793.7	5.5	0.45	0.50	1.86	8.5	9.4	35.
10 (2)	1551.8	761.5	3.2	0.60	0.75	3.40	19.4	24.1	103.
11 (2)	1953.2	978.0	6.4	0.20	0.24	1.06	3.3	3.7	16.
12 (3)	1691.8	867.3	4.5	0.23	0.27	1.53	5.5	6.4	34.
13 (1)	1157.0	533.0	3.2	0.36	0.42	3.54	11.2	13.0	110.
Locality mean[4]	1676.5 A	817.7 AB	4.8 B	0.37 B	0.43 B	2.05 BC	9.0 A	10.5 B	51.
LA CROSSE, WIS.; 11 SPECIMENS FROM 5 NESTS									
14 (1)	2009.0	940.0	6.7	0.34	0.45	1.72	5.1	6.7	25.
15 (2)	1649.5	819.5	4.8	0.43	0.53	1.84	8.7	10.7	38.
16 (3)	1783.0	913.3	4.9	0.69	0.84	5.46	13.9	16.8	110.
17 (3)	1017.2	420.3	3.4	0.81	0.88	0.98	27.0	28.8	31.
18 (2)	776.5	322.0	3.8	0.52	0.61	2.52	19.1	21.9	96.
Locality mean[2]	1387.4 A	656.7 B	4.5 B	0.61 B	0.71 B	2.71 B	16.7 A	19.0 AB	65.

[1] Locality means that do not share the same letters are significantly different ($P < 0.05$) from each other (Duncan's Multiple Range Test).
[2] Locality means based on weighted nest means.
[3] This chick was found on the ground with a broken wing and was excluded from all statistical comparisons (see Methods).
[4] Locality mean based on weighted nest means, but excludes first bird listed for this locality.

and low lipid content that it was starving. Another heron that was found on the ground in the Wabasha heronry (Table 1, nest 13) was included as a separate nest because the bird apparently had fallen while collectors were in the colony, although its fall was not observed. Weight, lipid content, and organochlorine residues in this bird were generally similar to those in herons from nest 10. However, the fallen bird was found under a different tree than that containing nest 10, and DDT was not detected in this bird whereas DDT was found in both young from nest 10.

The birds were frozen after collection. Whole body weights were determined before feet, beaks, wing tips, skin, and gastrointestinal tracts were removed; carcasses were then weighed, ground, and frozen until analysis.

ANALYTICAL PROCEDURES

Herons were analyzed for PCBs, DDE, TDE, and DDT by WARF Institute, Inc. (now Raltech Scientific Services, Inc.), Madison, Wisconsin. The individual carcasses were ground and mixed well before subsampling; then a 20-g subsample of each was mixed with about 100 g anhydrous sodium sulfate, covered with aluminum foil, and dried in a hood. The sample was extracted with 50 ml ethyl ether in 50 ml petroleum ether for 10 hours in a Soxhlet extractor.

A 10-ml aliquot of the extract was eluted twice thro a column of previously standardized Florisil, first 150 ml of 5 percent ethyl ether in petroleum ether next with 250 ml of 15 percent ethyl ether in petrol ether. The second elution was injected into a chromatograph and quantitated for insecticides. first elution was separated into three fractions by age through a silica CC–4 column. The first frac eluted with 200 ml petroleum ether, contained s late-eluting PCBs. The second fraction, eluted 400 ml petroleum ether, contained PCBs and s amounts of DDE. The third fraction, eluted wi mixture of 2 ml acetronitrile, 38 ml hexane, and ml methylene chloride, contained DDE, TDE, DDT. Each fraction was injected into a gas chrom graph for quantitation.

Samples were analyzed on a Hewlett-Packard M 5710 A gas chromatograph equipped with a linea Ni^{63} electron-capture detector and an automatic jector. Instrument and operating conditions follow

Column:	glass, 122 cm long × 4 mm ID, packed w mixture of 1.5 percent SP-2250 and 1.95 p SP-2401 on a 100–120-mesh Supelcoport
Temperatures:	column 213°C injector 250°C detector 300°C
Carrier gas:	95 percent argon and 5 percent methane fl at 45 ml/minute

idues in 12 samples were confirmed by gas chroma-raphy-mass spectrometry.

Hewlett-Packard Model 3352 C data system was l for quantitation. PCBs were calculated against clor 1254 on the basis of all peaks except the one a retention time near DDE. Lower limits of detec- were 0.005 ppm for DDE, TDE, and DDT, and ppm for PCBs.

d percentages were determined on 5-ml subsamples he Soxhlet extract.

ISTICAL PROCEDURES

iors ran a nested analysis of variance—mixed el (*12*, pp. 248, 261) for weight, lipid content, and chemical; collection locations were fixed effects nests within locations were random effects. When ors found statistically significant differences among locations, they used Duncan's multiple range test eparate locations. In addition, correlation coeffi-ts and linear regressions were calculated for pairs ariables. Statistical Analysis System (SAS) pro-res were used to perform the analyses (*1*). Locality is reported in Table 1 are weighted averages of means; each nest mean is weighted by the number hicks from that nest. The level of significance is pted as $P \leq 0.05$ unless otherwise indicated.

Results

n whole body weights of herons from the four ities were not signifieantly different, but the mean ss weight of the birds from South St. Paul was ficantly greater than means for Royalton or La se birds (Table 1). Mean carcass weight of the from Wabasha was not significantly different that of birds from the other three localities. ass weights of the birds averaged 46.2–48.7 per-of their whole body weights at each locality ex-South St. Paul, where carcasses averaged 52.8 nt of the body weight.

n lipid content in the herons from South St. Paul significantly higher than in birds from the other ties.

lue data are presented here on a wet-weight basis, ipid-weight concentrations also are listed in Table ean concentrations of PCBs, DDE, and ΣDDT in s from South St. Paul were significantly greater in chicks from all other localities, and the PCB for La Crosse chicks was higher than that for lton chicks. However, the mean PCB concentra-in herons from Wabasha was not signifieantly ent from mean concentrations in birds from La e and Royalton. There were no differences in ntrations of DDE or of ΣDDT among the birds Royalton, Wabasha, and La Crosse.

Residues of DDT *per se* were detected in all herons from La Crosse and South St. Paul, but in only one of the 10 birds from Royalton (Table 1). Highest wet-weight concentration of DDT was 0.1 ppm in a South St. Paul heron. DDT also was detected in five of 12 herons from Wabashha; two were from nest 10 and three were from nest 12. TDE was found in all herons from South St. Paul at levels up to 0.72 ppm, in all from La Crosse; in eight of 12 from Wabasha, and in one of the 10 from Royalton.

When the 42 birds were considered individually, lipid content correlated significantly with carcass weight ($R^2 = 0.48$; $P < 0.0001$); heavier birds had a higher percentage of lipids in their bodies. However, the regression of lipid content against carcass weight (Table 2, Fig. 2) for the birds from South St. Paul was significantly different from that of the birds from the other three localities which did not differ from each other. This relationship further demonstrates the significant differences in carcass weights and lipid contents of birds from the four localities.

Because of the significant differences in residue concentrations among localities (Table 1), authors tested the relationship between wet-weight residue concentrations and carcass weights separately for each locality. Except for PCBs in La Crosse herons, the regression slope was negative; residue concentrations for each chemical at each loeality tended to decrease as the birds increased in weight. However, the regression slope was not statistically significant at the $P = 0.05$ level (Table 2, Fig. 3). The negative regression slope of

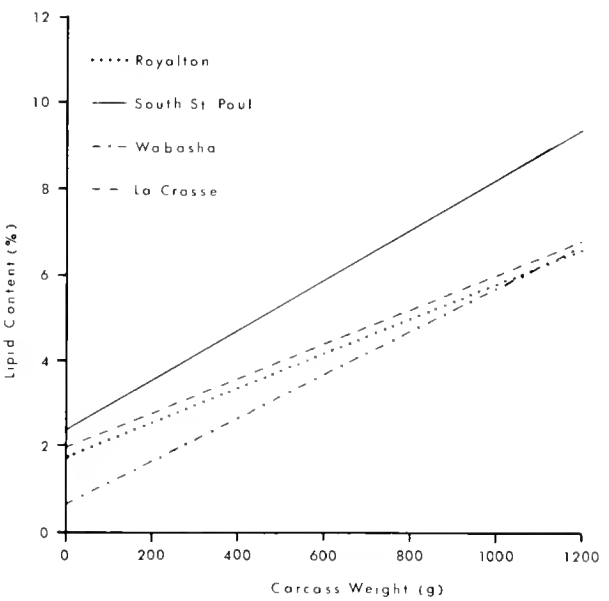


FIGURE 2. *Regression of lipid content against carcass weight in young great blue herons from the upper Mississippi River—1976. See Table 2 for regression equations.*

TABLE 2. *Regression of lipid content and residue concentrations against carcass weight in great blue herons from four upper Mississippi River localities—1976*

Location (Number of Birds)	Lipid Content, %	Residues, ppm Wet Weight		
		DDE	ΣDDT	PCBs
Royalton, Minn. (N = 10; 4 nests)	$Y = 1.76 + 0.004X$	$Y = 0.68 - 0.0005X$	$Y = 0.67 - 0.0005X$	$Y = 0.27 - 0.0000$
South St. Paul, Minn. (N = 10; 4 nests)	$Y = 2.18 + 0.006X$	$Y = 1.65 - 0.0004X$	$Y = 2.40 - 0.0005X$	$Y = 8.74 - 0.002X$
Wabasha, Minn. (N = 11; 5 nests)	$Y = 0.68 + 0.005X$	$Y = 0.76 - 0.0005X$	$Y = 0.90 - 0.0006X$	$Y = 5.40 - 0.004X$ [1]
La Crosse, Wis. (N = 11; 5 nests)	$Y = 1.99 + 0.004X$ [2]	$Y = 0.76 - 0.0002X$ [2]	$Y = 0.79 - 0.0001X$ [2]	$Y = 0.47 + 0.003X$ [3]
(N = 10; 5 nests)	$Y = 2.44 + 0.003X$	$Y = 0.84 - 0.0003X$	$Y = 0.85 - 0.0002X$	$Y = -1.29 + 0.00$ [5]

[1] Significant at $P = 0.08$.
[2] Regression equation when one of the two young in nest 18 that apparently was starving is omitted from the analysis.
[3] Significant at $P = 0.12$.
[4] Significant at $P = 0.05$.

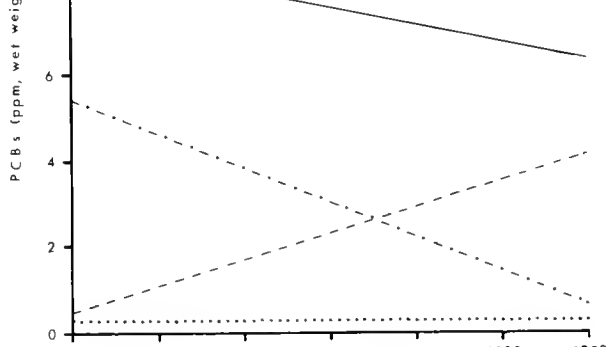


FIGURE 3. *Regression of PCBs against carcass weight in young great blue herons from the upper Mississippi River—1976. See Table 2 for regression equations.*

PCBs against carcass weight for birds from Wabasha, however, was significant at $P = 0.08$. In contrast, the regression slope of PCBs against carcass weight for birds from La Crosse was positive. Residues increased as body weight increased, and the regression slope was significant at $P = 0.12$.

One of the two birds in nest 18, La Crosse, apparently was starving. Its 418 g body weight and 2.0 percent lipid content were much lower than the 1135 g body weight and 5.7 percent lipid content of its sibling. Furthermore, the residue concentrations were much higher in the smaller bird. When the smaller bird was omitted from the analysis, the regression slope for PCBs at La Crosse was significantly positive.

Discussion and Conclusions

Heron chicks from the Royalton nesting colony stream from the Minneapolis-St. Paul metropo area contained the lowest PCB burdens, suggesting the chicks were being fed prey containing signific lower residue levels than prey in heronries below metropolitan area. Authors found the highest org chlorine residue levels in herons from colonies South St. Paul and La Crosse; residue levels tend be lower, although the differences were not statisti significant, in herons from the more rural are Wabasha than in herons from La Crosse. The r sources of PCBs are associated with the Minnea St. Paul and La Crosse metropolitan areas (*3, 4*). ΣDDT residues in the birds may have resulted the past spraying of DDT for control of Dutch disease in Minneapolis-St. Paul and in La Crosse.

Because of reported high residue levels in fish Lake Pepin (*3, 4, 6*), authors expected PCB res in herons from Wabasha to be higher than in the from South St. Paul. However, herons nesting i Wabasha colony, which is downstream from Pepin, apparently feed on cleaner prey than do from South St. Paul. Most birds from the Wal colony probably do not feed in Lake Pepin durin nesting season because the downstream portion o lake does not provide many favorable shallow- feeding sites near the colony. Furthermore, there a ently are differences in contamination levels within Pepin; PCB residues are higher at the upper end o lake than they are at the lower end (*6*).

The negative regression of PCBs against carcass w of chicks from the Wabasha heronry was signific $P = 0.08$. This indicates that herons nesting i colony feed more extensively in Lake Pepin befor after the nesting season than they do while the feeding their chicks. Great blue herons do not o their breeding areas immediately after spring migr and they disperse soon after the young can fly p. 396). The young herons at Wabasha, therefore have received higher concentrations of PCBs i egg, but the residues were being diluted by grow

reater rate than were residues in birds at other lities.

ough there was no statistically significant difference hole body weights of birds from the four locations, herons from South St. Paul were heavier after ction, i.e., a smaller proportion of their weight removed. The significant difference in carcass hts was partly due to the greater amount of lipids he South St. Paul birds, which indicates that the s were somewhat older than those from the other lities. Heavy deposition of fat, and hence, increased ht, is typical of late pre-fledging development (*13*, 37). If the chicks from South St. Paul were older, would have had more time to accumulate resi-, and because they were also fatter they would accumulated more residues from the same intake hicks at other localities.

n comparing residue levels in animals from dif-nt geographic areas, it is important to determine her the lipid content in samples from the various lities is the same. If residue concentrations are not ented on both wet-weight and a lipid-weight basis, percentage lipid in the samples should be given to v readers to make the appropriate conversions.

he beginning of the present study, authors assumed residues acquired within the egg from the female ld have been diluted by growth and that most of contaminant burden in the heron chicks was ired through the local food supply. If, for example, -g heron egg contained 1000 μg (14.3 ppm) of aminant, the chick would have only 1 ppm when ached 1000 g, owing to dilution alone. Residues hicks then would indicate local differences in con-nant occurrence along the river.

nochlorine residues decreased in ducklings as the increased in weight (*2*). Those residues were ably transferred through the egg by the parent because no residues were detected in the duck-food.

residues were positively correlated with the weight oung herons at La Crosse, undoubtedly reflecting ted PCB levels in local food sources. Residues ased significantly as the birds grew. At the other localities, however, the trend was toward lower ues of all chemicals as the birds increased in ht. At these localities the rate of residue accumula-therefore, was less than the rate of dilution caused owth.

ors conclude that there are differences among the localities, and that the residue levels in birds col-l upstream from the metropolitan areas were icantly lower than those affected by pollution stream. Authors also conclude that birds nesting in Wabasha Colony were not feeding on the heavily contaminated fish in Lake Pepin during the nesting season.

Acknowledgments

K. Butts, S. Cornelius, D. L. Peterson, and J. L. Smith collected the young herons, and J. P. Hughes dissected them. The Nature Conservancy granted permission for collections at the Royalton site. The Environmental Chemistry Project at the Patuxent Wildlife Research Center analyzed cross-check samples. Authors appreciate reviews and helpful suggestions by T. W. Custer, A. S. Federighi, G. H. Heinz, L. F. Stickel, and W. H. Stickel.

LITERATURE CITED

(*1*) *Barr, A. J., J. H. Goodnight, J. P. Sall, and J. T. Helwig. 1976.* A user's guide to SAS 76. Statistical System Institute, Raleigh, N.C. 329 pp.

(*2*) *Charnetski, W. A. 1976.* Organochlorine insecticide residues in ducklings and their dilution by growth. Bull. Environ. Contam. Toxicol. 16(2):138–144.

(*3*) *DeGurse, P., and V. Duter. 1975.* Chlorinated hydrocarbon residues in fish from major waters of Wisconsin. Wisconsin Department of Natural Resources, Fish Management Section Rept. No. 79. 21 pp.

(*4*) *DeGurse, P., and J. Ruhland. 1972.* Occurrence of chlorinated biphenyls in Mississippi River fish. Wisconsin Department of Natural Resources, Fish Management Rept. No. 52. 13 pp.

(*5*) *Mauck, W. L., and L. E. Olson. 1977.* Polychlorinated biphenyls in adult mayflies (*Hexagenia bilineata*) from upper Mississippi River. Bull. Environ. Contam. Toxicol. 17(4):387–390.

(*6*) *Minnesota-Wisconsin PCB Interagency Task Force. 1976.* Polychlorinated biphenyls (PCBs) in the Upper Mississippi River Basin. Minnesota Pollution Control Agency, Roseville, Minn. 55 pp.

(*7*) *Ohlendorf, H. M., E. E. Klaas, and T. E. Kaiser. 1978.* Environmental pollutants and eggshell thinning in the black-crowned night heron. Pp. 63–82 *in* A. Sprunt, IV, J. C. Ogden, and S. Winckler, eds. Wading Birds National Audubon Research Rept. No. 7. National Audubon Society, New York, N.Y.

(*8*) *Ohlendorf, H. M., E. E. Klaas, and T. E. Kaiser. 1978.* Organochlorine residues and eggshell thinning in anhingas and waders. Pp. 185–195 *in* W. E. Southern, compiler. Proc. 1977 Conf. Colonial Waterbird Group. National Audubon Society, Tavernier, Fla.

(*9*) *Ohlendorf, H. M., E. E. Klaas, and T. E. Kaiser. 1978.* Organochlorine residues and eggshell thinning in wood storks and anhingas. Wilson Bull. 90(4):608–618.

(*10*) *Ohlendorf, H. M., E. E. Klaas, and T. E. Kaiser. 1979.* Environmental pollutants and eggshell thickness: anhingas and wading birds in the eastern United States. Fish and Wildlife Service Special Scientific Rept.–Wildlife No. 216, U.S. Department of the Interior, Washington, D.C.

(*11*) *Palmer, R. S., ed. 1962.* Handbook of North American Birds, Vol. 1, Loons through Flamingos. Yale University Press, New Haven, Conn. 567 pp.

(*12*) *Scheffé, H. 1959.* The Analysis of Variance. John Wiley & Sons, Inc., New York, N.Y. 477 pp.

(*13*) *Welty, J. C. 1963.* The Life of Birds. Alfred A. Knopf, Inc., New York, N.Y. 546 pp.

WATER

Herbicide Contamination and Decontamination of Well Waters in Ontario, Canada, 1969–78 [1]

Richard Frank, George J. Sirons, and Brian D. Ripley

ABSTRACT

Over the 10-year period 1969–78, the waters of 237 wells were analyzed because of contamination from herbicide spillage in or near the well, complaints of impaired water flavor, or injury to seedling plants moistened with the well water. Herbicides were identified in 159 wells: 98 had a single herbicide, 46 had two, 12 had three, one had four, and another had five separate herbicides contributing to the contamination. Wells were grouped according to the mode of entry of the contaminant. Entry occurred most commonly as an aerial spray drift or in runoff. Serious contaminations were caused by spillage of herbicide concentrates and spray solutions in or around the well.

Twenty-four of the contaminated wells were further investigated to determine the persistence of the contaminant and how to remove it. Some wells were decontaminated adequately to allow reuse within nine weeks, others required three years, and yet others had to be abandoned. Particularly persistent contaminants were amitrole, dinoseb, and picloram.

Introduction

In Ontario, water for spraying herbicides is drawn from wells, ponds, ditches, and creeks. The normal procedure is to fill the spray equipment directly from a water source, although filling from a nurse tank is quite common. According to the Pesticide Act of 1973, an anti-backflow device should be used when drawing from public waters. Mixing of the herbicides is advisably performed away from the water source. These procedures are not always followed, and as a result a number of wells have become contaminated with herbicides. In some cases, this has had detrimental effects when the well water was applied to seedling plants. In addition, herbicide treatment of croplands and weeds in close proximity to the well have impaired the water flavor.

Over the past 10 years, the Ontario Ministry of A culture and Food and the Ontario Ministry of Environment have offered an analytical service to vestigate well contaminations and to advise on clea Records have been maintained on many of the wel determine how long it took the owners to decont nate their wells.

In the present study, 237 wells suspected of cont nation were sampled and analyzed between 1969 1978.

Methods and Materials

SAMPLING

Field staff of the Ontario Ministries of Agriculture Food and of the Environment responded to reques sample wells where herbicide contaminations known or suspected. Composite water samples collected from several pumpings, and 1-liter quant for each herbicidal group suspected, were collecte the time of sampling. Repeated water sampling occu until the well had been decontaminated or until well was abandoned for a new one.

Water sampling was often part of a larger investig into sources of plant injury especially where well had been used to raise seedlings in a greenhouse. I often, herbicide spills had occurred into or aroun well while water was being drawn for a spray o tion; often humans and/or animals used the same for drinking purposes. In many other cases, contar tion was suspected when weeds had been sprayed the well.

In some cases, single analyses were performed w the contamination was known. In others, mu analyses were performed before the contaminants be identified. Follow-up analyses were performed comitant with the owners' attempts to decontam the wells.

ANALYSES

One-liter water samples were extracted within 24 h of receipt by the laboratory. The procedures for e

[1] Provincial Pesticide Residue Testing Laboratory, Ontario Ministry of Agriculture and Food, c/o University of Guelph, Guelph, Ontario, Canada N1G 2W1.

