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

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

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FISH, WILDLIFE, AND ESTUARIES

Polychlorinated Biphenyls and Other Organic Chemical Residues in Fish from Major United States Watersheds Near the Great Lakes, 1978

Gilman D. Veith,[1] Douglas W. Kuehl,[2] Edward N. Leonard,[1] Kenneth Welch,[1] and Glenn Pratt[3]

ABSTRACT

wenty-six composite samples of fish were collected during 978 from United States watersheds near the Great Lakes nd analyzed for polychlorinated biphenyls (PCBs) and elated organic chemicals. PCB mixtures resembling Aroclor 254 were found in all samples, and mixtures resembling roclor 1242 (or 1016) were found in 77 percent of the mples. Total PCB concentrations in the whole-fish composite samples ranged from 0.13 to 14.6 ppm; 65 percent of ie samples contained > 2 ppm PCBs. DDT and its metabolites were also found in all samples. ΣDDT concentration as 1.66 ppm, and 81 percent of the samples contained 1.0 ppm ΣDDT. Chlordane ranged from < 0.001 to 2.57 pm in 38 percent of the samples. Hexachlorobenzene was ound in 65 percent of the samples, ranging from <0.005 0.447 ppm. Other chemicals identified by gas chromaography/mass spectrometry included petroleum hydrocarbons and chlorobenzenes, chlorostyrenes, chlorophenols, nd chlorinated aliphatic compounds. Fish from the Ashtaula River (Ohio), Rocky River (Ohio), and Wabash River Indiana) contained extremely complex residues of chlorated and other organic chemicals.

Introduction

n 1976, authors extended their gas-liquid chromatography/mass spectrometry (GLC/MS) exploratory studies f organic chemical residues in Great Lakes fish to include residues in fish from major United States rivers or the purpose of tabulating polychlorinated biphenyls PCBs) and other xenobiotic chemicals accumulating in ie aquatic environment. A previous work (*6*) showed iat the types and concentrations of chemical residues i fish varied immensely among rivers in the same area f the country. Fish in some rivers in eastern Michigan nd Ohio contain PCB residues almost exclusively, whereas fish from the Ashtabula River nearby in Ohio contain at least 19 major chlorinated chemicals in addition to PCBs. Fish from rivers a few miles apart differ in hexachlorobenzene (HCB) residues by a factor of almost 3,000.

The wide variation in both the types and amounts of chemicals in different waters suggests that it is not cost-effective to apply trend-monitoring programs to the problem of determining the extent of contamination by toxic chemicals. Trend monitoring requires a predetermined list of chemicals to monitor, precise methods for measuring small differences in concentration, and, to minimize biological variability, a fairly rigid sampling protocol with respect to species and size. In contrast, the initial problem regarding toxic industrial chemicals is the identification of every major chemical component of residues from hundreds of industrial areas. Such areas may not have diverse fish populations because of the contamination. Finally, order-of-magnitude estimates of residue concentrations by GLC/MS may be used to direct enforcement-related field studies to "hot-spots" for more intensive studies.

A previous work (*6*) indicated that taking composite samples of any fish near the mouth of a river provides a convenient, enriched sample of bioaccumulable chemicals being discharged into the entire watershed and excludes the bulk of the less persistent, nonaccumulable chemicals attributable to natural products and sanitary wastes. Because the accumulation of chemicals in fish species varies considerably less than the concentration of chemicals in rivers and areas of rivers, composite samples also provide adequate estimates of relative concentrations in the sampling areas. This paper presents the results of exploratory studies of chemicals in fish from rivers in Minnesota, Wisconsin, Indiana, Michigan, Ohio, and New York (Figure 1).

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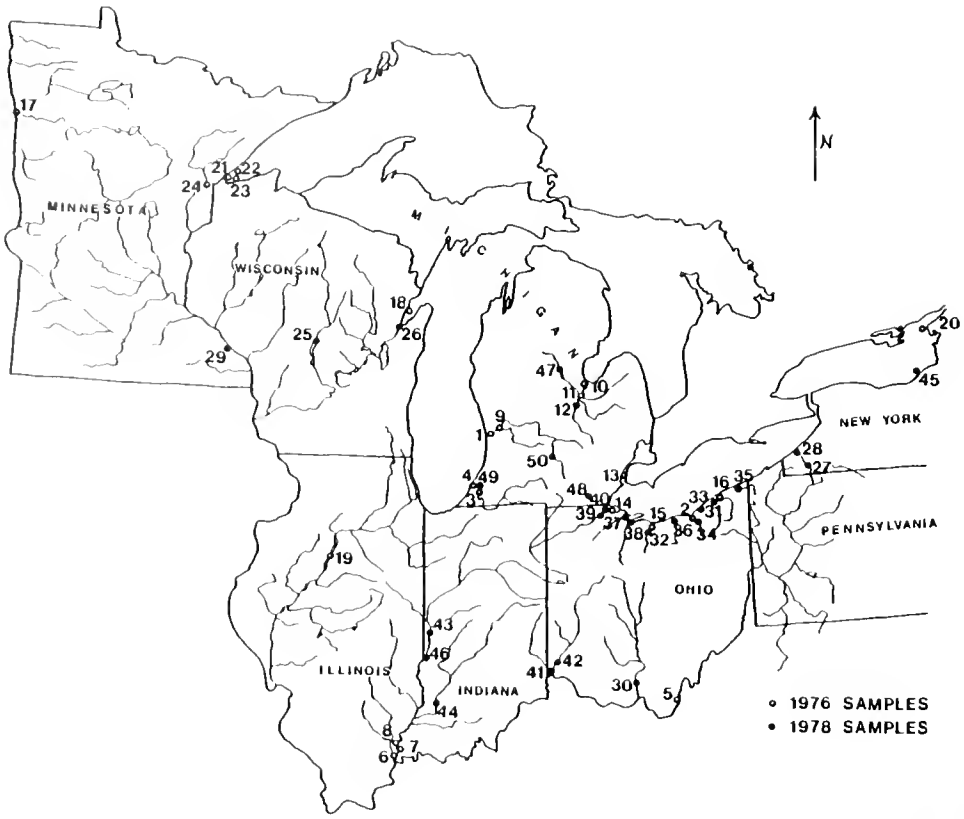

FIGURE 1. *Map of U.S. EPA Region V showing sites where fish samples were collected for GLC/MS analysis bioaccumulating hazardous organic chemical residues*

Materials and Methods

COLLECTION OF FISH

The areas that were sampled for detailed GLC/MS analyses in 1976 and the 26 sampling areas for the present study (1978) are shown in Figure 1. Table 1 gives a brief description of the 1978 sampling locations.

State and federal field personnel used nets and other conventional apparatus to collect fish. Sampling areas included known problem areas disclosed by previous studies as well as rivers for which little data were available. Where possible, samples were collected near mouths of rivers or confluence of major tributaries. Sample areas are designated as general areas of rivers rather than exact locations because of the migratory nature of many fish and the tendency of bioaccumulable chemicals to contaminate large areas near the discharge. Samples were wrapped in solvent-rinsed aluminum foil, frozen, and shipped with dry ice to the Environmental Research Laboratory in Duluth, Minnesota.

PREPARATION OF SAMPLES

The procedures for preparation and analysis of samples have been described previously (*6*). Composite whole-fish samples were homogenized with a Hobart