TABLE 1. *Analytical procedures followed for determining herbicides in well water samples, Ontario, Canada—1969–78*

Herbicides	Extracting Solvent	Cleanup	Quantification [1]	Recovery, %	References
role	none	ion-exchange	colorimetry	83	(9)
ridyl	none	ion-exchange	colorimetry	90	(1)
carbamates	isooctane	none	GLC–FPD (sulfur)	95	(3)
rinated phenols	benzene	methylation Florisil	GLC–ECD	95	(8)
pon	diethyl ether	none	GLC–ECD	90	(4)
rophenols	benzene	Florisil	methylation GLC–ECD	96	(11)
oxy and benzoic acids	chloroform	Methylation Florisil	GLC–ECD	95	(10)
vlureas	*n*-hexane	hydrolysis distillation	GLC–CCD	90	(2)
ram	diethyl ether	none	methylation GLC–ECD	90	(6)
ines	chloroform	none	GLC–CCD	95	(7)

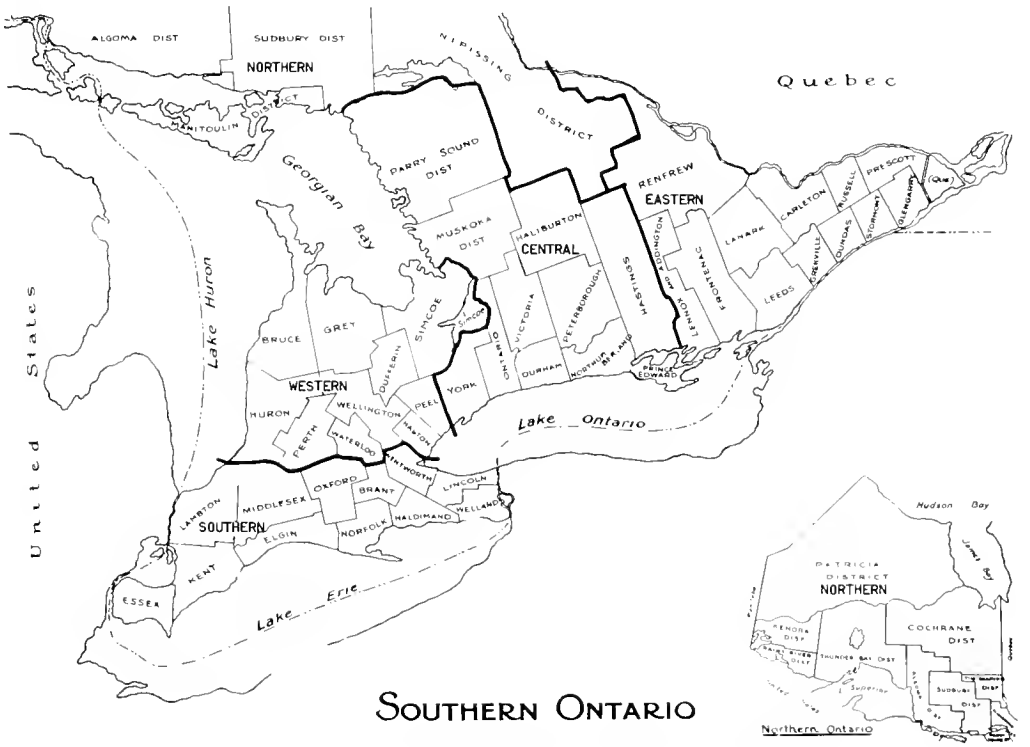
C = gas-liquid chromatography, FPD = flame photometric detection, ECD = electron-capture detection, CCD = Coulson conductivity tion.

isolation, and quantitation of the 10 herbicide ips essentially followed the references presented in le 1 with only minor revision. Identities were con- ed by the techniques given in the references or by of alternative detection systems or different column ings in the gas-liquid chromatographic column.

Results

veen 1969 and 1978, 237 wells were sampled in counties and districts throughout the Province of rio. The occurrence by region was 107 from the south, 54 from the west, 43 from the central, 21 from the east, and 12 from the north (Fig. 1). During the 10-year period, 505 samples were analyzed as follows: 161 for triazine, 204 for phenoxy and benzoic acids and chlorinated phenols, 39 for picloram, and 101 for a number of other herbicide groups (Table 2).

Where herbicides were used near the well, no identifiable contaminant could be found in 78, or 33 percent, of the wells (Table 2). In almost all cases of non-contamination, herbicides had been spilled or were noticed near the well. However, personnel applying



SOUTHERN ONTARIO

FIGURE 1. *Counties, districts, and regions of Ontario*

TABLE 2. *Farm and private rural wells analyzed for herbicide contamination, Ontario, Canada—1969–78*

Year of Initial Samples	Number of Wells Sampled	Number of Wells Free of Herbicides	Number of Wells Contaminated	Investigation: Number of Samples	Investigation: Number of Analyses
1969	9	1	8	11	11
1970	12	5	7	13	13
1971	19	8	11	22	24
1972	32	11	21	35	43
1973	27	4	23	47	58
1974	31	4	27	42	45
1975	35	12	23	87	108
1976	19	10	9	39	56
1977	35	13	22	56	75
1978	18	10	8	41	72
Total	237	78	159	393	505

the herbicides could not be sure whether the herbicides had actually entered the well, although soil near the well was contaminated.

Atrazine and 2,4-D were the herbicides reportedly spilled in about half the cases. Most of the remainder involved herbicides closely related to these two.

In 159, or 69 percent, of the wells, contaminants were positively identified. In 98 wells, a single ingredient was detected; in 46, two herbicides were found; in 12, three herbicides were found; and in one well each, four and five herbicides were present (Table 3). Twenty-two different herbicides were identified with levels of contamination covering eight orders of magnitude, i.e., 0.01 μg/liter to 150 mg/liter (Table 4).

Wells ranged in depth from sand points of 2.5 m to drilled wells of up to 40 m.

MODE OF ENTRY

From the investigations conducted on each site it was possible to divide the contaminations into five distinct types, depending on the mode of entry of the herbicides:

Type I—Herbicide concentrate entered the well as: IA, a single spill event directly into the water; or IB, an extended spill event that entered the water directly and indirectly.

Type II—Diluted herbicide solutions entered the well as: IIA, a single spill event directly into the water especially as back-siphoning from spray equipment; or IIB, an extended spill event which included direct and indirect entry into water especially where spray equipment was overfilled, or tanks were emptied or rinsed.

Type III—Herbicide drift entered the well during the spraying of vegetation adjacent to the well. This situation occurred especially where wells were located close to rights-of-way or where farmers sprayed weeds around their wells.

Type IV—Herbicide residues entered the well during storm runoff events as: IVA, rainwater carrying herbicides from past spills near the well; or IVB, rainwater carrying residues from recently treated fields or vegetation adjacent to the well.

TABLE 3. *Identity of herbicides contaminating 159 o farm and private wells in Ontario, Canada—1969–7*

Number of Incidences of Each Herbicide Combination	Total Number of Wells Contaminated	Herbicides
SINGLE CONTAMINANT		
32	32	atrazine
23	23	2,4-D
17	17	PCP
5	5	2,4,5-T
4	4	picloram
3	9	amitrole, dinoseb, pebulate
2	2	paraquat
1	6	alachlor, butylate, dalapon, dicamba, MCPA, simazine
Subtotal	98	
TWO CONTAMINANTS		
12	12	2,4-D/2,4,5,-T
5	5	atrazine/alachlor
3	6	atrazine/simazine; 2,4-D/PCP
2	18	atrazine/cyanazine; atrazine/2,4-D; atrazine/P atrazine/2,4,5-T; 2,4-D/dicamba; 2,4-D/dichlorprop; 2,4-D/fenoprop; 2,4-D/mecoprop; dicamba/fenoprop
1	5	2,4-D/TCA; dicamba/PCP; dinoseb/PCP; 2,4,5-T/PCP; linuron/prometone
Subtotal	46	
THREE CONTAMINANTS		
2	4	2,4-D/dicamba/mecoprop; 2,4-D/picloram/PCP
1	8	atrazine/2,4-D/simazine; atrazine/2,4-D/2,4,5-T; 2,4-D/dinoseb/PCP; 2,4-D/2,4,5-T/fenoprop; 2,4-D/2,4,5-T/PCP; 2,4-D/mecoprop/PCP; 2,4,5-T/fenoprop/PCP; dicamba/fenoprop/mecopr
Subtotal	12	
FOUR CONTAMINANTS		
1	2	2,4-D/dinoseb/mecoprop/P 2,4,5-T/fenoprop/mecopro
Subtotal	2	
FIVE CONTAMINANTS		
1	1	2,4-D/dicamba/fenoprop/M mecoprop
Subtotal	1	
Grand total	159	

Type V—Subterranean movement into a well from mally used or spilled herbicides.

Well water contained herbicide residues that ra from 0.01 μg/liter to 150 mg/liter and these grouped according to initial concentrations (Tabl The initial concentrations of Type I and II conta tions ranged from 0.1 μg/liter to a high of 14.6 liter for 2,4-D. On the other hand, initial concentra of Type III contaminations ranged from 0.01 to μg/liter for 2,4-D and Type IV from 0.01 to 30 liter for atrazine. Only picloram could be identifi a Type V contamination. In this latter case, re ranged from 0.1 to 1.5 μg/liter. Where indirect

ination occurred, the residues in water were below μg/liter compared to the much higher residues of o 150 mg/liter that occurred from direct contamina-. Type III and IV contaminations occurred most uently and reflected the closeness to wells that herbi-s had been sprayed; in general, herbicides were hormone-types applied to existing vegetation, or other types applied pre-emergence to cropland (Table 5).

CASE HISTORIES

Twenty-four case histories are given in Table 6. Only those wells for which details of the mode-of-entry and

TABLE 4. *Number of herbicides by concentration and type of entry among 159 wells found contaminated in Ontario between 1969–78*

	Concentration, μg/Liter, and Number of Wells Contaminated and Type of Entry [1]							
Herbicide	0.01–0.1	0.1–1.0	1.1–10	11–100	101–1,000	1,001–10,000	10,000–+	Total
)	3(III–IV)	28(II–IV)	12(II–IV)	10(I–III)	6(I–III)[2]	1(I)	1(II)[3]	61
ine	0	21(II–IV)	7(II–IV)	6(I–IV)	11(I–IV)[4]	4(I,II)	1(I)[5]	50
rinated phenols	12	16	4	1(I)	0	0	0	33
T	0	13(III, IV)	7(II–IV)	3(I–III)	1(I)	1(II)	0	25
nba	1(IV)	5(III,IV),	1(IV)	1(II)	1(II)	1(I)	0	10
prop	0	6(III)	0	2(II)	1(I)	0	0	9
prop	2(III)	2(III)	0	4(II,III)	0	0	1(I)[6]	9
seb	2(III)	0	1(IV)	1(IV)	1(II)	1(I)	0	6
ram	0	3(III,V)	2(IV,V)	1(III)	0	0	0	6
ilor	0	1(IV)	2(IV)	0	2(II)	1(II)	0	6
ine	0	3(IV)	1(II)	0	0	0	1(II)[7]	5
role	0	1(III)	0	0	0	2(II)	0	3
ate	0	0	3(IV)	0	0	0	0	3
azine	0	1(IV)	1(II)	0	0	0	0	2
orprop	0	0	1(III)	0	1(II)	0	0	2
A	0	0	1(III)	0	0	1(I)	0	2
quat	0	0	0	1(II)	0	1(I)	0	2
ate	0	1(II)	0	0	0	0	0	1
on	0	1(II)	0	0	0	0	0	1
on	0	0	1(IV)	0	0	0	0	1
etone	0	0	0	1(II)	0	0	0	1
	0	1(IV)	0	0	0	0	0	1
	20	103	44	31	24	13	4	239

e of entry: I, concentrated herbicide; II, diluted herbicide; III, drift during spraying; IV, during storm runoff; V, subterranean.
test Type III, 370 μg/liter 2,4-D.
test Type I and II contamination, 14.6 mg/liter 2,4-D.
test Type IV, 300 μg/liter atrazine.
test contamination was 22.4 mg/liter.
test contamination was 150 mg/liter.
test contamination was 12.6 mg/liter.

TABLE 5. *Number of herbicides involved in the five types of well contaminations, Ontario, Canada, 1969–78*

	Type of Entry [1]					
	I	II	III	IV	V	Total
Herbicide	Number of Contaminants					
2,4-D	5	6	22	28	0	61
Atrazine	1	16	8	25	0	50
Chlorinated phenols [2]	1				0	33
2,4,5-T	2	3	18	2	0	25
Dicamba	1	2	5	2	0	10
Fenoprop	1	2	6	0	0	9
Mecoprop	1	1	7	0	0	9
Dinoseb	1	1	2	2	0	6
Picloram	0	0	3	1	2	6
Alachlor	0	4	0	2	0	6
Simazine	0	2	0	3	0	5
Amitrole	0	2	1	0	0	3
Pebulate	0	0	0	3	0	3
Cyanazine	0	1	0	1	0	2
Dichlorprop	0	1	1	0	0	2
MCPA	1	0	1	0	0	2
Paraquat	1	1	0	0	0	2
Butylate	0	1	0	0	0	1
Dalapon	0	1	0	0	0	1
Linuron	0	0	0	1	0	1
Prometone	0	1	0	0	0	1
TCA	0	0	0	1	0	1
Total	15	(45)	(74)	(71)	(2)	239

[1] Type of entry: I, concentrated herbicide; II, diluted herbicide; III, drift during spraying; IV, during storm runoff; V, subterranean.
[2] Source and modes of entry not determined.

TABLE 6. *Case histories of 24 farms with private wells investigated for herbicide contamination, Ontario, Canada—1969–78*

Case No.	Well	Herbicide Spill	Days After Contamination	Concentration µg/Liter	Impact	Well Cleanup
			1A. HERBICIDE CONCENTRATE ENTERED WELLS DIRECTLY			
1	Drilled, 20 m	50 ml 50 percent 2,4-D amine from container, May 1974	0 316 375	610 0.5 Reused	Killed or distorted tobacco seedlings	Pumped dry sev times over one
2	Shallow, 3 m	2.5 liters each 35 percent 2,4-D and dichlorprop, August 1973	0 6 10 28 46 61	2,4-D dichlorprop 140 240 1,350 4,660 100 960 0.z 0.4 Reused	Impaired water flavor	Emptied three ti 15,000 liters Pumped continu for 4 weeks, wal washed.
3	Shallow 4 m deep	50 ml 50 percent 2,4-D amine, May 1977	0 64 132	780 5.6 Reused	Killed greenhouse plants	Pumped dry inte mittently for 4 months.
			1B. HERBICIDE CONCENTRATE ENTERED WELLS DIRECTLY AND INDIRECTLY			
4	Sand point, 4 m	23 liters 36 percent dinoseb from container, May 1973	0 52 86 111 237 285	2,330 2,240 61 72 150 3,800	Killed tobacco seedlings	Pumped until ye color disappeare color returned a pumping continu Spring thaw wat deep yellow.
5	Cased well, 22 m	50 ml 60 percent 2,4,5-T from container, August 1975	Well abandoned 0 86 1,028	26.3 5.5 Not used	Impaired water flavor for 34 months	Pumped on and for 6 months an abandoned.
			IIA. DILUTED HERBICIDES ENTERED WELLS DIRECTLY			
6	Drilled, 25 m	About 50 liters 1 percent solution atrazine back-siphoned, June 1974	0 1 11 68	— 610 barn, 1,840 house 9 barn, 29 house Reused	Continuously fed to swine with no visible effects.	Pumped continu for 11 days, ther intermittently.
7	Medium depth, 10 m	About 25 liters 1 percent solution atrazine back-siphoned, June 1977	0 2 8 21 49 64	— 833 50 14 5.7 Reused	Stopped use for livestock and house	Pumped continu for about 60 day Well sides scrap
8	Shallow, 4.5 m	About 100 liters 1 percent solution atrazine back-siphoned, June 1977	0 2 32 338	— 6,670 212 Reused	Stopped use for livestock and house	Pumped dry onc sampled. Pumpe continually for 3 days. Periodicall pumped for nine months.
9	Drilled, 17 m	Unknown quantity of atrazine/alachlor mixture back-siphoned, May 1975	0 1 3 64 0	— 370 5,690 14 54 Reused	Stopped use for livestock and house	Pumped dry and sampled, contin pumping for five and then intermi for two months.
10	Drilled, 21 m	About 100 liters of 1 percent solution of atrazine–alachlor backsiphoned, June 1978	13 47 160	4,040 5,690 1,031 1,827 90 130 Reused	Continued use for cattle; stopped use for humans	Pumped continu for 47 days then intermittently.
11	Sand point, 5 m	About 50 liters of 1.5 percent solution of amitrole back-siphoned, April 1974	0 11 67 358 1,092	Reused 1,320 540 50	Killed all tobacco seedlings in greenhouse after well was pumped dry once	Pumped dry inte mittently for ove two years.
12	Sand point, 5 m	About 1 liter of 1 percent solution of picloram back-siphoned, May 1976	0 130 450 706 749	— 7.2 1.7 0.08 Reused	Tobacco seedlings wiped out initially; at 706 days, seedlings still affected	Pumped dry con tinually first yea then intermitten second year. Pur continually for 5 days before reus
			IIB. DILUTED HERBICIDES ENTERED WELLS DIRECTLY OR INDIRECTLY			
13	Medium depth, 9 m	Atrazine from an over-filled sprayer spilled around the lip of the well and into well, May 1976	0 4 100 110	1,792 67 ND Reused	Vegetation around well killed.	Well pumped dr scraped, and sec removed.
14	Drilled, 10 m	Spray tank containing a mixture of 3 percent 2,4-D/dicamba was spilled around well, July 1977	0 2 32 39 49 70 95 294	93 90 600 267 447 35 71 ND 374 49 4.5 4.8 Reused	Domestic use stopped; water flavor impaired	Pumped out 35 in 4 months, the emptied periodi

(*Continued next page*)

TABLE 6. (Cont'd.) *Case histories of 24 farms with private wells investigated for herbicide contamination, Ontario, Canada—1969–78*

Well	Herbicide Spill	Days After Contamination	Concentration µg/Liter	Impact	Well Cleanup
IIB. DILUTED HERBICIDES ENTERED WELLS DIRECTLY OR INDIRECTLY (*Cont'd.*)					
Shallow, 4 m	Spray tank of 1.5 percent solution dicamba spilled around well	0	60	Tobacco seedlings wiped out or injured two years in a row	Pumped out regularly at first then periodically. New well dug nearby.
		48	4.2		
		220	1.2		
		272	11.3		
		570	3.5		
		617	<0.1		
		abandoned for new well of 8 m deep			
Sand point, 2.5 m	Most of 900-liter tank of 1.5 percent amitrole, April 1975	0		Tobacco seedlings wiped out for over 2 years	
		30	2,800		
		71	1,100		
		109	800		
		192	610		
		441	30		
		723	40		
		1,093	3 (reused)		
III. AERIAL HERBICIDE DRIFT ENTERED WELLS					
Shallow, 3.5 m	2,4-D drift of 1 percent solution, June 1974	0	—	Water flavor impaired	Well emptied three times after detection of residue.
		4	370		
		38	ND		
		78	Reused		
Shallow, 4 m	A 1 percent solution of 2,4-D/2,4,5-T drifted 7.5 m from rights of way, June 1975	0	— —	Water flavor impaired	Well emptied twice after detection.
		2	42 34		
		16	<0.1 <0.1		
		20	Reused		
IV. HERBICIDES ENTERED WITH RUNOFF					
Sand point, 2.5 m	Heavy rains carried atrazine from spill near well, June 1969	0	22	Killed tobacco seedlings	Occassionally pumped dry over nine months.
		103	15		
		281	ND		
Sand point, 2.5 m	Spring thaw carried atrazine and desethyl atrazine from adjacent field, April 1973	0	15 22	Continued use for livestock	Emptied well once.
		389	1 2		
Shallow, 4.5 m	Storm runoff carried atrazine and metabolite from treated field, May 1975	0	0.4 0.1	Continued use for livestock	Emptied several times in first year.
		50	6.4 2.1		
		134	1.2 2.2		
		379	0.4 1.6		
Shallow, 4.5 m	Storm runoff carried atrazine and metabolite from treated field, October 1977	0	0.6 4.6	Stopped use for livestock	
		38	ND ND		
		173	Reused		
Shallow, 5.0 m	2,4-D linked to runoff from weeds treated around well, October, 1971	0	—	Killed seedlings during Spring 1972	Pumped regularly over two-month period with no pesticides detected.
		158	2.5		
		205	1.6		
		227	ND Reused		
V. SUBTERRANEAN MOVEMENT OF HERBICIDES INTO WELL					
Shallow, 4 m	Picloram used some distance from well, surplus dumped nearby, June 1974	0	—	Killed seedlings during spring 1975 and each year until 1977. Abandoned June 1977	Pumped intermittently between Spring 1975 and June 1977.
		287	1.5		
		301	0.2		
		333	7.5 & 10.9		
		344	3.0 & 5.9		
		357	0.8		
		370	0.6		
		377	0.3		
		386	2.3		
		411	0.2		
		414	0.3		
		420	0.3		
		435	0.3		
		439	<0.1		
		493	0.4		
		498	0.7		
		523	0.2		
		704	ND		
		781	0.4		
		1,040	0.4		
		1,101	ND		

ND = none detected.

decontamination procedures could be clearly documented have been chosen.

Type IA, herbicide concentrates entered wells directly. Three cases are cited in Table 6. In one, a container stored over a well leaked into the water; in the other two, herbicide concentrate was spilled into the well during handling. In all three cases, decontamination was difficult until the sides of the well were scraped and cleansed of spilled herbicide. Even after the well was pumped dry once or twice, large numbers of plant seedlings were killed in two instances because the decontamination had been inadequate. Only continued pumping over an extended period removed the contamination.

Type IB, herbicide concentrate entered wells directly and indirectly. Two cases are cited in Table 6; in both, the concentrate leaked from containers stored near the well. In one case, dinoseb soaked into the ground around the well as well as running directly into the well. During the spring thaw and runoff period, when the ground was saturated with water, dinoseb entered with runoff and drainage waters to seriously contaminate the well for a second year. In the second case, 2,4,5-T leaked behind the casing of the well and impaired the water flavor for 34 months after the event.

Type IIA, diluted herbicide entered wells directly. Seven cases are cited and all involved accidental back-siphoning of diluted solutions of herbicides into the wells (Table 6). Cleanup involved pumping out water with existing small equipment that emptied the wells slowly. Decontamination took as little as two months in some wells but as long as two to three years in others.

Type IIB, diluted herbicides entered wells directly or indirectly. Four cases were investigated, and in all, the herbicides were spilled into and around the well mouth while spray equipment was being filled (Table 6). The contaminated water severely damaged seedling plants in greenhouses before it was adequately decontaminated. Cleanup operations involved pumping water out of the wells during an extended period of 100–1093 days. In the one well that was decontaminated in 100 days, the walls and the bottom of the well were scraped and the soil and sediment were removed.

Type III, aerial herbicide drift entered wells. Two wells were investigated in which aerial drift of chlorophenoxy herbicides had entered the water and impaired its flavor. Both wells were located within 7 to 10 m of the treated areas. Cleanup was effected in two to five weeks by emptying the well two to three times.

Type IV, herbicides entered with storm water runoff. Five cases are cited in Table 6. Heavy rains producing runoff carried atrazine into well water from a spill near the well that had occurred 10 days before the rains. In three other cases, atrazine from treated corn fields 4–15 m from the wells was deposited in the wells by storm runoff waters. In one other case, heavy rains w 2,4-D into well water from recently sprayed tall adjacent to the well. Seedling plants were dest following the use of water from these contami wells. Two farmers continued to use the contami water for livestock when it was discovered that at levels were relatively low. No adverse effects a animals were reported. Four of the five wells decontaminated in periods ranging from 38 da just over one year.

Type V, subterranean movement of herbicides wells. Continued distortion of plant seedlings mo ized for three years by water from a well could be explained by the subterranean movement of picl Picloram had been used to spray vegetation som tance from the well, and the unused portion was du in the same area. A possible connection betwee well and the treated site was an aquifer close t surface.

Discussions and Conclusions

Use or misuse of herbicides around wells result contamination of 67 percent of the examined wel 159 wells, 22 herbicides were found as single or mu contaminants, for 239 individual contamination e Contamination levels were greatest where concen or diluted spray solutions were spilled directly int well. However, these were not necessarily the most cult to decontaminate. The mode-of-entry did infl the time required for decontamination. Contami entering as drift were relatively rapidly removed pared to subterranean contaminants which were pa larly persistent in spite of their initial low levels.

Schneider et al. (5) found that both atrazine and ram moved freely through an aquifer to contam wells 9 m and 20 m away but not 45 m fror injection site. Up to 90 percent of the injected l cides were recovered. Picloram took 84 hours to in the well 20 m from the injection. Concentr increased and decreased over the pumping period days, reaching a high of 135 ppb (5) when pur rates were 82 m^3/hour. The picloram concentr were considerably more attenuated in the case of terranean movement reported in the present pape the distance from the area of use to the well was s hundred meters. Few wells in the present study pumped continuously day and night for extended p or at the high rates available to Schneider et al. These differences probably explain why cleanup to much longer in the present study.

Where herbicide was spilled down the wall of the (case 2), and/or around the lip of the well (cas and 15), concentrations first declined and then incr as more herbicide entered the water. In case 2, re in water rapidly declined after the walls had scraped. In case 4, dinoseb was spilled in qu

nd a well, and it soaked into the soil where it ined with little movement as long as the soil was t to dry. However, during the spring thaw, the was saturated with water and the herbicide leaked the well (case 4). Atrazine continued to degrade ne well (case 21) where the ratio of atrazine to bolite was 4:1 in May 1975 and 1:4 in June 1976.

type of compound involved had an important bear- n the time required for decontamination. Amitrole, eb, and picloram were particularly difficult to re- from water supplies, but alachlor, atrazine, and) were removed more rapidly.

tying the well of water was not always possible. n the well could be emptied, cleanup was facilitated moving soil around the well or from the sides or m of the well. In cases 2, 7, and 13, the wells were ied, and contaminated soils and sediments were re- d. Hence decontamination was rapid, i.e., 61–100 Where only water was removed, decontamination 20–1093 days. It should be pointed out that owners ved their own procedures for well decontamination. combination of differences in well depths, soil , refilling rates, and initial herbicide concentrations most of the 159 contaminated wells unique events. e the decontamination of 24 wells makes it diffi- o generalize on the best practical procedures.

Acknowledgments

uthors thank the fields staffs of the Ontario Minis- f Agriculture and Food and the Ontario Ministry e Environment for supplying the samples and nation on the wells discussed in this paper.

LITERATURE CITED

Calderbank, H., and S. H. Yuen. 1965. An ion exchange method for determining paraquat residues in food crops. Analyst 90(1067):99–106.

(2) *Dalton, R. L., and H. L. Pease. 1962.* Determination of residues of diuron, monuron, fenuron, and neburon. J. Assoc. Off. Agric. Chem. 45(2):377–381.

(3) *Frank, R., H. E. Braun, G. J. Sirons, M. V. H. Holdrinet, B. D. Ripley, D. Onn, and R. Coote. 1978.* Stream flow quality—Pesticides in 11 agricultural watersheds in southern Ontario, Canada, 1974–77. International Reference Group on Great Lakes Pollution from Land Use Activities, International Joint Commission, Windsor, Ontario.

(4) *Getzendaner, M. E. 1969.* Gas chromatographic determination of residues of dalapon in several substrates. J. Assoc. Off. Anal. Chem. 52(4):824–831.

(5) *Schneider, A. D., A. F. Wiese, and O. R. Jones. 1977.* Movement of three herbicides in a fine sand aquifer. Agron. J. 69(3):432–436.

(6) *Sirons, G. J., R. Frank, and R. M. Dell. 1977.* Picloram residues in sprayed MacDonald-Cartier Freeway right-of-way. Bull. Environ. Contam. Toxicol. 18(5): 526–533.

(7) *Sirons, G. J., R. Frank, and T. Sawyer. 1973.* Residues of atrazine, cyanazine, and their phytotoxic metabolites in a clay loam soil. J. Agric. Food Chem. 21(6): 1016–1020.

(8) *Sirons, G. J., and Y. J. Paik. 1978.* Extraction and quantitation of chlorinated phenols in aquatic substrates. Presented at International Symposium for the Analysis of Hydrocarbons and Halogenated Hydrocarbons in the Aquatic Environment, May, Hamilton, Ontario, Canada.

(9) *Sutherland, G. L. 1964.* 3-Amino-s-triazole. *In* Analytical Methods for Pesticides, Plant Growth Regulators, and Food Additives. G. Zweig., Ed., Vol. IV, Chapt. 3, Academic Press, New York, N.Y.

(10) *Yip, G. 1971.* Improved method for determination of chlorophenoxy acid residues in total diet samples. J. Assoc. Off. Anal. Chem. 54(4):966–969.

(11) *Yip, G., and S. F. Howard. 1968.* Extraction and cleanup procedure for the gas chromatographic determination of four dinitrophenolic pesticides. J. Assoc. Off. Anal. Chem. 51(1):24–28.

Triazine Herbicide Residues in Central European Streams [1]

W. D. Hörmann,[2] J. C. Tournayre,[3] and H. Egli[2]

ABSTRACT

*Triazine herbicide residues were monitored in the rivers Adour, Danube, Garonne, Herault, Loire, Marne, Oise, Rhine, and Rhône from spring 1976 to fall 1977 to determine whether the continued use of the compounds resulted in accumulations of undesirable residues in the streams. Samples were generally collected monthly or bimonthly and analyzed for the parent compounds atrazine, simazine, terbumeton, terbuthylazine, and dealkylated metabolites GS 26571 (2-amino-4-*tert*-butylamino-6-methoxy-1,3,5-triazine) and G 30033 (2-amino-4-chloro-6-ethylamino-1,3,5-triazine). The compounds were extracted into dichloromethane and quantitated by gas chromatography (GC) with nitrogen-specific detection. Selected results were verified by GC with mass fragmentographic detection. Limit of detection was usually 0.4 mg/m³; 80 percent of all results were below 0.4 mg/m³, 14 percent were 0.4–1 mg/m³, 6 percent were 1–10 mg/m³, and 0.3 percent were higher than 10 mg/m³. Detectable residues were mainly atrazine from the downstream sampling sites. Residues usually peaked during June.*

Introduction

Triazine compounds, especially atrazine, have been widely used as herbicides for many years. The compounds, under the trade names Gesatop, Gesaprim, and Caragard, mainly have been applied to maize, orchards, and vine. Because they might reach surface waters via runoff or even via leaching, residues of the compounds could accumulate in streams. To gather information about the actual residue situation in Central European streams draining the main cultivation regions of maize, vine, and fruits, a monitoring program was initiated in Austria, France, Germany, and Switzerland during spring 1976. Concentrations of the following compounds were monitored: atrazine, simazine, terbumeton, terbuthylazine, GS 26571 (2-amino-4-*tert*-butylamino-6-methoxy-1,3,5-triazine), and G 30033 (2-amino-4-chloro-6-ethylamino-1,3,5-triazine).

Water samples were collected monthly or bimonthly between spring 1976 and fall 1977. At each site a total of 6–12 samples were taken, which the authors felt would reasonably indicate the actual residue situation and the seasonal fluctuations.

Three samples across the profile of a river were s to result in the same average as did 10 sample reduce the effect of potential outliers, the numb samples, however, should not be less than thre Newby and B. G. Tweedy, CIBA-GEIGY Corp., G boro, North Carolina, private communication, 1 Therefore the following procedure was chosen:

Ten-liter samples each were taken at a depth of 50 cm from either bank and from the center of th by means of a metal bucket. Two liters of each s were combined and mixed. From the mixed sa 1-liter aliquots were transferred into aluminum b deep frozen, and shipped to the residue laborator

Until analysis, samples were stored at −20°C. zines stored at this temperature have been shown stable for many years in neutral aqueous solutio as well as in soil and crop materials (*2*).

Depending on stream length, one to four samplin were selected. Locations are shown on the map i ure 1. Information on drained area, upstream o sampling site, and main cultures is given in Tabl

Analytical Procedures

The entire contents of one bottle, 1 liter, was t and the water was filtered to remove sediment filtrate was transferred to a 2-liter separatory and extracted with three consecutive portions chloromethane which had been used previously t the sample container. After passage over a plug ton to remove excess water, the extracts were co and evaporated to dryness in a rotary evaporator a 30°C water bath. The residue was dissolved appropriate volume, 0.5–2 ml, of a 1:1 mixt hexane-ethanol and the solution was injected int chromatograph equipped with a nitrogen-specif or Coulson detector. Instrument parameters and ing conditions follow:

Columns:	glass, 1 m long × 3 mm ID packed wi 3 percent Carbowax 20M on 0.15–0.18 r Chrom Q or 2 percent FFAP on 0.15–0 Gas-Chrom G	
Temperatures:	injector	250°C
	columns	190°–210°C isothermal
	interface	250°C
	detector oven	800°C
Carrier gas:	helium flowing at 60 cm³/minute	

[1] Presented in part at the Fourth International Congress of Pesticide Chemistry, IUPAC, Zurich, Switzerland, 1978.
[2] CIBA-GEIGY Ltd., Agricultural Division, 4002 Basel, Switzerland.
[3] CIBA-GEIGY SA, 30670 Aigues-Vives, France.

JRE 1. *Map showing location of sample sites along al European streams—spring 1976–fall 1977 (see Table 1 for key)*

TABLE 1. *Sites on Central European rivers sampled for triazine herbicide residues, spring 1976–fall 1977*

Stream	Sampling Site [1]	Drainage Area, km²	Main Cultures	Remarks
Adour	1 Urt	17,000	maize vineyard fruits	main maize cultivation region of France
Danube	2 Deggendorf	39,000	fruits fodder crops vineyard	vineyard downstream of Deggendorf
Garonne	4 Le Mas d'Agenais	50,000	vineyard maize	
Herault	5 Bessan	2,300	vineyard	
Loire	6 St. Benoit	73,000	vineyard	
	7 Savennieres	110,000	fodder crops fruits	
Marne	8 Meaux	13,000	vineyard	Champagne
Oise	9 La Verberie	15,000	fodder crops fruits	
Rhine	10 Laufenburg	31,000	fodder crops	(L)[2] upstream of
	11 Augst	31,000	vineyard	CIBA-GEIGY pro-
	12 Basel	32,000	fruits	duction plants
	13 Mainz	94,000		(B)[2] downstream of plants
Rhone	14 Bouveret	5,400	vineyard	between (B)[2] and
	15 Geneve	8,000	fruits	(G)[2]: Lake of
	16 Donzere	67,000		Geneva, viticulture
	17 Pin Fourcat	95,000		at borders

[1] Numbers refer to Figure 1.
[2] Letters refer to Figure 1.

mum detection levels were 0.1–0.4 mg/m³ except few cases where relatively high concentrations of fering materials were present. Recoveries for all ounds were 80–120 percent at 5 mg/m³ and 10 n³ fortification levels.

al samples showing residues above the detection were confirmed by gas chromatography/mass spectry. Instrument parameters and operating conditi- follow:

strument:	Finnigan Model 3000, equipped with programmable multiple ion monitor	
asses selected:	atrazine	215
	simazine	201
	terbumeton	225
lumn:	glass, 1 m long × 2 mm ID, packed with 2 percent SP 1000 on 0.15–0.18 mm Chromosorb G	
mperatures:	injector	240°C
	column	220°C isothermal
	separator	220°C
	transfer	180°C
	manifold	120°C
ctron energy:	70 eV	
rrier gas:	helium flowing at 30 cm³/minute	

TABLE 2. *Number of samples from Central European streams, containing atrazine residues at four given mg/m³ ranges, spring 1976–fall 1977*

	Sampling Site [1]	< 0.4	0.4–1.0	1.1–10	> 10
1	Adour (Urt)	2	1	2	0
2	Danube (Deggendorf)	3	3	3	0
3	Danube (Hainburg)	0	1	4	2
4	Garonne (Le Mas d'Agenais)	1	2	2	0
5	Herault (Bessan)	2	3	0	0
6	Loire (St. Benoit)	2	3	1	0
7	Loire (Savennieres)	2	3	1	0
8	Marne (Meaux)	4	1	1	0
9	Oise (La Verberie)	2	3	1	0
10	Rhine (Laufenburg)	9	0	0	0
11	Rhine (Augst)	8	1	0	0
12	Rhine (Basel)	7	2	0	0
13	Rhine (Mainz)	1	2	0	0
14	Rhone (Bouveret)	12	0	0	0
15	Rhone (Geneve)	12	0	0	0
16	Rhone (Donzere)	1	1	2	0
17	Rhone (Pin Fourcat)	2	2	1	0

[1] Numbers refer to Figure 1.

Results and Discussion

s 2–6 present all values found, expressed as numf results within given concentration ranges of , 0.4–1.0, 1.1–10, and >10 mg/m³; values are not cted for recovery. Where two or more sampling or the same river are listed, the upstream sampling re listed first. No table for G 30033 was included se no residues of the compound were found in f the samples.

08 values measured, two, or 0.3 percent, were 10 mg/m³; 43, or 6.1 percent, were between 1.1 and 10 mg/m³; 98, or 13.8 percent, were between 0.4 and 1 mg/m³; and 565, or 79.8 percent, were below 0.4 mg/m³, showing that transfer from treated areas to the rivers via runoff or leaching is very small.

Where different sites of a river were sampled, samples from the downstream sites normally showed higher residues than did samples from the upstream sites.

Residue levels peaked in June (Fig. 2) as they did in similar studies in the United States (*3*) and Canada (*4*).

TABLE 3. *Number of samples from Central European streams, containing simazine residues at four given mg/m³ ranges, spring 1976–fall 1977*

	Sampling Site [1]	< 0.4	0.4–1.0	1.1–10	> 10
1	Adour (Urt)	0	4	1	0
2	Danube (Deggendorf)	9	0	0	0
3	Danube (Hainburg)	6	1	0	0
4	Garonne (Le Mas d'Agenais)	0	4	1	0
5	Herault (Bessan)	1	4	0	0
6	Loire (St. Benoit)	5	1	0	0
7	Loire (Savennieres)	4	2	0	0
8	Marne (Meaux)	5	1	0	0
9	Oise (La Verberie)	3	2	1	0
10	Rhine (Laufenburg)	9	0	0	0
11	Rhine (Augst)	9	0	0	0
12	Rhine (Basel)	6	3	0	0
13	Rhine (Mainz)	3	0	0	0
14	Rhone (Bouveret)	11	0	1	0
15	Rhone (Geneve)	12	0	0	0
16	Rhone (Donzere)	1	2	1	0
17	Rhone (Pin Fourcat)	2	1	2	0

[1] Numbers refer to Figure 1.

TABLE 4. *Number of samples from Central European streams, containing terbumeton residues at four given mg/m³ ranges, spring 1976–fall 1977*

	Sampling Site [1]	< 0.4	0.4–1.0	1.1–10	> 10
1	Adour (Urt)	1	3	1	0
2	Danube (Deggendorf)	9	0	0	0
3	Danube (Hainburg)	7	0	0	0
4	Garonne (Le Mas d'Agenais)	3	0	2	0
5	Herault (Bessan)	3	2	0	0
6	Loire (St. Benoit)	4	1	1	0
7	Loire (Savennieres)	5	0	2	0
8	Marne (Meaux)	3	2	1	0
9	Oise (La Verberie)	3	1	2	0
10	Rhine (Laufenburg)	9	0	0	0
11	Rhine (Augst)	9	0	0	0
12	Rhine (Basel)	8	1	0	0
13	Rhine (Mainz)	3	0	0	0
14	Rhone (Bouveret)	12	0	0	0
15	Rhone (Geneve)	12	0	0	0
16	Rhone (Donzere)	3	1	0	0
17	Rhone (Pin Fourcat)	2	2	1	0

[1] Numbers refer to Figure 1.

TABLE 5. *Number of samples, from Central European streams, containing terbuthylazine residues at four given mg/m³ ranges, spring 1976–fall 1977*

	Sampling Site [1]	< 0.4	0.4–1.0	1.1–10	> 10
1	Adour (Urt)	3	2	0	0
2	Danube (Deggendorf)	9	0	0	0
3	Danube (Hainburg)	4	1	2	0
4	Garonne (Le Mas d'Agenais)	2	2	1	0
5	Herault (Bessan)	5	0	0	0
6	Loire (St. Benoit)	5	1	0	0
7	Loire (Savennieres)	5	1	0	0
8	Marne (Meaux)	4	1	1	0
9	Oise (La Verberie)	5	1	0	0
10	Rhine (Laufenburg)	9	0	0	0
11	Rhine (Augst)	9	0	0	0
12	Rhine (Basel)	8	1	0	0
13	Rhine (Mainz)	3	0	0	0
14	Rhone (Bouveret)	12	0	0	0
15	Rhone (Geneve)	12	0	0	0
16	Rhone (Donzere)	4	0	0	0
17	Rhone (Pin Fourcat)	4	1	0	0

[1] Numbers refer to Figure 1.

TABLE 6. *Number of samples from Central Eur streams, containing GS 26571 residues at four given n ranges, spring 1976–Fall 1977*

	Sampling Site [1]	< 0.4	0.4–1.0	1.1–10
1	Adour (Urt)	1	3	1
2	Danube (Deggendorf)	9	0	0
3	Danube (Hainburg)	7	0	0
4	Garonne (Le Mas d'Agenais)	0	5	0
5	Herault (Bessan)	3	2	0
6	Loire (St. Benoit)	6	0	0
7	Loire (Savennieres)	4	1	1
8	Marne (Meaux)	4	1	1
9	Oise (La Verberie)	3	2	1
10	Rhine (Laufenburg)	9	0	0
11	Rhine (Augst)	9	0	0
12	Rhine (Basel)	9	0	0
13	Rhine (Mainz)	3	0	0
14	Rhone (Bouveret)	12	0	0
15	Rhone (Geneve)	12	0	0
16	Rhone (Donzere)	0	4	0
17	Rhone (Pin Fourcat)	2	3	0

[1] Numbers refer to Figure 1.

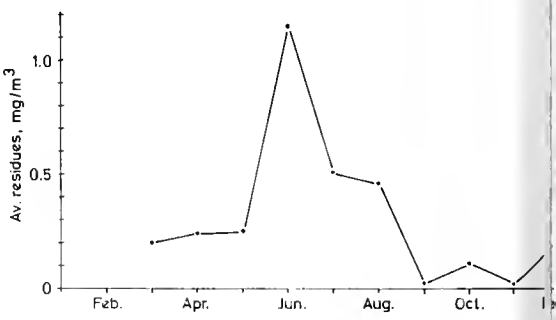


FIGURE 2. *Sum of the concentration of all compo analyzed by month. Values below the limit of determin were taken as zero.*

This maximum must be caused by runoff after sp herbicide applications, because leaching of compo would have resulted in more delayed and more con residues. River volumes could not account for the peak, because rivers rising in the Alps show their g est volumes in June when snow melts. The resu water volumes should dilute residues, thereby causi June minimum. So, river volumes influence the re situation only to a small extent. The main contribu to the June peak obviously comes from runoff with short time after application.

The results from Laufenburg, upstream of two tri production plants, from Augst, in between the pl and from Basel, downstream of both plants, demons that residues are not increased by those plants.

Where residues were present at all, those of atra were highest. This was expected because atrazine i most commonly used triazine herbicide. From this the conclusion can be drawn that in future monito programs it is sufficient to analyze only for atrazi a tracer.

LITERATURE CITED

urkhard, N., and J. A. Guth. 1978. Chemical hydroly-
s of 2-chloro-4,6-bis(alkylamino)-1,3,5-triazine herbi-
des and their breakdown in soil under the influence
absorption. Abstr. Vol. Fourth International Con-
ess of Pesticide Chemistry, IUPAC, Zürich, Switzer-
nd. Abstr. No. V–605.

gli, H., and N. Burkhard. 1978. Deep freeze stability
some pesticide residues in biological material and soil. Abstr. Vol. Fourth International Congress of Pesticide Chemistry, IUPAC, Zürich, Switzerland. Abstr. No. VI–707.

(*3*) *Frank, R., and G. J. Sirons. 1978.* Atrazine: Its use and entry into stream water. Abstr. Vol. Fourth International Congress of Pesticide Chemistry, IUPAC, Zürich, Switzerland, Abstr. No. VI–815.

(*4*) *Newby, L., and B. G. Tweedy. 1976.* Atrazine residues in major rivers and tributaries. 172nd Meeting, American Chemical Society, Abstr. Papers PEST 102.

APPENDIX

Chemical Names of Compounds Discussed in This Issue

ALACHLOR	2-Chloro-2′,6′-diethyl-*N*-(methoxymethyl)-acetanilide
AMITROLE	3-Amino-*s*-triazole
AROCLOR 1254	PCB, approximately 54% chlorine
ATRAZINE	2-Chloro-4-(ethylamino)-6-(isopropylamino)-*s*-triazine
AZODRIN	Dimethyl phosphate of 3-hydroxy-*N*-methyl-*cis*-crotonamide
BHC (Benzene Hexachloride)	1,2,3,4,5,6-Hexachlorocyclohexane (mixture of isomers)
BOTRAN	2,6-Dichloro-4-nitroaniline
BUTYLATE	*S*-Ethyl diisobutylthiocarbamate
CARBARYL	1-Naphthyl methylcarbamate
CIPC	Isopropyl *N*-(3-chlorophenyl)carbamate
CYANAZINE	2-[[4-Chloro-6-(ethylamino)-*s*-triazin-2-yl]amino]-2-methyl-proprionitrile
2,4-D	2,4-Dichlorophenoxyacetic acid
DALAPON	2,2-Dichloropropionic acid
2,4-DB	4-(2,4-Dichlorophenoxy)butyric acid
DDE	Dichlorophenyl dichloro-ethylene (degradation product of DDT); *p,p′*-DDE: 1,1-Dichloro-2,2-bis(*p*-chlor 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 possi some are present in the commercial product. *o,p′*-DDT: [1,1,1-Trichloro-2-(*o*-chlorophenyl)-2-(*p*-chloro ethane]
DESETHYL ATRAZINE	2-Chloro-4-amino-6-isopropylamino-1,3,5-triazine
DIAZINON	*O,O*-Diethyl *O*-(2-isopropyl-6-methyl-4-pyrimidinyl) phosphorothioate
DICAMBA	3,6-Dichloro-*o*-anisic acid
DICHLORPROP	2-(2,4-Dichlorophenoxy)propionic acid
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-d anonaphthalene
DINOSEB	2-*sec*-Butyl-4,6-dinitrophenol
ENDOSULFAN	Hexachlorohexahydromethano-2,4,3-benzodioxathiepin 3-oxide
ENDRIN	Hexachloroepoxyoctahydro-*endo,endo*-dimethanonaphthalene
FENOPROP	2-(2,4,5-Trichlorophenoxy)propionic acid

(*Continued next page*)

	Hexachlorobenzene
CHLOR EPOXIDE	1,4,5,6,7,8,8-Heptachloro-2,3-epoxy-3a,4,7,7a-tetrahydro-4,7-methanoindan
PHOS	*O*-(4-Bromo-2,5-dichlorophenyl) *O*-methyl phenylphosphonothioate
NE	*Gamma* isomer of 1,2,3,4,5,6-hexachlorocyclohexane
ON	3-(3,4-Dichlorophenyl)-1-methoxy-1-methylurea
THION	*O,O*-Dimethyl dithiophospbate of diethyl mercaptosuccinate
	See MCPA
	2-Methyl-4-chlorophenoxyacetic acid
ROP	2-(2-Methyl-4-chlorophenoxy)propionic acid
OXYCHLOR	2,2-Bis(*p*-methoxyphenyl)-1,1,1-trichloroethane 88% and related compounds 12%
YL PARATHION	*O,O*-Dimethyl *O*-*p*-nitrophenyl phosphorothioate
	Dodecachlorooctahydro-1,3,4-metheno-1*H*-cyclobuta[cd]pentalene
HLOR EPOXIDE	1-*exo*-2-*endo*-4,5,6,7,8,8a-Octachloro-2,3-*exo*-*epoxy*-2,3,3a,7,7a-hexahydro-4,7-methanoindene
UAT	1,1′-Dimethyl-4,4′-bipyridilium ion (as dichloride salt)
HION	*O,O*-Diethyl *O*-*p*-nitrophenyl phosphorothioate
	Pentachloroaniline
olychlorinated Biphenyls)	Mixtures of chlorinated biphenyl compounds having various percentages of chlorine
	Pentachloronitrobenzene
	Pentachlorophenol
ATE	*S*-Propyl butylethylthiocarbamate
EL	See Leptophos
AM	4-Amino-3,5,6-trichloropicolinic acid
TON	2,4-Bis(isopropylamino)-6-methoxy-*s*-triazine
L	*O,O*-Dimethyl *O*-(2,4,5-trichlorophenyl) phosphorothioate
NE	2-Chloro-4,6-bis(ethylamino)-*s*-triazine
	2,4,5-Trichlorophenoxyacetic acid
	Trichloroacetic acid
	1,2,4,5-Tetrachloro-3-nitrobenzene
	2,2-Bis(*p*-chlorophenyl)-1,1-dichloroethane (including isomers and dehydrochlorination products)
METON	2-(*tert*-Butylamino)-4-(ethylamino)-6-methoxy-*s*-triazine
THYLAZINE	2-(*tert*-Butylamino)-4-chloro-6-(ethylamino)-*s*-triazine
ENE	Chlorinated camphene (67–69% chlorine). Product is a mixture of polychlor bicyclic terpenes with chlorinated camphenes predominating.
	2-(2,4,5-Trichlorophenoxy)propionic acid

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

Articles are grouped under seven headings. Five follow the basic environmental components of the National Pesticide Monitoring Program: Pesticide Residues in People; Pesticide Residues in Water; Pesticide Residues in Soil; Pesticide Residues in Food and Feed; and Pesticide Residues in Fish, Wildlife, and Estuaries. The sixth is a general heading; the seventh encompasses briefs.

Monitoring is defined here as the repeated sampling and analysis of environmental components to obtain reliable estimates of levels of pesticide residues and related compounds in these components and the changes in these levels with time. It can include the recording of residues at a given time and place, or the comparison of residues in different geographic areas. The Journal will publish results of such investigations and data on levels of pesticide residues in all portions of the environment in sufficient detail to permit interpretations and conclusions by author and reader alike. Such investigations should be specifically designed and planned for monitoring purposes. The Journal does not generally publish original research investigations on subjects such as pesticide analytical methods, pesticide metabolism, or field trials (studies in which pesticides are experimentally applied to a plot or field and pesticide residue depletion rates and movement within the treated plot or field are observed).

Authors are responsible for the accuracy and validity of their data and interpretations, including tables, charts, and references. Pesticides ordinarily should be identified by common or generic names approved by national or international scientific societies. Trade names are acceptable for compounds which have no common names. Structural chemical formulas should be used when appropriate. Accuracy, reliability, and limitations of sampling and analytical methods employed must be described thoroughly, indicating procedures and controls used, such as recovery experiments at appropriate levels, confirmatory tests, and application of internal standards and interlaboratory checks. The procedure employed should be described in detail. If reference is made to procedures in another paper, crucial points or modifications should be noted. Sensitivity of the method and limits of detection should be given, particularly when very low levels of pesticide residues are b
reported. Specific note should be made regardin
rection of data for percent recoveries. Numerical
plot dimensions, and instrument measurements
be reported in metric units.

PREPARATION OF MANUSCRIPTS

——Prepare manuscripts in accord with the *CBE*
Manual, third edition, Council of Biologica
tors, Committee on Form and Style, Am
Institute of Biological Sciences, Washington,
and/or the *U.S. Government Printing Office*
Manual. For further enrichment in languag
style, consult Strunk and White's *Elements of*
second edition, MacMillan Publishing Co.,
York, N.Y., and *A Manual of Style,* twelft
tion, University of Chicago Press, Chicago,

——On the title page include authors' full name
affiliations and addresses footnoted; the
author's name should appear first. Autho
those individuals who have actually writt
made essential contributions to the manuscri
bear ultimate responsibility for its conten
the Acknowledgment section at the end
paper for crediting secondary contributors

——Preface each manuscript with an informati
stract not to exceed 200 words. Constru
piece as an entity separate from the paper
it is potential material for domestic and
secondary publications concerned with the t
study. Choose language that is succinct b
detailed, summarizing reasons for and res
the study, and mentioning significant trends
in mind the literature searcher and his/he
for key words in scanning abstracts.

——Forward original manuscript and three co
first-class mail in flat form: do not fold or

——Type manuscripts on 8½-by-11-inch pape
generous margins on all sides, and end eac
with a completed paragraph. Recycled p
acceptable if it does not degrade the qua
reproduction. Double-space all copy, in
tables and references, and number each pag

——Place tables, charts, and illustrations, p
titled, at the end of the article with notat
the text to show where they should be ir
Treat original artwork as irreplaceable m
Lightly print author's name and illustration
with a ballpoint pen on the back of each
Wrap in cardboard to prevent mutilation;
use paperclips or staples.

——Letter charts distinctly so that numbers and
will be legible when reduced. Execute draw

ack ink on plain white paper. Submit original awings or sharp glossy photographs: no copies ll be accepted.

umber literature citations in alphabetical order cording to author. For journal article include, spectively, author, year, title, journal name as breviated in *Chemical Abstracts Service Source dex*, and volume, issue, and page numbers. For ook references cite, respectively, author, year, apter title, pages, and editor if pertinent, book le, and name and city of publisher. For Governent manuals list originating agency and relevant bgroup, year, chapter title and editor if pertint, manual title, and relevant volume, chapter, d/or page numbers. Do not list private comunications among Literature Cited. Insert them renthetically within the text, including author, te, and professional or university affiliation incating author's area of expertise.

urnal welcomes brief papers reporting monitora of a preliminary nature or studies of limited A section entitled Briefs will be included as ry to provide space for short papers which prely and informative data. These papers must be to two published pages (850 words) and should n to the format for regular papers accepted by urnal.

cripts require approval by the Editorial Advisory When approved, the paper will be edited for and style. Editors will make the minimum changes required to meet the needs of the general Journal audience, including international subscribers for whom English is a second language. Authors of accepted manuscripts will receive edited typescripts for approval before type is set. After publication, senior authors will receive 100 reprints.

Manuscripts are received and reviewed with the understanding that they have not been accepted previously for publication elsewhere. If a paper has been given or is intended for presentation at a meeting, or if a significant portion of its contents has been published or submitted for publication elsewhere, notations of such should be provided. Upon acceptance, the original manuscript and artwork become the property of the *Pesticides Monitoring Journal.*

Every volume of the Journal is available on microfilm. Requests for microfilm and correspondence on editorial matters should be addressed to:

Paul Fuschini (TS-793)
Editorial Manager
Pesticides Monitoring Journal
U.S. Environmental Protection Agency
Washington, D.C. 20460

For questions concerning GPO subscriptions and back issues write:

Superintendent of Documents
U.S. Government Printing Office
Washington, D.C. 20402

The Administrator of the U.S. Environmental Protection Agency has determined that the publication of this periodical is necessary in the transaction of public business required by law of this Agency. Use of funds for printing this publication approved by the Director of the Office of Management and Budget, May 19, 1976.

ORDER BLANK
FOR PMJ

To: Superintendent of Documents
Government Printing Office
Washington, D.C. 20402

Please enter my Subscription for Pesticides Monitoring Journal. I am enclosing Money Order ☐ Check ☐ for this subscription. ($7.90 a year; $2.00 additional for foreign mailing)

*Please address the PMJ as follows.*_____

_____

_____

UNITED STATES GOVERNMENT PRINTING OFFICE, WASHINGTON, D. C. 1967

For sale by the Superintendent of Documents, U.S. Government Printing Office, Washington, D. C. 20402. Subscription price $7.90 a year, $2.00 additional for foreign mailing. Price for a single copy of this issue is $2.00.

United States
Environmental Protection
Agency
Washington DC 20460
TS-793

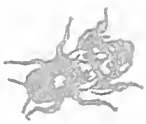
Postage and
Fees paid
Environmental
Protection
Agency
EPA 335

Official Business
Penalty for Private Use $300

Third-Class
Bulk Rate

If you do not desire to continue receiving this publication, please CHECK HERE ☐; cut off this label and return it to the above address. Your name will be removed from the mailing list.

PESTICIDES MONITORING JOURNAL



MARCH 1980

VOLUME 13 NUMBER 4

PEMJAA (13) 137–176 (1980)

ANNUAL INDEX

Vol. 13, June 1979—March 1980

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

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

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

The *Pesticides Monitoring Journal* is published by the Chemical Information Division, Office for Program Integration and Information, Office of Pesticides and Toxic Substances, U.S. Environmental Protection Agency.

Pesticide monitoring activities of the Federal Government, particularly in those agencies represented on the Monitoring Panel which participate in operation of the national pesticides monitoring network, are expected to be the principal sources of data and articles. However, pertinent data in summarized form, together with discussions, are invited from both Federal and non-Federal sources, including those associated with State and community monitoring programs, universities, hospitals, and nongovernmental research institutions, both domestic and foreign. Results of studies in which monitoring data play a major or minor role or serve as support for research investigation also are welcome; however, the Journal is not intended as a primary medium for the publication of basic research. Publication of scientific data, general information, trade names, and commercial sources in the *Pesticides Monitoring Journal* does not represent endorsement by any Federal agency.

Manuscripts received for publication are reviewed by an Editorial Advisory Board established by the Monitoring Panel. Authors are given the benefit of review comments prior to publication. For further information on Journal scope and manuscript preparation, see Information for Contributors at the back of this issue.

Address correspondence to:

Paul Fuschini (TS-793)
Editorial Manager
Pesticides Monitoring Journal
U. S. Environmental Protection Agency
Washington, D.C. 20460

CONTENTS

Volume 13 March 1980 Numbe

FISH, WILDLIFE, AND ESTUARIES

Dieldrin and Heptachlor Residues in Dead Gray Bats, Franklin County, Missouri—1976 Versus 1977

Donald R. Clark, Jr.,[1] Richard K. LaVal,[2] and Alexander J. Krynitsky[1]

ABSTRACT

l dieldrin concentrations were found in the brains of gray bats (Myotis grisescens) *collected during 1976 977 beneath a maternity roost in a Missouri cave. In on, residues of heptachlor epoxide, oxychlordane,* cis-*lane, and* trans-*nonachlor increased significantly in brains and carcasses of bats collected during 1977. increases appear to reflect a switch by local farmers aldrin, dieldrin's parent compound, to heptachlor for ontrol of cutworms. They also constitute an additional to this colony of this endangered bat species.*

Introduction

l concentrations of dieldrin were found in brains ay bats (*Myotis grisescens*) found dead beneath nity roosts in two Missouri caves in late June arly July 1976 (*2*). The apparent source of the in was its parent compound, aldrin, which had applied to cornfields to control cutworms (larvae eral moth species of the family Noctuidae). Hepta- and toxaphene are being recommended as sub- s for aldrin in Missouri (*3*). On July 8, 1977, found 74 dead gray bats when one of the two es was revisited; the other colony was not re- l at this time. In the present study, authors com- he organochlorine residues found in the 1977 sam- dead bats with those found in the 1976 sample he same cave.

Materials and Methods

ave is located in Franklin County, Missouri. Be- its precise location is confidential, it will be :d to by its number, 048, assigned by the Fish Wildlife Service, U.S. Department of the Interior.

ıd Wildlife Service, U.S. Department of the Interior, Patuxent : Research Center, Laurel, Md. 20811.
ri Department of Conservation, Fish and Wildlife Research Columbia, Mo. 65201.

A brief description of cave 048 has been published (*2*). All gray bats found dead in 1976 were juveniles. The 1977 sample contained 23 juveniles and 51 adults; of these, four juveniles and four adults showed no signs of decomposition and, therefore, were analyzed. Bats were recovered under authority of the Federal Endangered Species Permit PRT–8–31–C.

By the same procedures as used in 1976, the dead bats collected in 1977 were frozen, shipped to the Patuxent Wildlife Research Center, and dissected into brain and carcass components as described previously (*1*). Each brain and carcass was analyzed for *p,p'*-DDT, *p,p'*-TDE, *p,p'*-DDE, dieldrin, heptachlor epoxide, oxychlordane, *cis*-chlordane, *trans*-nonachlor, endrin, hexachlorobenzene (HCB), toxaphene, mirex, and polychlorinated biphenyls (PCB). The recovered PCB resembled Aroclor 1260. Hexane extracts of samples were cleaned by Florisil column chromatography, and the eluate containing the pesticides and PCBs was fractionated by SilicAr column chromatography (*4*). Four fractions were collected to facilitate partitioning of endrin and dieldrin in a separate fraction. Analyses were performed on a Hewlett-Packard Model 5753 gas-liquid chromatograph as described by Prouty et al. (*5*).

Residues in 15 percent of the samples were confirmed by gas chromatography-mass spectrometry. Average percentage recoveries from spiked bald eagle (*Haliaeetus leucocephalus*) tissues were: DDE, 107; TDE, 100; DDT, 107; dieldrin, 100; heptachlor epoxide, 93; oxychlordane, 91; *cis*-chlordane, 100; *trans*-nonachlor, 100; endrin, 85; HCB, 78; mirex, 66; and PCB, 120 percent. Residue data were not adjusted on the basis of these recoveries.

Lipid levels were determined from weights of dried hexane extracts of carcasses (*4*). The lower limit of

sensitivity for residues in carcasses was 0.1 ppm pesticides and 0.5 ppm PCB; in brains, it was 0.5 ppm pesticides and 2.5 ppm PCB. Additional details of the analytical procedure are given by Clark et al. (*2*).

Geometric means are given for residues because the data were positively skewed. Residue levels reported as not detected (ND) were entered as zeros. Significance levels are: one asterisk, $0.05>P>0.01$; two asterisks, $0.01>P>0.001$; and three asterisks, $P<0.001$. For compounds which were not detected in the majority of samples for either year, comparisons between years (Table 1) were based on frequencies of occurrence rather than mean concentrations.

Dieldrin levels in the brains of all eight bats in the 1977 sample were within the lethal range as identified previously (*2*). However, among the 12 bats collected during 1976, the brains or carcasses of only ten contained lethal dieldrin levels, and dieldrin levels in the brains of two of the ten were undetermined because of laboratory errors (*2*). Therefore, the present study compares all 1977 dieldrin levels in eight brains and carcasses with just the 1976 lethal dieldrin levels found in eight brains and 10 carcasses.

Results

RESIDUES VERSUS LIPIDS IN CARCASSES

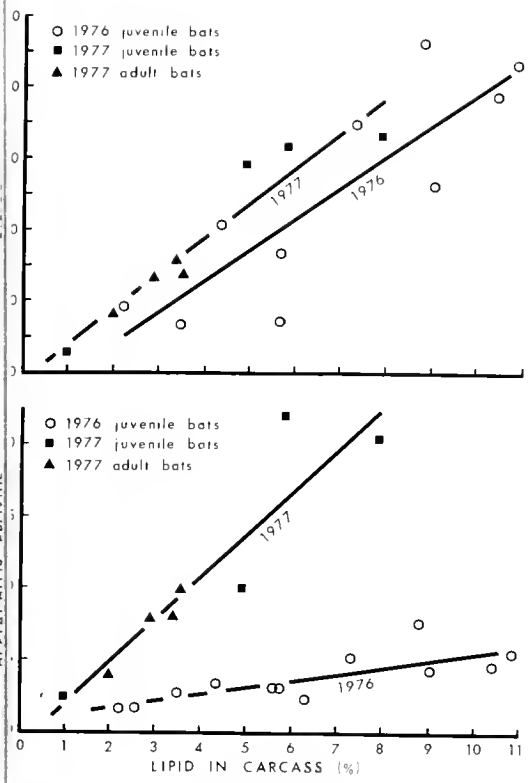
Initial examination of the residue and lipid data for casses indicated that the residue levels of most pounds were positively related to the amount of f the bat. To quantify the relationships, regressions calculated between ppm wet weight (fresh weight residue and percentage fat in the carcass for the compounds found in the majority of samples. Re for dieldrin (1976, $r = 0.858$**; 1977, $r = 0.953$ and heptachlor epoxide (1976, $r = 0.788$**; 1977, 0.924**) are illustrated in Figure 1. Among th other compounds, only *trans*-nonachlor had signif regressions for both years (1976, $r = 0.645$*; 1977 0.744*). Four compounds showed a significant re sion only for 1977: *cis*-nonachlor ($r = 0.773$*); chlordane ($r = 0.799$*); *cis*-chlordane ($r = 0.7$ and DDE ($r = 0.729$*). PCB showed no significa lationship for either year.

To account for this variation due to fat level, au expressed residues as ppm lipid weight rather tha ppm wet weight (Table 1). Organochlorine residu brains are unaffected by this problem, and are com as ppm wet weight (Table 1).

TABLE. 1. *Organochlorine residues and fat levels in gray bats found dead in cave 048, Franklin County, Missouri, in 1976 and 1977* [1]

Compound	Brains, ppm Wet Weight			Carcasses, ppm Lipid Weight		
	1976	1977	t or χ^2	1976	1977	t or χ^2
Dieldrin						
Geometric mean	7.5	8.6	0.909	650	867	1.596
Range	5.0–10	4.6–13		239–1050	560–1182	
Heptachlor epoxide						
Geometric mean	0.10	2.4	4.759***	59	257	13.123*
Range	ND–1.5	0.85–3.7		36–86	204–375	
Oxychlordane						
Frequency or geometric mean	2 of 12	5 of 8	4.432*	31	68	3.577*
Range	ND–1.4	ND–2.3		16–70	21–167	
cis-Nonachlor						
Frequency or geometric mean	1 of 12	5 of 8	6.706**	36	63	2.605*
Range	ND–0.86	ND–1.0		15–70	42–108	
trans-Nonachlor						
Frequency or geometric mean	0 of 12	7 of 8	16.154***	7.6	159	4.901*
Range	ND	ND–2.1		ND–45	91–252	
cis-Nonachlor						
Geometric mean	ND	ND	—	1.5	24	4.456*
Range	—	—		ND–11	14–38	
K chlordane						
Frequency	0 of 12	1 of 8	1.579	0 of 12	7 of 8	15.772*
Range	ND	ND–0.84		ND	ND–25	
PCB (Aroclor 1260)						
Frequency or geometric mean	0 of 12	4 of 8	7.500**	163	295	2.077
Range	ND	ND–9.3		71–425	86–1000	
DDE						
Frequency or geometric mean	6 of 12	2 of 8	1.250	38	44	0.450
Range	ND–4.9	ND–1.7		13–80	6.4–160	
DDT						
Geometric mean	ND	ND	—	0.41	2.2	1.644
Range	—	—		ND–9.1	ND–19	
% Fat						
Mean	—	—	—	6.38	3.92	2.010
Range	—	—		2.21–10.83	0.96–7.88	

NOTE: ND = not detected. Significance levels are indicated as follows: * = $0.05 > P > 0.01$; ** = $0.01 > P > 0.001$; and *** = $P <$ [1] Twelve bats were analyzed in 1976 but, for dieldrin, only the eight brains containing lethal levels and the 10 carcasses containing letha are compared. For all other compounds, $n = 12$ bats. For 1977, $n = 8$ bats.



URE 1. *Dieldrin and heptachlor epoxide in carcasses gray bats in relation to lipid levels: 1976 versus 1977*

levels averaged higher in 1976, but the difference not significant (Table 1).

OUE CHANGES BETWEEN 1976 AND 1977

een 1976 and 1977, heptachlor epoxide, oxychlor- *cis*-chlordane, and *trans*-nonachlor increased sig- ntly in mean concentration or frequency of occur- in both brains and carcasses; *cis*-nonachlor and K dane increased significantly in carcasses; and PCB red significantly more often in brains of 1977 bats in brains of 1976 bats (Table 1).

ts of covariance analyses for heptachlor epoxide 1) and *trans*-nonachlor were similar; 1976 and regressions differed significantly in both slope and ion (heptachlor epoxide, slope $F = 38.63^{***}$, ion $F = 27.83^{***}$; *trans*-nonachlor, slope $F =$, elevation $F = 41.25^{***}$). However, there were ch differences for dieldrin (Fig. 1). Plots for oxy- lane and *cis*-nonachlor showed relationships be- 1976 and 1977 that resembled the one for hepta- epoxide (Fig. 1). However, statistical comparisons en years were not possible because the 1976 re- ons for oxychlordane and *cis*-nonachlor were not ically significant.

Discussion

ata in Table 1 and Figure 1 suggest that heptachlor is being substituted for aldrin over the feeding area of the gray bats from this colony, because heptachlor epoxide, oxychlordane, *cis*-chlordane, *trans*-nonachlor, *cis*-nonachlor, and K chlordane are either present in or degrade from commercial heptachlor. Similarly, the residues could result from the use of commercial chlordane; authors assume heptachlor was used because Missouri Farm Management Specialists are recommending it as a substitute for aldrin (*3*). Two factors indicate local usage. First, other analytical data from this laboratory show residues of heptachlor epoxide, *cis*-chlordane, and dieldrin in the insect prey of these bats at known feeding localities adjacent to crop fields. Second, the cave where the bats spend the winter is in Shannon County, Missouri, which is approximately 75 percent forested and has almost no row crop agriculture.

The data in Table 1 and Figure 1 also indicate that dieldrin levels have not declined. Authors cannot explain the apparent increase in PCB levels.

In cowbirds (*Molothrus ater*), red-winged blackbirds (*Agelaius phoeniceus*), grackles (*Quiscalus quiscula*), and starlings (*Sturnus vulgaris*) that were fed commercial chlordane, brain levels of heptachlor epoxide and oxychlordane appeared to be the primary cause of death (*6*). Heptachlor epoxide residues in brains of birds that died after chlordane dosage ranged from 3.4 to 8.3 ppm whereas residues in brains of survivors ranged from 0.87 to 3.2 ppm (*6*). Among the 1977 bats (Table 1), only one contained heptachlor epoxide residues (3.7 ppm) that reached or exceeded 3.4 ppm. Oxychlordane residues in brains of birds that died after chlordane dosage ranged from 1.1 to 5.0 ppm, and residues in brains of survivors ranged from 0.18 to 1.7 ppm. (*6*). Among the 1977 bats (Table 1), one contained 2.3 ppm oxychlordane but all others had 0.76 ppm or less. In sum, authors doubt that heptachlor residues contributed to the deaths of these 1977 bats because heptachlor concentrations were generally below lethal levels, whereas 1977 dieldrin levels in brains were lethal. However, if the heptachlor residues continue to increase, they could contribute to deaths in future years. Authors believe that these insecticides are a major threat to the continued existence of this maternity colony.

Acknowledgments

We thank V. Brack, M. LaVal, and T. Zinn for field assistance and A. Federighi and L. Stickel for critical readings of the manuscript.

LITERATURE CITED

(*1*) *Clark, D. R., Jr., T. H. Kunz, and T. E. Kaiser. 1978.* Insecticides applied to a nursery colony of little brown bats (*Myotis lucifugus*): lethal concentrations in brain tissues. J. Mammal. 59(1):84–91.

(2) *Clark, D. R., Jr., R. K. LaVal, and D. M. Swineford. 1978.* Dieldrin-induced mortality in an endangered species, the gray bat (*Myotis grisescens*). Science 199 (4335):1357–1359.

(3) *Craig, W. L., J. L. Huggans, S. G. Jones, and G. W. Thomas. 1979.* 1979 Missouri Insect Control Recommendations. University of Missouri, Columbia, Mo. 163 pages.

(4) *Cromartie, E., W. L. Reichel, L. N. Locke, A. A. Belisle, T. E. Kaiser, T. G. Lamont, B. M. Mulhern, R. M. Prouty, and D. M. Swineford. 1975.* Residues of organochlorine pesticides and polychlorinated biphenyls and autopsy data for bald eagles, 1971–72. Pe Monit. J. 9(1):11–14.

(5) *Prouty, R. M., W. L. Reichel, L. N. Locke, A. Belisle, E. Cromartie, T. E. Kaiser, T. G. La B. M. Mulhern, and D. M. Swineford. 1977.* Residu organochlorine pesticides and polychlorinated bipl and autopsy data for bald eagles, 1973–74. Pe Monit. J. 11(3):134–137.

(6) *Stickel, L. F., W. H. Stickel, R. D. McArthur D. L. Hughes. 1979.* Chlordane in birds: a stu lethal residues and loss rates. Pages 387–396 *in* cology and Occupational Medicine. Organized by Deichmann. Elsevier North Holland, New York, N

Residues of Polychlorinated Biphenyls and DDT in Water and Sediment of the Indian River Lagoon, Florida—1977–78[1]

Tsen C. Wang, Robert S. Johnson,[2] and Joe L. Bricker

ABSTRACT

r and sediment samples collected during 1977–78 from ıdian River lagoon between Vero Beach, Indian River ty, and Fort Pierce, Saint Lucie County, Florida, were zed for PCBs and DDT. Sample locations were chosen e basis of proximity to major tributaries, sewage out- or municipal areas. Concentrations in water samples below 0.01 ppb ΣDDT and 0.5 ppb PCBs. Small nts of PCBs and DDT were found in most sediment es, ranging from <1.0 ppb to 0.63 ppm Aroclor 1254 rom <0.1 ppb to 0.081 ppm ΣDDT. Samples from the r Creek tributary and from the Fort Pierce power and municipal docking area contained higher PCB ntrations then did samples from other locations. DDT CB levels in most samples indicate little contamination se compounds of the Indian River Waterway between Beach and Fort Pierce.

Introduction

hlorinated biphenyls (PCBs) and ΣDDT are itous environmental contaminants. Reports of pread distribution of organochlorine pesticide resi- in the global ecosystem are increasing (*3–5, 8, 9,* Iowever, little information is available in the litera- egarding organochlorine levels in the water and ent of the Indian River lagoon.

ndian River is a lagoonal estuary situated along ıst central coast of Florida. This estuary extends m, from Titusville, Brevard County, in the north nt Lucie Inlet, Martin County, in the south (Fig. uthors investigated the occurrence of organochlo- in the Indian River lagoon between Vero Beach, ı River County, and Fort Pierce, Saint Lucie y (Fig. 2), during 1977 and early 1978.

Methods and Materials

: 2 indicates approximate locations of seven sam- stations which were chosen on the basis of prox- to major tributaries, sewage plant outfalls, or ipal areas.

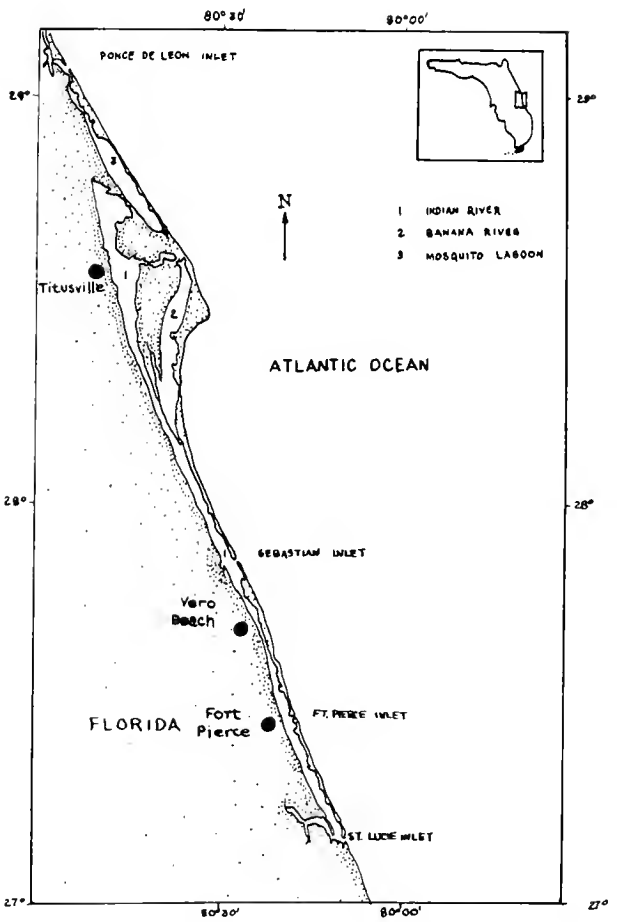


FIGURE 1. *Location of Indian River lagoon, Florida*

Surface water samples were collected at each station in a precleaned solvent bottle. The water samples were brought back to the authors' laboratory and refrigerated at 4°C overnight. Samples were analyzed the day after collection.

Each 3-liter water sample was drained at 250 ml/minute through a glass column containing 50 ml Amberlite XAD-2 resin (*2*). The column was eluted with 200 ml

- Branch Foundation, Inc., RR 1, Box 196, Fort Pierce, Fla.
Contribution No. 163.
: address: Varian Corporation, Boston, Mass.

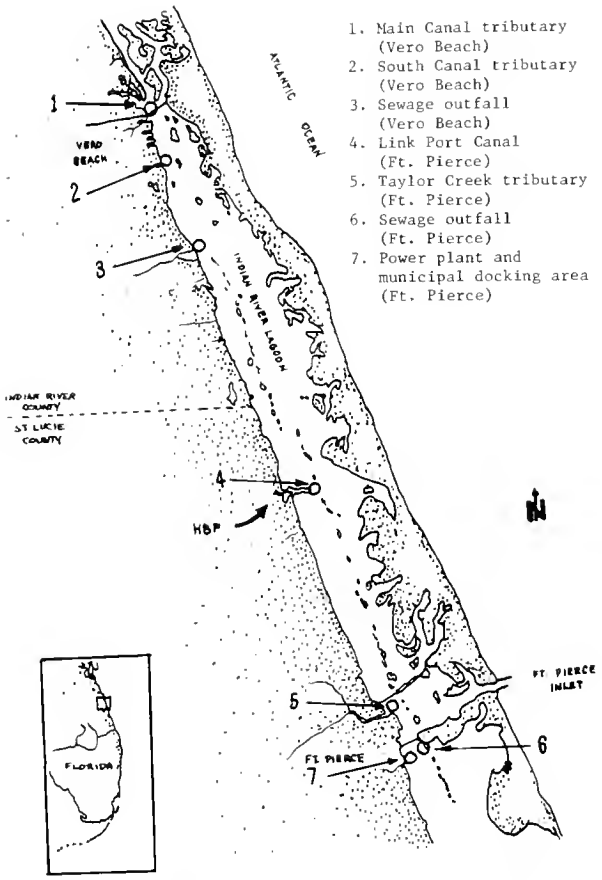


FIGURE 2. *Map of sampling stations, Indian River lagoon, Florida*

acetonitrile at full gravity flow, followed by 500 ml distilled water. The combined solvent was then extracted twice with 50 ml hexane. The hexane extracts were cleaned on a Florisil microcolumn (*6*) and eluted with 6.5 ml of 10 percent ethyl ether in hexane. The sample was concentrated to 1 ml before gas chromatographic analysis.

The 100-g composited sediment samples were air dried for about two days at ambient temperature. The sample was then shaken in a wrist-action shaker for 2 hours with isopropyl alcohol followed by hexane to recover the isopropyl alcohol together with the desorbed material. The extract was washed with distilled water, dried through a Na_2SO_4-Celite column and concentrated to 1 ml before cleanup (*10*). The hexane extract was passed through a Florisil column and eluted with 100 ml of 10 percent methylene chloride in hexane. PCBs were separated from chlorinated pesticides on a silicic acid column (*1*). Activated copper was added to remove any sulfur from the sediment extracts before they were applied to the silicic acid column. Residues in the samples were further treated with potassium hydroxide for confirmation and sample cleanup (*12*). The analytical scheme for sediment samples is shown in Figure 3.

Compounds were identified by gas-liquid chroma graphic analysis and confirmed by thin-layer chro tography (*7*) when sample size and concentration sufficient. Analyses were performed on a Perkin-E Model 900 gas chromatograph with the followin strument parameters and operating conditions:

Detector:	^{63}Ni
Dual columns:	6 ft × 2 mm ID glass, packed with a mixtu 1.5 percent OV–17 and 1.95 percent QF–1 a mixture of 4 percent SE–30 and 6 percent 210 on 100–120-mesh Chromosorb Q
Temperatures:	column 185°C injector 205°C detector 220°C
Carrier gas:	95 percent argon in methane flowing at 2 minute.

The minimum detectable concentrations for Ar 1254 and DDT residues were 0.5 ppb and 0.01 pp water and 1.0 ppb and 0.10 ppb in sediment sam respectively.

Recoveries

Water and sediment samples were spiked with 2 PCB and 75 pg ΣDDT. Duplicate analyses produce following recoveries:

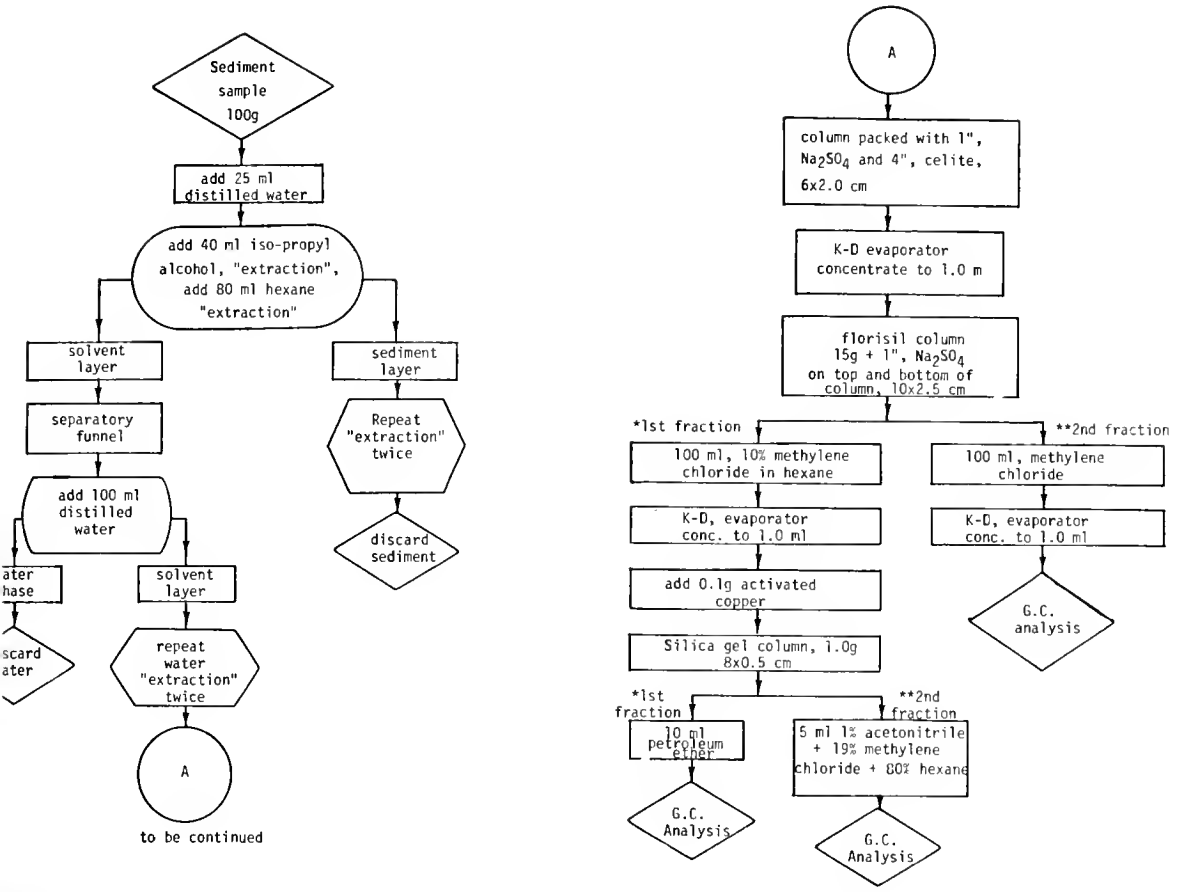
Compound	% Recovery	
	Water (± SD, $n = 5$)	Sedimen (± SD, $n =$
Aroclor 1254	95 ± 4	92 ± 4
o,p'–DDT	90 ± 10	91 ± 3
p,p'–DDT	92 ± 8	91 ± 8
p,p'–DDE	83 ± 15	98 ± 14
p,p'–TDE	90 ± 7	106 ± 21

The results reported in this paper were not corrected for recoveries.

Results and Discussion

After water and sediment samples were collected the Indian River lagoon, duplicate residue analyses performed. The arithmetic means of PCB and Σ concentrations for each sample are presented in Ta Residues ranging from <1.0 ppb to 0.63 ppm Ar 1254 and from <0.1 ppb to 0.081 ppm ΣDDT wer tected in most sediment samples. However, PCB ΣDDT residues were below detection limits in the samples: less than 0.50 ppb Aroclor 1254 and 0.0 ΣDDT.

Table 1 illustrates the amounts of PCB and Σ found in the sediment samples. Main Canal and Canal in Indian River County are two major tribu to the lagoon through which agricultural runoff o The results show that samples from the Main Cana utary area had slightly higher PCB and ΣDDT c



RE 3. *Analytical scheme for cleanup and extraction of organochlorines from sediment samples from the Indian River lagoon, Florida*

lid samples from the South Canal tributary. PCB DDT residue concentrations in the Main Canal es ranged from not detectable to 210 ppb and not detectable to 5.62 ppb, respectively. Residue ıtrations in South Canal samples ranged from not ıble to 8.67 ppb PCBs and from not detectable to ppb ΣDDT. The frequency with which PCB and appeared at both sampling sites was 60 percent. aylor Creek tributary in Saint Lucie County is an- major source of agricultural runoff to the lagoon. es from Taylor Creek had the highest PCB resi- ı the study area. Residues ranged from 20 to 570 roclor 1254 and from 0.96 to 19.9 ppb ΣDDT. ierce power plant and municipal docking area also latively high PCB and ΣDDT residues. Aroclor anged from 39 to 278 ppb and ΣDDT from 1.90 0 ppb in the sediment samples. Both compounds ound in all samples from Taylor Creek and Fort municipal docking area. Samples from near the Beach sewage outfall contained 1.0–16.2 ppb r 1254 with 100 percent frequency occurrence; levels ranged from not detectable to 0.38 ppb in cent of samples. Residues in samples from near rt Pierce sewage outfall ranged from not detecta- ble to 11.1 ppb Aroclor 1254 and from not detectable to 1.70 ppb ΣDDT. Of six samples analyzed, 83 percent contained both compounds.

Conclusions

Low concentrations of PCB and ΣDDT residues were found only in the sediment samples. Sediment samples collected from Taylor Creek tributary and Fort Pierce municipal docking area had higher PCB and ΣDDT residue levels than did other sample sites. The source of the compounds is not known. The data from this survey do not show any clear correlation between sampling site and sampling date.

LITERATURE CITED

(*1*) *Armour, J. A., and J. A. Burke. 1970.* Method for separating polychlorinated biphenyls from DDT and its analogs. J. Assoc. Off. Anal. Chem. 53(4):761–768.

(*2*) *Harvey, G. R. 1972.* Absorption of chlorinated hydrocarbons from seawater by a crosslinked polymer. Technical Report, Woods Hole Oceanographic Institution, Woods Hole, Mass. pp. 1–17.

(*3*) *Holden, A. V. 1970.* Source of polychlorinated biphenyl contamination in the marine environment. Nature 228(5277):1220–1221.

TABLE 1. *Polychlorinated biphenyls and ΣDDT residues in sediment of the Indian River lagoon between Vero Beach and Fort Pierce, Florida, 1977–78*

Sampling Site	Sampling Date	Residues, ppb Dry Weight					
		Aroclor 1254	*p,p'*-DDE	*o,p'*-TDE	*p,p'*-TDE	*p,p'*-DDT	ΣD
Main Canal tributary, Vero Beach	2–07–77	5.33	ND	ND	ND	ND	N
	3–07–77	ND	ND	ND	ND	ND	N
	4–18–77	ND	ND	0.96	2.40	ND	3.
	1–11–78	210	ND	ND	2.13	ND	2.
	4–12–78	20.76	4.51	ND	1.11	1.97	5.
South Canal tributary, Vero Beach	2–07–77	8.67	ND	ND	ND	ND	N
	3–07–77	1.95	ND	ND	ND	ND	N
	4–18–77	ND	ND	ND	ND	ND	N
	1–11–78	0.61	0.40	ND	0.10	ND	0.
	4–12–78	ND	0.14	ND	0.09	0.10	0.
Sewage outfall, Vero Beach	2–07–77	16.2	ND	ND	ND	ND	N
	3–07–77	1.36	ND	ND	ND	ND	N
	4–18–77	10.1	ND	ND	ND	ND	N
	4–12–78	1.0	0.17	ND	0.21	ND	0.
Link Port, Fort Pierce	2–07–77	23.7	ND	ND	ND	ND	N
	3–07–77	2.5	ND	ND	ND	ND	N
	12–15–77	ND	1.47	ND	1.80	ND	2.
	1–11–78	1.89	0.07	ND	0.35	ND	0.
	4–12–78	ND	0.03	ND	0.12	ND	0.
Taylor Creek, Fort Pierce	2–07–77	20.6	ND	0.96	ND	ND	0.
	3–07–77	32.3	ND	7.5	ND	ND	7.
	4–18–77	82.0	1.1	3.5	3.5	0.2	8.
	12–15–77	41.4	13.3	5.9	0.60	ND	19.
	1–11–78	570	0.50	0.50	0.91	ND	10.
Sewage outfall, Fort Pierce	2–07–77	1.44	ND	ND	ND	ND	N
	3–07–77	11.1	ND	ND	0.5	ND	0.
	4–18–77	5.0	ND	0.37	1.33	ND	1.
	12–05–77	ND	0.15	ND	0.38	0.06	0.
	1–11–78	3.1	0.28	ND	0.36	ND	0.
	4–12–78	2.21	0.14	0.26	0.79	0.06	1.
Fort Pierce power plant and municipal docking area	3–07–77	278	ND	1.9	ND	ND	1
	4–18–77	140	ND	6.2	16.5	ND	22.
	12–15–77	39	13.3	5.99	33.1	28.6	81.
	1–11–78	120	0.5	ND	1.00	3.20	4.
	4–12–78	61	6.25	5.50	13.0	1.46	26

NOTE: ND = not detectable.

(4) *Jensen, S., A. G. Johnels, M. Olsson, and G. Otterlind. 1969.* DDT and PCB in marine animals from Swedish waters. Nature 224(5216):247–250.

(5) *Korte, F. 1976.* Global input and trends of chemical residues in the biosphere. Environ. Qual. Safety 5(1): 183–196.

(6) *Law, L. M., and D. F. Goerlitz. 1970.* Minicolumn chromatographic cleanup for the analysis of pesticides in water. J. Assoc. Off. Anal. Chem. 53(6):1276–1286.

(7) *Oliver, B. M. 1972.* TLC systems for identification of pesticides. Paper TSD–1, Chemical and Biological Investigation Branch, U.S. Environmental Protection Agency. pp. 1–5.

(8) *Risebrough, R. W., and L. deLappe. 1972.* Accumulation of polychlorinated biphenyls in ecosystems viron. Health Perspect. No. 1. p. 39.

(9) *Risebrough, R. W., P. Rieche, D. B. Peakall, Herman, and M. N. Kriven. 1968.* Polychlor biphenyls in the global ecosystem. Nature 220(5 1098–1102.

(10) *U.S. Environmental Protection Agency. 1972.* L tory Manual National Soils Testing Laboratory St. Louis, Miss.

(11) *Warster, C. F. 1969.* Chlorinated hydrocarbon i cides and world ecosystem. Biol. Conserv. 1(1) 129.

(12) *Young, S. J., and J. A. Burke. 1972.* Microscale treatment for use in pesticide residue confirmat sample cleanup. Bull. Environ. Contam. Toxicol. 160–167.

Organochlorine Pesticide, PCB, and PBB Residues and Necropsy Data for Bald Eagles from 29 States—1975–77[1]

T. Earl Kaiser, William L. Reichel, Louis N. Locke,[2] Eugene Cromartie, Alexander J. Krynitsky, Thair G. Lamont, Bernard M. Mulhern, Richard M. Prouty, Charles J. Stafford, and Douglas M. Swineford

ABSTRACT

g 1975–77, 168 bald eagles (Haliaeetus leucocephalus) *moribund or dead in 29 states were analyzed for ochlorine pesticides and polychlorinated biphenyls s); 32 specimens from 13 states were analyzed for poly-inated biphenyls (PBBs). PCBs were present in 166 bald carcasses and DDE was found in 165. TDE and diel-were identified in 137 samples,* trans-*nonachlor in 118, xychlordane in 90. Brains of five eagles contained pos-lethal levels of dieldrin, and two eagles possibly died drin poisoning. Nine eagle livers, analyzed because of ted lead poisoning, contained high levels of lead. y percent of the eagles died from shooting, the most on cause of death; this cause of death, however, has ed.*

Introduction

paper is the sixth in a series (*1, 2, 5–7*) evaluating ide residues and necropsy data on bald eagles *aeetus leucocephalus*), and it covers the years -77.

Sampling and Necropsy

undred sixty-eight moribund or dead bald eagles collected in 29 states (Table 1). Sampling, ng, and storage procedures have been reported Eagles found in the field were packed in Dry Ice ipped air express to the Fish and Wildlife Service, Department of the Interior, National Wildlife h Laboratory, Madison, Wisconsin, for necropsy Following necropsy, the brain and the remaining s, except skin, feet, wings, liver, kidney, and gas-estinal tract, were packed in Dry Ice and shipped press to the Patuxent Wildlife Research Center, l, Maryland, for chemical residue analysis.

Analytical Procedures

e preparation, extraction, lipid removal, and chemical separations have been reported (*2*). The procedure for eluting pesticides from the SilicAr column was modified to isolate dieldrin and endrin in a discrete fraction from the following number of samples: 8 of 49 eagles collected in 1975, 13 of 50 collected in 1976, and 52 of 69 collected in 1977. The modification involved collecting four fractions as follows:

Fraction 1: 80 ml petroleum ether, contained HCB and mirex

Fraction 2: 320 ml petroleum ether, contained PCBs, PBBs, and DDE

Fraction 3: 275 ml of 15 percent methylene chloride in hexane contained the remaining organochlorine compounds except endrin and dieldrin

Fraction 4: 200 ml mixture of 1 percent acetonitrile, 19 percent hexane, and 80 percent methylene chloride, contained endrin and dieldrin.

TABLE 1. *Distribution, by state and year of death, of bald eagles collected during 1975–77*

State	No. of Eagles Collected		
	1975	1976	1977
Alaska	3	5	5
California	2		
Colorado		1	4
Florida	7	2	4
Georgia			1
Idaho			2
Illinois			1
Indiana		1	
Iowa	5	2	1
Kansas		3	3
Maine	3	1	4
Maryland	2	2	
Michigan	4	1	1
Minnesota	2	4	7
Missouri		5	2
Nebraska	5	9	5
New Mexico	2		
New York		1	
Ohio	1	1	
Oklahoma	2	2	1
Pennsylvania			1
South Carolina			1
South Dakota	1	2	4
Texas	1		
Utah	2	2	11
Virginia	3		1
Washington		1	
Wisconsin	4	5	9
Wyoming			1
TOTAL	49	50	69

nd Wildlife Service, U.S. Department of the Interior, Patuxent e Research Center, Laurel, Md. 20811.
nd Wildlife Service, U.S. Department of the Interior, National e Health Laboratory, Madison, Wisc. 53706.

Other compounds normally analyzed for were chlordane, DDT, heptachlor epoxide, nonachlor, oxychlordane, TDE, and toxaphene. Samples were analyzed on a Hewlett-Packard Model 5713 or 5840A gas-liquid chromatograph equipped with a Ni^{63} detector, automatic sampler, and digital processor. The first 21 samples received in 1975 were analyzed on column 1. The remainder of the 1975 samples and all 1976 and 1977 samples were analyzed on column 2 to effect a separation of *cis*-chlordane and *trans*-nonachlor. Instrument parameters and operating conditions were:

Columns:	(1) 1.83 m × 4 mm ID, packed with a mixture of 4 percent SE-30 and 6 percent QF-1 (2) 1.83 m × 4 mm ID, packed with a mixture of 1.5 percent OV-17 and 1.95 percent QF-1
Temperature:	columns 190°C
Carrier gas:	5 percent methane in argon, flowing at 60 ml/minute

Fraction 2, which was analyzed for PBBs, was gas chromatographed on a 3 percent OV-1 column at 245°C with a 100-ml/minute flow rate. Under these conditions, the hexabromobiphenyl (HBBP) compound eluted after the PCBs. The pesticides were measured by digital integration of peak areas; PCBs were estimated by comparing total peak area with that of Aroclor 1254 or 1260, depending on the gas chromatographic profile of the sample. PBB values were based on the HBBP peak. Toxaphene measurements were semiquantitative estimates made from two peak areas as previously described (*6*).

Average percentage recoveries from spiked pheasant carcass tissue were: DDE, 104; TDE, 92; DDT, 100; dieldrin, 89; heptachlor epoxide, 93; oxychlordane, 92; *cis*-chlordane, 92; *trans*-nonachlor, 91; endrin, 90; HCB, 80; mirex, 90; and Aroclor 1260, 90. Residue levels were not corrected for recovery. The lower limit of reportable residues was 0.05 ppm pesticides, 0.10 ppm PCBs, and 0.02 ppm PBBs.

Residues in 56 specimens, or 33 percent, were confirmed on an LKB 9000 or a Finnigan 4000 series gas chromatograph/mass spectrometer (GC/MS). Operating parameters for the LKB have been described (*1*). The procedures followed with the Finnigan model were:

Column:	1.83 m × 2 mm ID, packed with a mixture of 1.9 percent OV-17 and 1.95 percent QF-1	
Temperatures:	column	programmed at 2°C/minute from 140°C to 225°C
	injector	215°C
	separator	235°C
	ion source	300°C
Carrier gas:	helium flowing at 30 ml/minute	

Results and Discussion

Table 2 shows the results of the tissue analyses of the 168 bald eagles. PCBs were present in 166 carcass samples, DDE in 165, and dieldrin in 137. Thirty-tw the 69 specimens collected during 1977 were exam for PBBs; low residue levels were detected in 11 s imens from Maine, Virginia, Florida, Missouri, Mi sota, and Wisconsin.

A comparison of residue data from year to year is cult because a systematic sampling procedure coul be considered and also because of the wide rang residue levels. However, median values for DDE, drin, and PCBs in the carcasses collected during were lower than in any previous year (*1, 2, 5–7*). ing 1972–77, the frequency of detection of residu the brains of this species has steadily declined as lows: DDE from 100 to 83 percent, dieldrin from 46 percent, and PCBs from 92 to 84 percent.

Five eagles may have died of dieldrin poisoning (T 3). Dieldrin levels in the brains ranged from 6.8 to ppm. A study of several series of experimental killed by dieldrin indicated that when death was pri ily caused by the neurotoxic action of dieldrin, the end of the distribution curve fell at about 5 ppm published data: W. H. Stickel (Patuxent Widlife search Center, Laurel, Md.), November 27, 1978). study concluded that death may be due to dieldrin soning at the 5 ppm level but that the probabili dieldrin-caused mortality increases as the levels incr at 9 ppm and above, the probability of dieldrin po ing is high.

The 11-ppm reading of the present study was fro immature female collected in Wisconsin. The bird weak, unable to fly, and died the next day. It ha subcutaneous or abdominal fat; the coronary fat wa dergoing resorption and the pectoral muscles wer duced. Bacteriological and virological tests were tive.

In two possible cases of death caused by endrin po ing (Table 3), brains contained 0.71 ppm and 1.2 endrin. The known lethal range begins at about 0.6 and evidence of death caused by endrin becomes s at 0.8 ppm, as reported by Stickel et al. (*8*). Neith the two eagles had subcutaneous, abdominal, or nary fat. The lack of fat is often seen in organochl pesticide poisoning, although it can be caused by factors.

Livers of specimens that had lead shot pellets i stomach, were emaciated, or had signs of diarrhea analyzed for lead by the Central Animal Health La tory, Madison, Wisconsin. High levels were found i specimens (Table 4), suggesting lead poisoning. ever, the lethal level of lead in bald eagles is not k and is currently being studied. Longcore (*4*) conc

TABLE 2. *Residues of organochlorine pesticides, PCBs, and PBBs in 168 bald eagles from 29 states, 1975–77*

		Residues, ppm Wet Weight					
		Carcass			Brain		
ompound	Year	No. of Specimens [1]	Median	Range	No. of Specimens [1]	Median	Range
)DE	1975	49	4.5	0.17– 74.0	45	0.81	0.05– 35.0
	1976	49	6.8	0.18–120.0	42	0.93	0.07– 52.0
	1977	67	4.0	0.10– 65.0	57	0.98	0.05–100.0
DE	1975	44	0.42	0.05– 10.0	18	0.51	0.07– 1.9
	1976	43	0.45	0.08– 12.0	14	0.32	0.06– 1.2
	1977	50	0.26	0.06– 4.5	19	0.23	0.05– 2.3
)DT	1975	13	0.11	0.06– 0.73	4	0.07	0.05– 0.09
	1976	12	0.13	0.05– 0.58	1	0.05	
	1977	6	0.09	0.06– 0.12	2	0.10	0.06– 0.13
in	1975	44	0.60	0.06– 12.0	32	0.23	0.05– 11.0
	1976	40	0.66	0.05– 12.0	25	0.38	0.05– 9.8
	1977	53	0.22	0.05– 4.0	32	0.27	0.05– 6.8
:hlor epoxide	1975	27	0.17	0.05– 1.8	11	0.22	0.07– 1.6
	1976	29	0.15	0.05– 2.8	12	0.17	0.05– 2.1
	1977	29	0.11	0.05– 1.4	14	0.18	0.05– 0.77
ordane	1975	28	0.18	0.05– 0.78	15	0.23	0.07– 0.68
	1976	28	0.14	0.06– 2.3	12	0.18	0.06– 2.6
	1977	34	0.13	0.05– 1.2	16	0.29	0.08– 1.7
ordane and/or -nonachlor	1975	17[2]	0.55	0.11– 6.5	13	0.11	0.05– 3.1
ordane	1975	20[3]	0.32	0.11– 4.5	9	0.19	0.07– 1.3
	1976	27	0.24	0.05– 1.7	13	0.09	0.05– 1.2
	1977	19	0.22	0.07– 2.2	20	0.19	0.06– 6.4
lonachlor	1975	26[3]	0.38	0.06– 6.0	13	0.20	0.06– 2.2
	1976	41	0.38	0.05– 4.0	18	0.22	0.06– 3.4
	1977	51	0.28	0.05– 5.6	22	0.33	0.05– 7.4
achlor	1975	29	0.14	0.05– 1.7	12	0.17	0.06– 0.75
	1976	27	0.10	0.05– 0.83	9	0.13	0.05– 0.41
	1977	30	0.15	0.05– 1.3	14	0.17	0.06– 4.0
	1975	5[4]	0.16	0.09– 1.0	3	0.44	0.12– 0.50
	1976	6	0.48	0.18– 3.0	6	0.32	0.15– 0.71
	1977	5	0.07	0.06– 2.5	5	0.14	0.05– 1.2
ene	1975	20	0.30	0.06– 2.5	8	0.24	0.13– 1.2
	1976	11	0.11	0.05– 0.55	7	0.25	0.05– 0.31
	1977	22	0.22	0.06– 0.88	13	0.16	0.06– 2.7
	1975	11	0.08	0.05– 0.12	4	0.06	0.05– 0.07
	1976	8	0.08	0.05– 0.40	4	0.07	0.05– 0.16
	1977	4	0.08	0.07– 0.12	6	0.06	0.05– 0.17
	1975	22	0.19	0.06– 1.9	13	0.14	0.06– 0.98
	1976	24	0.24	0.05– 2.5	8	0.13	0.09– 0.57
	1977	29	0.25	0.05– 5.3	18	0.21	0.05– 5.5
	1977	10[5]	0.07	0.03– 0.27	7	0.05	0.03– 0.17
	1975	49	7.7	0.20–220.0	46	1.2	0.13–160.0
	1976	50	12.0	0.18–560.0	44	2.2	0.10–240.0
	1977	67	5.5	0.21–190.0	58	1.5	0.07–160.0

er of specimens containing residues; median is based on this number. Total samples numbered 49 in 1975, 50 in 1976, and 69 in 1977.
y of the 49 specimens were analyzed for *cis*-chlordane and/or *trans*-nonachlor.
y-nine of the 49 specimens were analyzed separately for *cis*-chlordane and for *trans*-nonachlor.
y-nine of the 49 specimens were analyzed for endrin.
-two of the 69 specimens were analyzed for PBBs.

experimental studies, and from results reported in erature for lead-poisoned waterfowl, that 6–20 ead in the liver of mallards indicated acute expo- o lead. The two eagles from northern California observed regurgitating a fluorescent green material ere found dead the next day. Necropsy failed to indicate cause of death but both esophagi were stained with bile. Livers contained 38 ppm and 29 ppm lead. Organochlorine residues in carcasses and brains were low. The Maryland specimen that contained 75 lead shot pellets in the stomach has been studied in detail by Jacobsen et al. (*3*).

TABLE 3. *Data on five suspected cases of dieldrin poisoning and two suspected cases of endrin poisoning of bald eagles from six states, 1975–77*

State	Year	Sex	Age	Residues in Brain, ppm	Necropsy Findin
			DIELDRIN		
Minnesota	1975	M	adult	7.5	Open; no fat deposits
Wisconsin	1975	F	immature	11.0	Open; no fat deposits
Missouri	1976	F	immature	9.8	Emaciation; no fat d
Florida	1976	M	immature	8.7	Open; no fat deposits
Wisconsin	1977	F	adult	6.8	Open; no fat deposits
			ENDRIN		
Minnesota	1976	M	adult	0.71	Open; no fat deposits
Iowa	1977	M	immature	1.2	Open; no fat deposits

[1] Open = No diagnosis could be made on the basis of necropsy findings.

TABLE 4. *Data on nine bald eagles that contained high lead levels in the liver, 1975–77*

State	Year	Sex	Age	Residue in Liver, ppm	Necropsy Findin
California	1975	F	adult	38.1[1]	Open; bile-stained es
California	1976	F	adult	29.0[1]	Open; bile-stained es
Florida	1975	F	adult	26.2	Open
Maine	1975	F	adult	34.0	Open; nine shot pe bile-stained stomach
Nebraska	1976	F	adult	23.7	Open; one pellet in
Maryland	1976	F	immature	22.9	Open; 75 shot pellets stomach
South Dakota	1976	F	adult	36.9	Open; no fat, intestir with bile
South Dakota	1977	M	adult	28.0	Open; no fat
Wisconsin	1977	M	immature	30.4	Open; no fat, liver green with bile

[1] Analysis at Patuxent Wildlife Research Center, Laurel, Maryland; remainder analyzed by Central Animal Health Laboratory, Wiscon partment of Agriculture, Madison, Wisconsin for National Wildlife Health Laboratory.

TABLE 5. *Probable causes of death of 168 bald eagles collected in 29 states, 1975–77*

Cause of Death	No. of Eagles
Shot	33
Impact injuries	22
Electrocution	17
Lead poisoning	9
Pneumonia	6
Trapping wounds	6
Dieldrin poisoning	5
Drowning	3
Peritonitis	3
Endrin poisoning	2
Enteritis	2
Septicemia	2
Strychnine poisoning	2
Aspiration of fish	1
Avian cholera	1
Aspergillosis	1
Cyanide poisoning [1]	1
Dieldrin/pneumonia	1
Hepatic necrosis	1
Impaction of cloaca and large intestine	1
Laceration of lung	1
Myocardial infarction	1
Penetration wound	1
Open [2]	46
TOTAL	168

[1] Cyanide analysis was performed by Central Animal Health Laboratory, Wisconsin Department of Agriculture, Madison, Wisconsin.
[2] No diagnosis could be made on the basis of necropsy findings or chemical analysis.

Shooting remained the most frequent cause of death, but the proportion of mortalities due to shooting has declined steadily: 1966–68, 41 percent; 1969–70, 46 percent; 1971–72, 35 percent; 1973–74, 24 percen 1975–77, 2 percent (Table 5).

Conclusions

The presence of organochlorine residues, some at l lethal levels, in bald eagles shows the continuing ence of contamination on the environment. The d dicate that the residue levels are declining.

Acknowledgments

Authors acknowledge and appreciate the help many organizations, individuals, and Special A Division of Law Enforcement, Fish and Wildlife ice, who submitted specimens and provided field Authors also thank Marian Kreamer, who assist assembling data.

LITERATURE CITED

(1) *Belisle, A. A., W. L. Reichel, L. N. Locke, T. mont, B. M. Mulhern, R. M. Prouty, R. B. D and E. Cromartie. 1972.* Residues of organoch pesticides, polychlorinated biphenyls, and mercu autopsy data for bald eagles, 1969 and 1970. Monit. J. 6(3):133–138.

(2) *Cromartie, E., W. L. Reichel, L. N. Locke, Belisle, T. E. Kaiser, T. G. Lamont, B. M. Mu R. M. Prouty, and D. M. Swineford. 1975.* Resid organochlorine pesticides and polychlorinated bip and autopsy data for bald eagles, 1971–72. Monit. J. 9(1):11–14.

acobsen, E., J. W. Carpenter, and M. Novilla. 1977. uspected lead toxicosis in a bald eagle. J. Am. Vet. Med. Assoc. 171(9):952–954.

ongcore, J. R., L. N. Locke, G. E. Bagley, and R. An-rews. 1974. Significance of lead residues in mallard issues. Fish and Wildlife Service, U.S. Department of he Interior, Special Science Report, Wildl. No. 182, 4 pp.

Iulhern, B. M., W. L. Reichel, L. N. Locke, T. G. La-nont, A. A. Belisle, E. Cromartie, G. E. Bagley, and R. M. Prouty. 1970. Organochlorine residues and au-opsy data from bald eagles, 1966–68. Pestic. Monit. J. (3):141–144.

routy, R. M., W. L. Reichel, L. N. Locke, A. A. Belisle, E. Cromartie, T. E. Kaiser, T. G. Lamont, B. M. Mulhern, and D. M. Swineford. 1977. Residues of organochlorine pesticides and polychlorinated biphenyls and autopsy data for bald eagles, 1973–74. Pestic. Monit. J. 11(3):134–137.

(7) *Reichel, W. L., E. Cromartie, T. G. Lamont, B. M. Mulhern, and R. M. Prouty. 1969.* Pesticide residues in eagles. Pestic. Monit. J. 3(3):142–144.

(8) *Stickel, W. H., W. L. Reichel, and D. L. Hughes. 1979.* Endrin in birds: lethal residues and secondary poisoning. Pages 397–406 *in* W. B. Deichmann, ed., Toxicology and Occupational Medicine, Elsevier North Holland, New York, N.Y.

SOILS

Heavy Metal Concentrations in Soils of Five United States Cities, 1972 Urban Soils Monitoring Program

Ann E. Carey,[1] Jeanne A. Gowen,[1] Terrell J. Forehand,[2] Han Tai,[2] and G. Bruce Wiersma[3]

ABSTRACT

Lead, mercury, cadmium, and arsenic levels were determined in soil samples from Des Moines, Iowa, Fitchburg, Massachusetts, Lake Charles, Louisiana, and Reading and Pittsburgh, Pennsylvania, as part of the 1972 Urban Soils Monitoring Program. Sampling sites within each Standard Metropolitan Statistical Area (SMSA) were defined as urban or suburban based on their position either within or outside the official city limits, respectively. In addition, each site was classified lawn or waste according to the maintenance it received. Except in Fitchburg, urban soils of each SMSA contained significantly higher mean concentrations of cadmium, lead, and mercury than did suburban soils. Mean urban soil concentrations of arsenic were similar to suburban concentrations in each SMSA except Des Moines and Reading, where urban levels were significantly higher. Generally, the metal concentrations in lawn and waste areas did not differ significantly. The results indicate a general contamination of these areas, probably as a result of fallout of airborne metal aerosols from industrial processes and/or fossil-fuel combustion.

Introduction

Although arsenic, cadmium, lead, and mercury occur naturally, they can be detrimental to plant and animal life at high concentrations. Industrial wastes, auto emissions, and pesticide and fertilizer applications (*5, 6*) all contribute to heavy metal contamination of soils. Trace element contamination of urban soils is often from many sources (*18*).

Lead concentrations from these sources are generally highest in the surface soil layers and decrease rapidly with either soil depth or distance from the surface (*7, 12, 16*). The lead content of soils near highways increases with increased traffic volume (*1, 7, 15, 24*).

Mercury accumulates in soil via various industrial processes, pesticide use, and the combustion of fossil fuels (*20, 24*).

Cadmium contamination of the soil occurs through the use of phosphate fertilizers and cadmium-contaminated pesticides, and through the discharge of liquid or solid waste from metallurgical and industrial activities (*17*). Higher traffic volumes in urban areas probably contribute to the cadmium burden in urban soils because cadmium is used in lubricating oils, diesel fuel, and tires (*13*). Urban refuse disposal is another likely source because cadmium is a component of both paper and plastics, which comprise a major portion of urban refuse (*17*).

The main sources of arsenic contamination are mining, smelting and combustion of fossil fuels (*14*), and pesticide applications (*9, 10*).

The present study was undertaken as part of the Environmental Protection Agency's Urban Soils Monitoring Program. Reported here are arsenic, cadmium, lead, and mercury concentrations detected during 1972 in soils of five United States Standard Metropolitan Statistical Areas (SMSAs), including Des Moines, Iowa; Fitchburg, Massachusetts; Lake Charles, Louisiana; Reading and Pittsburgh, Pennsylvania.

Sampling Procedures

Five SMSAs were randomly selected from a list provided by the Bureau of the Census, U.S. Department of Commerce (*23*). Within each SMSA, sampling sites were randomly allocated within the city limits to

[1] Field Studies Branch, Survey and Analysis Division, Office of Pesticide and Toxic Substances, U.S. Environmental Protection Agency, TS-793, Washington, D. C. 20460.
[2] Field Studies Branch, Survey and Analysis Division, Office of Pesticides and Toxic Substances, U.S. Environmental Protection Agency, Pesticides Monitoring Laboratory, NASA/NSTL, Bay St. Louis, Miss. 39529.
[3] Chief, Pollutant Pathways Branch, Environmental Monitoring and Support Laboratory, U.S. Environmental Protection Agency, Las Vegas, Nev. 89114.

nsity of one site per 2.6 km² or one square mile were designated as urban sites. In the remainder of SMSAs, sites were randomly allocated to yield a ity of one site per 51.8 km² or 20 square miles and designated as suburban sites. In addition, each site described as either lawn or waste according to the ria used by Wiersma et al. (*26*) to indicate whether ite received regular maintenance.

sampling sites were 231 m², usually a 15.2 m by m plot (50 ft by 50 ft). Sixteen soil cores, each cm in diameter by 7.6 cm deep, were collected ughout the site on a 4 by 4 grid pattern. The cores composited, sieved three times through a 6.3-mm anized mesh screen, and thoroughly mixed. A 2.3- subsample was drawn, packed in a new metal paint which had been rinsed previously with isopropyl hol, and was shipped to the Pesticides Monitoring oratory, Bay St. Louis, Mississippi. When the sam- arrived at the laboratory, soil for analysis was re- ed from the center of the cans to minimize any ible contamination from the cans.

Analytical Procedures

netals were determined by atomic absorption spec- notometry. For arsenic analysis, the soil sample was cted with 9.6*N* HCl, and arsenic was reduced to . As^{+3} was partitioned from the acid to benzene, and further partitioned from benzene to water for the rption measurement. A Perkin-Elmer Model 303 rophotometer was used, and absorbance was meas- with an arsenic cathode lamp at 197.0 nm with n as an aspirant to an air-hydrogen flame. Average very was 56 percent arsenic. Concentrations were cted for recovery; minimum detection limit, after ction, was 0.2 ppm.

cadmium, lead, and mercury analyses, soil samples dried at 50°C for 24 hours. A 10-g dry soil sam- vas weighed into a 125-ml Erlenmeyer flask, and ml of a mixture of 4*N* HNO_3 and 0.7*N* HCl was d. The capped flask was swirled and heated at 0°C for 2 hours in a water bath. After the mixture d and settled, cadmium and lead were determined Perkin-Elmer Model 306 spectrophotometer with t aspiration and an air-acetylene flame. Absorbance neasured at 229.0 nm for lead and at 283.3 nm for ium with background corrections. Lead recovery ged 90–95 percent with a detection limit of 0.5 l, equivalent to 0.5 ppm in 1 g of soil. Cadmium very averaged 85–90 percent with a detection limit 5 μg/ml, equivalent to 0.5 ppm in 1 g of soil.

he mercury determination, an aliquot of the acid ct, containing not more than 0.5 μg mercury, was ted into a 300-ml BOD bottle. Five milliliters of ntrated H_2SO_4 were added to the aliquot, and the volume was adjusted to 100 ml. Flameless AA by the method of Hatch and Ott (*8*) was followed. Mercury recovery averaged 60–100 percent, depending on soil type and percent organic matter. The detection limit was 0.05 μg/100 ml, equivalent to 0.2 ppm in 1 g of soil.

Values for all four metals were corrected for the appropriate percent recovery, as determined by recovery studies carried out in conjunction with the analyses. The recovery studies included fortifying selected samples with known quantities of each metal followed by analysis and determination of the amount recovered.

Results

Results of the metal analyses are presented in Tables 1 and 2. Both tables list the number of analyses for each category, percent occurrence of the element, the arithmetic mean, the estimated geometric mean, and the minimum and maximum positive concentrations detected within each metropolitan area.

The estimated geometric mean is routinely presented in the tables as an alternative to the arithmetic mean as a measure of central tendency of the data. Such data are seldom distributed normally, as shown by tests for skewness and/or kurtosis, but often approximate a log-normal distribution. The log $(X + 0.01)$ transformation was used to determine the logarithmic means. The antilogs of these figures, minus 0.01, were taken to estimate the geometric mean in the untransformed dimension. Differences between means were checked for significance by t-tests of the transformed variate log $(X + 0.01)$.

LEAD

All soil samples contained detectable amounts of lead. Geometric means for the SMSAs ranged from 12 ppm at Lake Charles to 71 ppm at Pittsburgh. Individual sample measurements ranged from 2.1 ppm in a Lake Charles sample to 11,700 ppm in a Reading sample. Most published estimates show that lead occurs naturally in soils at levels of 10–20 ppm (*13, 22*). Urban portions of each SMSA, except Fitchburg, had significantly higher mean concentrations of lead than did corresponding suburban portions. Lead concentrations were similar in urban lawn and waste areas of all cities except Des Moines, where lead concentrations were significantly higher in lawn areas than in waste areas. Suburban lawn and waste lead concentrations were similar except in Reading, which had significantly higher lead levels in waste areas than in lawn areas.

MERCURY

Mercury was detected in 68 percent of the samples, ranging from 0.02 to 15 ppm. The highest geometric mean concentration for the SMSAs was 0.25 ppm in Fitchburg; the lowest was 0.01 ppm at Lake Charles. Average mercury concentrations in soils in the United

TABLE 1. *Heavy metal concentrations in urban and suburban soils of five Standard Metropolitan Statistical Areas, 1972—Urban Soils Monitoring Program*

Location	No. of Samples		Heavy Metal	Concentration, ppm Dry Weight			Sam Cont Dete Amo
	Urban	Suburban		Arithmetic Mean	Estimated Geometric Mean	Extreme Positive Values	
Des Moines, Iowa	59	25	Lead				
			urban	89.0	55.0	9.8 – 488.0	10
			suburban	15.0	14.0**	7.2 – 26.0	10
			Mercury				
			urban	0.44	0.10	0.06– 15.0	
			suburban	0.01	<0.01**	0.06– 0.15	
			Cadmium				
			urban	0.89	0.64	0.1 – 3.6	10
			suburban	0.28	0.12**	0.1 – 1.8	
			Arsenic				
			urban	12.0	7.1	1.36– 119.0	
			suburban	2.8	2.2**	0.40– 14.0	10
Fitchburg, Mass.	26	10	Lead				
			urban	117.0	62.0	12.0 – 1230.0	10
			suburban	60.0	34.0	4.4 – 278.0	10
			Mercury				
			urban	0.34	0.29	0.08– 0.83	1
			suburban	0.24	0.17	0.70– 0.50	
			Cadmium				
			urban	0.13	0.06	0.12– 0.70	
			suburban	0.13	0.05	0.11– 0.38	
			Arsenic				
			urban	15.0	9.1	2.8 – 158.0	10
			suburban	7.4	5.8	2.0 – 18.0	10
Lake Charles, La.	16	54	Lead				
			urban	139.0	39.0	3.5 – 1330.0	10
			suburban	11.0	8.7**	2.1 – 61.0	10
			Mercury				
			urban	0.06	0.02	0.04– 0.29	
			suburban	0.01	<0.01**	0.04– 0.18	
			Cadmium				
			urban	0.36	0.02	0.11– 5.3	
			suburban	0.01	<0.01*	0.11– 0.1	
			Arsenic				
			urban	1.8	1.6	0.88– 5.7	10
			suburban	2.2	1.9	0.69– 8.2	10
Pittsburgh, Pa.	51	138	Lead				
			urban	444.0	267.0	45.0 – 2290.0	10
			suburban	52.0	44.0**	15.0 – 402.0	10
			Mercury				
			urban	0.64	0.46	0.1 – 2.1	10
			suburban	0.09	0.04**	0.02– 0.74	
			Cadmium				
			urban	1.2	0.74	0.11– 4.9	
			suburban	0.9	0.45*	0.11– 8.0	
			Arsenic				
			urban	15.0	12.0	3.2 – 54.0	10
			suburban	15.0	13.0	3.6 – 122.0	10
Reading, Pa.	10	41	Lead				
			urban	1400.0	172.0	21.0 –11,700.0	10
			suburban	40.0	40.0**	14.0 – 306.0	10
			Mercury				
			urban	0.63	0.29	0.04– 2.8	10
			suburban	0.10	0.07**	0.04– 0.4	
			Cadmium				
			urban	0.63	0.26	0.11– 1.7	
			suburban	0.25	0.04*	0.11– 2.5	
			Arsenic				
			urban	16.0	13.0	4.3 – 42.0	10
			suburban	8.6	7.0**	1.6 – 33.0	10

NOTE: Statistical significance of urban-suburban differences based on t-tests of the transformed variate log (X + 0.01), U.S. Environ Protection Agency.
* Differences statistically significant (P = 0.05).
** Differences statistically significant (P = 0.01).

TABLE 2. *Heavy metal concentrations in lawn and waste soils of five Standard Metropolitan Statistical Areas, 1972—Urban Soils Monitoring Program*

LOCATION	AREA	NO. OF SITES	CONCENTRATION, PPM DRY WEIGHT							
			LEAD		MERCURY		CADMIUM		ARSENIC	
			ARITHMETIC MEAN	GEOMETRIC MEAN	ARITHMETIC MEAN	GEOMETRIC MEAN	ARITHMETIC MEAN	GEOMETRIC MEAN	ARITHMETIC MEAN	GEOMETRIC MEAN
Moines, Iowa	Urban									
	lawn	39	102.0	68.0	0.61	0.14	0.85	0.68	14.7	9.9
	waste	20	65.0	38.0	0.11	0.05*	0.96	0.57	5.5	3.7**
	Suburban									
	lawn	15	13.0	12.0	ND	—	0.14	0.08	2.2	2.1
	waste	10	18.0	16.0	0.04	0.01	0.48	0.23	3.5	2.1
burg, Mass.	Urban									
	lawn	7	119.0	80.0	0.44	0.37	0.18	0.05	13.0	12.4
	waste	19	116.0	56.0	0.30	0.26	0.10	0.05	15.4	8.2
	Suburban									
	lawn	1	56.0	—	0.31	—	0.12	—	5.4	—
	waste	9	60.0	32.0	0.23	0.16	0.14	0.05	7.7	5.9
Charles, La.	Urban									
	lawn	9	224.0	68.0	0.09	0.03	0.63	0.03	2.3	1.9
	waste	7	29.0	19.0	0.02	0.01	0.02	<0.01	1.2	1.2
	Suburban									
	lawn	20	9.7	7.3	0.01	<0.01	0.01	<0.01	1.7	1.6
	waste	34	11.0	9.7	0.01	<0.01	0.01	<0.01	2.5	2.1
urgh, Pa.	Urban									
	lawn	22	398.0	219.0	0.51	0.38	1.2	0.79	11.9	10.1
	waste	29	480.0	310.0	0.74	0.53	1.2	0.71	17.0	13.4
	Suburban									
	lawn	14	75.0	51.0	0.08	0.02	0.93	0.64	21.0	15.1
	waste	123	49.0	43.0	0.09	0.05	0.90	0.43	13.9	12.9
ng, Pa.	Urban									
	lawn	1	48.0	—	0.11	—	0.11	—	16.4	—
	waste	9	1550.0	198.0	0.69	0.32	0.68	0.29	15.7	12.7
	Suburban									
	lawn	15	28.0	26.0	0.06	0.05	0.03	0.01**	8.4	7.5
	waste	26	72.0	50.0**	0.12	0.09	0.38	0.09**	8.7	6.8

: ND = Not detected.
Statistical significance based on t-tests of the transformed variate log (X + 0.01), U.S. Environmental Protection Agency.
ferences statistically significant (P = 0.05).
fferences statistically significant (P = 0.01).

's are reported to be about 0.07 ppm (*19, 25*). in portions of each SMSA, except Fitchburg, had ficantly higher mean mercury concentrations than corresponding suburban portions. Mercury concen- ons were not significantly different between lawn waste areas of either urban or suburban parts of SMSA except in Des Moines, where the mean mer- concentration in lawn sites was significantly higher in waste sites.

MIUM

nium was detected in 73 percent of the samples, ing from 0.11 to 8.0 ppm. Geometric mean concen- ons for the SMSAs ranged from less than 0.01 ppm ake Charles to 0.52 ppm at Pittsburgh. Cadmium rs naturally in soils at average concentrations of t 0.06 ppm (*14*). As with mercury and lead, mean ium concentrations were significantly higher at n sites except in Fitchburg. The only significant ences in cadmium concentrations between lawn waste sites were found in suburban Reading, where ntrations were significantly higher in lawn areas in waste areas.

ARSENIC

Arsenic was detected in 99.8 percent of the samples, at levels of 0.58–158 ppm. Geometric mean concentrations for the SMSAs ranged from 1.9 ppm at Lake Charles to 13 ppm in Pittsburgh. Arsenic occurs naturally in soil at an average concentration of 6 ppm (*3, 14, 26*). Urban and suburban arsenic concentrations were not significantly different for the SMSAs except in Des Moines and Reading, where urban concentrations were significantly higher than suburban concentrations. Urban lawn sites in Des Moines also contained significantly higher arsenic concentrations than did urban waste areas. In all other comparisons of lawn and waste areas of suburban and urban portions, no significant differences were detected.

Discussion

Other investigators have attributed elevated metal concentrations in urban soils to atmospheric fallout of aerosols from industrial processes and fossil-fuel combustion, especially motor vehicle emissions (*2, 4, 5, 11, 21*). The present study supports previous findings. Such sources

would normally occur less frequently in suburban areas and would, therefore, result in lower suburban soil metal concentrations, as shown in the present study.

Urban and suburban mean soil concentrations of metals in Fitchburg may be similar because the city limits there do not seem to separate areas of more and less dense population and industry. The city of Leominster and several towns are included in that portion of the SMSA designated as suburban.

Mercury concentrations in Fitchburg were high compared to mercury concentrations in the other four cities. Mercury compounds were registered for fungicidal uses before 1972, and many industries in Fitchburg are types which would have used mercurial fungicides before 1972. These concentrations also might have originated from higher background soil concentrations of mercury, as suggested by the results of Shacklette et al. (*19*).

Summary and Conclusions

This study shows that metal concentrations in urban soils of SMSAs are generally higher than concentrations in the corresponding suburban soils. The similarity of average metal concentrations in lawn and waste sites within urban and suburban areas of these SMSAs indicates a general contamination of these areas. The main source of this contamination appears to be fallout of airborne metal aerosols from industrial processes and/or fossil-fuel combustion.

Acknowledgments

Authors wish to thank the inspectors of the Plant Protection and Quarantine Programs, Animal and Plant Health Inspection Service, U.S. Department of Agriculture, who collected the soil samples, and the citizens of Des Moines, Fitchburg, Lake Charles, Reading, and Pittsburgh, whose willing cooperation allowed the accomplishment of this study.

LITERATURE CITED

(*1*) *Bohn, H. L. 1972.* Soil absorption of air pollutants. J. Environ. Qual. 1(4):372–377.

(*2*) *Buraiky, M. S., and C. J. Ritter. 1976.* Mercury in soil from the area of Dayton, Ohio. Environ. Geol. 1(5): 295–297.

(*3*) *Carey, A. E., J. A. Gowen, H. Tai, W. G. Mitchell, and G. B. Wiersma. 1978.* Pesticide residue levels in soils and crops, 1971—National Soils Monitoring Program (III). Pestic. Monit. J. 12(3):117–136.

(*4*) *Day, J. P., M. Hart, and M. S. Robinson, 1975.* Lead in urban street dust. Nature 253(5490):343–345.

(*5*) *Farmer, J. G., and T. D. B. Lyon. 1977.* Lead in Glasgow street dirt and soil. Sci. Total Environ. 8(1): 89–93.

(*6*) *Fishbein, L. 1974.* Mutagens and potential mutagens in the biosphere II. Metals—mercury, lead, cadmium, and tin. Sci. Total Environ. 2(4):341–371.

(*7*) *Goldsmith, E. C., P. F. Scanlon, and W. R. Pirie. 1*
Lead concentrations in soil and vegetation with
ways of different traffic densities. Bull. Environ.
tam. Toxicol. 16(1):66–70.

(*8*) *Hatch, W. R., and W. L. Ott. 1968.* Determinatio
submicrogram quantities of mercury by atomic ab
tion spectroscopy. Anal. Chem. 40(14):2085–208

(*9*) *Johnson, L. R., and A. E. Hiltbold. 1969.* Arsenic
tent of soils and crops following use of methanea
ate herbicides. Soil Sci. Amer. Proc. 33(2):279–2

(*10*) *Kearney, P. C., R. G. Nash, and A. R. Isensee. 1*
Persistence of pesticide residues in soils. Pages 5
In M. W. Miller and G. C. Berg, Eds. Chemical
out. Charles C. Thomas, Springfield, Ill.

(*11*) *Klein, D. H. 1972.* Mercury and other metals in u
soils. Environ. Sci. Technol. 6(6):560–562.

(*12*) *Lagerwerff, J. V. 1967.* Heavy-metal contaminatio
soils. *In* N. C. Brady, Ed., Agriculture and the qu
of our environment. Am. Assoc. Adv. Sci. Publ.
343–364.

(*13*) *Lagerwerff, J. V., and A. W. Specht. 1970.* Cont
nation of roadside soil and vegetation with cadm
nickel, lead, and zinc. Environ. Sci. Technol. 4
583–586.

(*14*) *Lisk, D. J. 1972.* Trace metals in soils, plants,
animals. Adv. Agron. 24:267–311.

(*15*) *Motto, H. L., R. H. Daines, D. M. Chilko, and C*
Motto. 1970. Lead in soils and plants: Its relatio
to traffic volume and proximity to highways. Env
Sci. Technol. 4(3):231–237.

(*16*) *Page, A. L., and T. J. Ganje. 1970.* Accumulatio
lead in soils for regions of high and low motor ve
traffic density. Environ. Sci. Technol. 4(2):140–14

(*17*) *Page, A. L., and F. T. Bingham. 1973.* Cadmium
dues in the environment. Residue Rev. 48:1–44.

(*18*) *Purves, D. 1977.* Trace-element contamination o
environment. Fundamental aspects of pollution
trol and environmental science series No. 1, Else
North Holland, Inc., New York, N.Y.

(*19*) *Shacklette, H. T., J. G. Boerngen, and R. L. Tu*
1971. Mercury in the environment-surficial mat
of the conterminous United States. U.S. Geolo
Survey Circ. 644, U.S. Department of the Interio

(*20*) *Smart, N. A. 1968.* Use and residues of mercury
pounds in agriculture. Residue Rev. 23:1–36.

(*21*) *Solomon, R. L., and J. W. Hartford. 1976.* Lead
cadmium in dusts and soils in a small urban con
nity. Environ. Sci. Technol. 10(8):773–777.

(*22*) *Swaine, D. J. 1955.* The trace element content of
Commonwealth Agriculture Bureau, Commonw
Bur. Soil Technol. Commun. No. 48, Harold Pri
Works, England.

(*23*) *U.S. Department of Commerce, Bureau of the Ce*
1967. County and City Data Book, 1967. U.S. Go
ment Printing Office, Washington, D.C. 673 pages.

(*24*) *U.S. Environmental Protection Agency. 1971.*
curial pesticides, man, and the environment. Sp
Pesticides Review Group. Office of Pesticide
grams. Washington, D.C. p. 88.

(*25*) *Wiersma, G. B., and H. Tai. 1974.* Mercury leve
soils of the eastern United States. Pestic. Moni
7(3/4):214–216.

(*26*) *Wiersma, G. B., H. Tai, and P. F. Sand. 1972.* I
cide residues in soil from eight cities—1969. P
Monit. J. 6(2):126–129.

WATER

Pesticides and PCB Residues in the Black Creek Watershed, Allen County, Indiana—1977–78 [1]

Daniel R. Dudley[2] and James R. Karr[3]

ABSTRACT

aquatic environment of a small agricultural drainage in ıeastern Indiana was surveyed during 1977–78 for pesti- and PCB contamination. A total of 45 water, sediment, ish samples from Black Creek watershed, Allen County, na were analyzed for seven pesticides and PCBs. Low s of dieldrin (mean 0.023 μg/g) and DDE (mean 0.016) were found in all fish samples, but were not detected ater or sediment samples. PCB concentrations in fish five times greater (0.102 μg/g) than were organochlo- pesticide concentrations. Two of seven water samples ined PCBs at 0.4 μg/liter and 0.2 μg/liter. Only the cide 2,4,5-T occurred in surface water samples during tream discharge, at concentrations of 0.2–7.7 μg/liter. ine, alachlor, carbofuran, and malathion were not de- l in any samples.

Introduction

48.5 km² Black Creek watershed in Allen County, ına, is typical of the land use, topography, and soils e larger Maumee River basin. Land use is 80 per- row crop agriculture and 4 percent urban.

rvey of the pesticide and PCB content of the water, ıent, and fish of this small agricultural drainage conducted in 1977. The study was a portion of a rch and demonstration project designed to identify reduce agricultural sources of non-point pollution The purpose of the survey was to assess toxic sub- e contamination of the aquatic environment at low n discharge, and the results are presented here.

Sampling Procedures

uly 18 and 19, 1977, 14 sediment samples, 7 water samples, and 18 fish samples were collected from various locations in the Black Creek drainage. The 39 samples were analyzed for PCBs (Aroclors 1242 and 1254), dieldrin, DDE, atrazine, alachlor, carbofuran, malathion, and 2,4,5-T. Grab water and sediment samples were collected in one-quart wide-mouth glass jars that had been rinsed with acetone. Sediment samples were collected by directly scooping the top 10 cm of bottom material into the glass jars. A single fish species, creek chub (*Semotilus atromaculatus*), was collected by seining, and individuals were analyzed separately. Sediment and water samples were placed on ice and refrigerated until analysis. Fish specimens were frozen at −20°C and analyzed as received after thawing. Samples were held no longer than 50 days before analysis. On June 5, 1978, six water samples were collected and analyzed for 2,4,5-T only.

Analytical Procedures

All laboratory work was done at the Pesticide Laboratory of the Section of Wildlife Research, Illinois Natural History Survey. Analytical and cleanup procedures outlined in the *Pesticide Analytical Manual* of the Food and Drug Administration, U.S. Department of Health, Education, and Welfare (*5*) were followed for each compound.

Compounds were extracted from the water samples by extracting each 1-liter sample with three 100-ml aliquots of methylene chloride. The combined extracts were dried with sodium sulfate and concentrated to 1 ml by refluxing under a three-ball Snyder column. The compounds were then partitioned into an equivalent volume of ethyl acetate for injection into the gas chromatograph.

The compounds were extracted from sediment samples by mixing 50 grams of sediment with 100 ml ethyl acetate on a magnetic stirrer for 1 hour. The ethyl acetate was decanted with rinsing, reduced in volume, dried

supported by the U.S. Environmental Protection Agency, under ın 108(a) Program, Grant G005103.

tic Biologist, Allen County Soil and Water Conservation Dis- 2010 Inwood, Fort Wayne, Ind. 46805. Present address: Ohio onmental Protection Agency, Division of Surveillance, 361 E. l St., Columbus, Ohio 43215.

iate Professor, Department of Ecology, Ethology, and Evolu- University of Illinois, Champaign, Ill. 61820.

over anhydrous sodium sulfate, and dissolved in hexane for injection into the gas chromatograph.

Twenty-gram subsamples representative of the whole fish were pulverized in a blender with 100 ml acetonitrile. The acetonitrile was swirled with 10 ml hexane to remove fish oil, blown dry with nitrogen, and dissolved in ethyl acetate for gas-liquid chromatographic analysis (GLC).

Alachlor, carbofuran, atrazine, and malathion were analyzed with an alkali flame ionization detector on a Varian 2100 gas chromatograph.

Instrument parameters and operating conditions were:

Column:	6 ft glass, packed with 3 percent OV–17 on 100–120-mesh Gas-Chrom Q, internal diameter 2 mm	
Temperatures:	column	210°C
	injection port	235°C
	detector	240°C
Carrier gas:	nitrogen flowing at 15 ml/minute	

Organochlorine pesticides and PCBs were measured by Ni^{63} electron-capture gas chromatography under the above conditions with one exception. The column was packed with a mixture of 3 percent OV–210 and 1.5 percent OV–17 on 100–120-mesh Gas-Chrom Q.

For 2,4,5-T analysis, a methyl ester derivative was prepared for GLC with 10 percent boron trichloride in methanol. GLC injection volumes were 1–10 μl. One milliliter final solution for GLC injection represented 1000 ml original water sample and 100 grams sediment or fish.

Appropriate recovery experiments were conducted according to the procedures in the *Pesticide Analytical Manual* (*5*). The results and the detection limits are shown in Table 1. Results reported are not corrected for percent recoveries.

TABLE 1. *Percent recovery and lower limits of dete of pesticides and PCBs from water, and sediment, and samples, Black Creek watershed, Allen County, Indiana—1977–78*

Compound	% Recovery [1]		Lower Lim Detection,
	Water and Sediment	Fish	
2,4,5-T	95	90	0.0002
PCBs, DDE, dieldrin	98	98	0.0002
Malathion	97.5	92	0.001
Atrazine, alachlor, carbofuran	95	90	0.1

[1] % Recovery = [amount of compound analyzed/(amount of com added − amount occurring in sample)] × 100

Results and Discussion

No organochlorine pesticide residues were detecte water or sediment samples (Table 2), reflecting botl current low use of the compounds within the water and a two-week period without storm runoff pric sampling. Despite the absence of pesticide residu the abiotic environment, low levels of dieldrin (r 0.023 ± 0.0048 μg/g (SE), $n = 18$) and DDE (r 0.016 ± 0.0017 μg/g (SE), $n = 18$) were found i fish samples. Similar DDE concentrations have bee ported in small-stream fishes from other waters where DDE was rarely detected in sediments or v (*4*). The source of the pesticide residues in the *S. maculatus* specimens collected in Black Creek cann ascertained at present. The absence of organochl residues in sediments plus evidence of seasonal upst movement of the older individuals of this species support the hypothesis that the pesticide residues assimilated in the Maumee River. However, the y age of the individuals collected and the species' dec preference for small-stream habitats suggests that fishes might occasionally be exposed to organochl pesticide residues in Black Creek during periods of s runoff.

TABLE 2. *Pesticide and PCB concentrations in the Black Creek aquatic environment, Allen County, Indiana— 1977–78* [1]

Compound	No. of Samples Collected	No. of Samples Containing Compound	Concentrations [2]		
			Maximum	Minimum	Me
WATER					
2,4,5-T	8	8	0.008	0.001	0.0
PCB					
Aroclor 1254	7	2	0.0004	0.0002	0.0
Aroclor 1242	7	0			
FISH					
Dieldrin	18	18	0.086	0.004	0.0
DDE	18	18	0.031	0.007	0.0
PCB					
Aroclor 1254	18	13	0.265	0.070	0.1
Aroclor 1242	18	1	0.140		

[1] Atrazine, alachlor, carbofuran, and malathion were not detected. No compounds were detected in any sediment samples.
[2] Water, mg/liter; fish, μg/g wet weight.

were detected in two of seven water samples at g/liter and 0.2 μg/liter. Almospheric inputs and/or ge outfall sources could account for the presence of in water (*1*). Sediments did not contain PCBs. Of sh sampled, 72 percent contained PCBs at a mean ntration (0.102 ± 0.0187 μg/g (SE), $n = 18$) mes higher than the organochlorine pesticide resi- in fish. These data suggest that PCBs are more lent than other organochlorine residues in the ic environment of this agricultural drainage. Ex- e of the fish to PCBs in the Maumee River is also sibility.

ine, alachlor, carbofuran, and malathion were not ed in any samples. Considering the rapid break- of these compounds and the low flow conditions existed for 15 days prior to sampling, these results ot unexpected.

77, the herbicide 2,4,5-T was detected in two water les at concentrations less than 3 μg/liter but was resent in sediment or fish samples. In 1978, a fish vas noted three days after application of 2,4,5-T stream banks. Surface water samples taken seven after spraying revealed 2,4,5-T concentrations rang- om 0.2 to 7.7 μg/liter. Based on field observations, rs predict frequent occurrence of 2,4,5-T in small is during summer low-flow periods. Widespread use of the herbicide to kill woody vegetation adjacent to streams, and the common methods of application, make contact with surface water inevitable.

Acknowledgments

The laboratory and field assistance of W. N. Bruce, J. G. Wilson, R. E. Duzan, K. E. Smith, and A. Shupe is gratefully acknowledged. K. E. Smith made helpful comments on the manuscript.

LITERATURE CITED

(*1*) *Crump-Wiesner, H. J., H. R. Feltz, and M. L. Yates. 1974.* A study of the distribution of polychlorinated biphenyls in the aquatic environment. Pestic. Monit. J. 8(3):157–161.

(*2*) *Karr, J. R., and O. T. Gorman. 1975.* Effects of land treatment on the aquatic environment. Non-point source pollution seminar: Pollution control in Great Lakes. U.S. Environmental Protection Agency Report 905/9–75–007. Pages 120–150.

(*3*) *Morrison, J. B. 1977.* Environmental impact of land use on water quality. U.S. Environmental Protection Agency Report 905/9–77–007–A–D. 4 vols.

(*4*) *Truhlar, J. F., and L. A. Reed. 1976.* Occurrence of pesticide residues in four streams draining different land-use areas in Pennsylvania, 1969–71. Pestic. Monit. J. 10(3):101–110.

(*5*) *U.S. Department of Health, Education, and Welfare. Food and Drug Administration. 1971.* Pesticide Analytical Manual. 3 vols.

Acknowledgments

The Editorial Advisory Board wishes to thank the following persons for their valuable assistance in reviewing papers submitted for publication in Volume 13 of the *Pesticides Monitoring Journal:*

U.S. ENVIRONMENTAL PROTECTION AGENCY
Ann E. Carey
Frederick W. Kutz

FOOD AND DRUG ADMINISTRATION
William J. Trotter
Sidney Williams
Martin P. Yurawecz

NOTIFICATION OF CONFERENCE CANCELLATION

The U.S. EPA International Conference on the *Application of Appropriate Technology to Chemical Dose and Chemical Residue Monitoring* scheduled for May 28–30, 1980 at the Sheraton International Conference Center in Reston, Virginia has been cancelled. All expressed interest is appreciated.

APPENDIX

Chemical Names of Compounds Discussed in This Issue

ALACHLOR	2-Chloro-2′,6′-diethyl-*N*-(methoxymethyl)-acetanilide
ALDRIN	Hexachlorohexahydro-*endo*, *exo*-dimethanonaphthalene 95% and related compounds
AROCLOR 1242	PCB, approximately 42% chlorine
AROCLOR 1254	PCB, approximately 54% chlorine
AROCLOR 1260	PCB, approximately 60% chlorine
ATRAZINE	2-Chloro-4-(ethylamino)-6-(isopropylamino)-*s*-triazine
CARBOFURAN	2,3-Dihydro-2,2-dimethyl-7-benzofuranyl methyl carbamate
CHLORDANE	1,2,3,4,5,6,7,8,8-Octachloro-2,3,3a,4,7,7a-hexahydro-4,7-methanoindene. The technical is a mixture of several compounds including heptachlor, chlordene, and two isomeri of chlordane.
DDE	Dichlorodiphenyldichloroethylene (degradation product of DDT); *p,p′*-DDE: 1,1-D 2,2-bis(p-chlorophenyl) ethylene; *o,p′*-DDE: 1,1-Dichloro-2-(*o*-chlorophenyl)-2-(*p* phenyl) ethylene
DDT	Main component (*p,p′*-DDT): ά-Bis(*p*-chlorophenyl) β,β,β-trichloroethane. Other are possible and some are present in the commercial product. *o,p′*-DDT: [1,1,1-Tric (*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 *exo*-5,8-dimethanonaphthalene
ENDRIN	Hexachloroepoxyoctahydro-*endo,endo*-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-methanoindan
MALATHION	*O,O*-Dimethyl dithiophosphate of diethyl mercaptosuccinate
MIREX	Dodecachlorooctahydro-1,3,4-metheno-1-*H*-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-2*H*-indeno(1,2-β)oxir
PPBs (Polybrominated Biphenyls)	Mixtures of brominated biphenyl compounds having various percentages of bromine
PCBs (Polychlorinated Biphenyls)	Mixtures of chlorinated biphenyl compounds having various percentages of chlorine
2,4,5–T	2,4,5-Trichlorophenoxyacetic acid
TDE	2,2-Bis(*p*-chlorophenyl)-1,1-dichloroethane (including isomers and dehydrochlorinatic ucts)
TOXAPHENE	Chlorinated camphene (67-69% chlorine). Product is a mixture of polychlor bicyclic with chlorinated camphenes predominating.

SUBJECT AND AUTHOR INDEXES

Volume 13, June 1979—March 1980

Preface

ıry headings in the subject index include pesticide ounds, media in which pesticide residues are moni- , and major concepts related to the monitoring of ides in the environment. Pesticide compounds are by common names; trade names are used for those ı have no common names.

dary headings cross-reference the primary head- For a paper which discusses five or more organo- nes or organophosphates the compounds are ed by class under media and concept headings but each compound appears individually under the primary headings for pesticide compounds.

In the author index all information on a paper appears in the senior author's citations: associate authors, title of the paper, and volume, issue, and pages where the article was published. Names of associate authors are cross-referenced as minor headings, but the reader is referred to the senior author's entry for the paper's complete citation.

With the exception of 13(3):87-98 in which no compounds are used as secondary headings. Each compound is listed as a primary head- ith Food as its only secondary heading.

A

B

C

E

N

Nonachlor

O

Octachlor Epoxide

Octachlorostyrene

Orthophenylphenol

Ovex

Oxychlordane

P

Paraffins

Paraquat

Parathion, see also Ethyl Parathion; Methyl Parathion

PBBs

PCA

PCBs

PCNs

PCNB

PCP

Q

QCB, see Pentachlorobenzene

R

S

T

Z

AUTHOR INDEX

Pesticides Monitoring Journal welcomes from all
es qualified data and interpretative information in
de monitoring. The publication is distributed
pally to scientists, technicians, and administrators
ated with pesticide monitoring, research, and
programs concerned with pesticides in the environ-
Other subscribers work in agriculture, chemical
facturing, food processing, medicine, public health,
nservation.

es are grouped under seven headings. Five follow
sic environmental components of the National
de Monitoring Program: Pesticide Residues in
; Pesticide Residues in Water; Pesticide Residues
il; Pesticide Residues in Food and Feed; and
de Residues in Fish, Wildlife, and Estuaries. The
is a general heading; the seventh encompasses

oring is defined here as the repeated sampling and
is of environmental components to obtain reliable
tes of levels of pesticide residues and related
unds in these components and the changes in
evels with time. It can include the recording of
es at a given time and place, or the comparison of
es in different geographic areas. The Journal will
results of such investigations and data on levels
ticide residues in all portions of the environment
icient detail to permit interpretations and con-
is by author and reader alike. Such investigations
be specifically designed and planned for moni-
purposes. The Journal does not generally publish
l research investigations on subjects such as
le analytical methods, pesticide metabolism, or
ials (studies in which pesticides are experimen-
pplied to a plot or field and pesticide residue de-
rates and movement within the treated plot or
re observed).

s are responsible for the accuracy and validity
data and interpretations, including tables, charts,
ferences. Pesticides ordinarily should be identi-
common or generic names approved by national
rnational scientific societies. Trade names are
ble for compounds which have no common
Structural chemical formulas should be used
ppropriate. Accuracy, reliability, and limitations
pling and analytical methods employed must be
ed thoroughly, indicating procedures and con-
ed, such as recovery experiments at appropriate
confirmatory tests, and application of internal
ds and interlaboratory checks. The procedure
ed should be described in detail. If reference is
o procedures in another paper, crucial points or
ations should be noted. Sensitivity of the method
and limits of detection should be given, particularly when very low levels of pesticide residues are being reported. Specific note should be made regarding correction of data for percent recoveries. Numerical data, plot dimensions, and instrument measurements should be reported in metric units.

PREPARATION OF MANUSCRIPTS

——Prepare manuscripts in accord with the *CBE Style Manual*, third edition, Council of Biological Editors, Committee on Form and Style, American Institute of Biological Sciences, Washington, D.C., and/or the *U.S. Government Printing Office Style Manual*. For further enrichment in language and style, consult Strunk and White's *Elements of Style*, second edition, MacMillan Publishing Co., New York, N.Y., and *A Manual of Style*, twelfth edition, University of Chicago Press, Chicago, Ill.

——On the title page include authors' full names with affiliations and addresses footnoted; the senior author's name should appear first. Authors are those individuals who have actually written or made essential contributions to the manuscript and bear ultimate responsibility for its content. Use the Acknowledgment section at the end of the paper for crediting secondary contributors.

——Preface each manuscript with an informative abstract not to exceed 200 words. Construct this piece as an entity separate from the paper itself; it is potential material for domestic and foreign secondary publications concerned with the topic of study. Choose language that is succinct but not detailed, summarizing reasons for and results of the study, and mentioning significant trends. Bear in mind the literature searcher and his/her need for key words in scanning abstracts.

——Forward original manuscript and three copies by first-class mail in flat form: do not fold or roll.

——Type manuscripts on 8½-by-11-inch paper with generous margins on all sides, and end each page with a complete paragraph. Recycled paper is acceptable if it does not degrade the quality of reproduction. Double-space all copy, including tables and references, and number each page.

——Place tables, charts, and illustrations, properly titled, at the end of the article with notations in the text to show where they should be inserted. *Treat original artwork as irreplaceable material.* Lightly print author's name and illustration number with a ballpoint pen on the back of each figure. Wrap in cardboard to prevent mutilation; do not use paperclips or staples.

——Letter charts distinctly so that numbers and words will be legible when reduced. Execute drawings in black ink on plain white paper. Submit original drawings or sharp glossy photographs: no copies will be accepted.

——Number literature citations in alphabetical order according to author. For journal article include, respectively, author, year, title, journal name as abbreviated in *Chemical Abstracts Service Source Index*, and volume, issue, and page numbers. For book references cite, respectively, author, year, chapter title, pages, and editor if pertinent, book title, and name and city of publisher. For Government manuals list originating agency and relevant subgroup, year, chapter title and editor if pertinent, manual title, and relevant volume, chapter, and/or page numbers. Do not list private communications among Literature Cited. Insert them parenthetically within the text, including author, date, and professional or university affiliation indicating author's area of expertise.

The Journal welcomes brief papers reporting monitoring data of a preliminary nature or studies of limited scope. A section entitled Briefs will be included as necessary to provide space for short papers which present timely and informative data. These papers must be limited to two published pages (850 words) and should conform to the format for regular papers accepted by the Journal.

Manuscripts require approval by the Editorial Advisory Board. When approved, the paper will be edited for clarity and style. Editors will make the mi changes required to meet the needs of the Journal audience, including international subs for whom English is a second language. Auth accepted manuscripts will receive edited typescri approval before type is set. After publication, authors will receive 100 reprints.

Manuscripts are received and reviewed with the standing that they have not been accepted pre for publication elsewhere. If a paper has been or is intended for presentation at a meeting, c significant portion of its contents has been pul or submitted for publication elsewhere, notati such should be provided. Upon acceptance, the o manuscript and artwork become the property *Pesticides Monitoring Journal*.

Every volume of the Journal is available on mic Requests for microfilm and correspondence on ed matters should be addressed to:

Paul Fuschini (TS-793)
Editorial Manager
Pesticides Monitoring Journal
U.S. Environmental Protection Agency
Washington, D.C. 20460

For questions concerning GPO subscriptions an issues write:

Superintendent of Documents
U.S. Government Printing Office
Washington, D.C. 20402

The Administrator of the U.S. Environmental Protection Agency has determined that the publication of this periodical is necessary in the transaction of public business required by law of this Agency. Use of funds for printing this publication approved by the Director of the Office of Management and Budget, May 19, 1976.

ORDER BLANK
FOR PMJ

To: Superintendent of Documents
Government Printing Office
Washington, D.C. 20402

Please enter my Subscription for Pesticides Monitoring Journal. I am enclosing Money Order ☐ Check ☐ for this subscription. ($7.90 a year; $2.00 additional for foreign mailing)

*Please address the PMJ as follows:*_____

_____

_____

UNITED STATES GOVERNMENT PRINTING OFFICE, WASHINGTON, D. C. 1967

For sale by the Superintendent of Documents, U.S. Government Printing Office, Washington, D. C. 20402. Subscription price $7.90 a year, $2.00 additional for foreign mailing. Price for a single copy of this issue is $2.00.

United States
Environmental Protection
Agency
Washington DC 20460
TS-793

Postage and
Fees paid
Environmental
Protection
Agency
EPA 335

Official Business
Penalty for Private Use $300

Third-Class
Bulk Rate

If you do not desire to continue receiving this publication, please CHECK HERE ☐; cut off this label and return it to the above address. Your name will be removed from the mailing list.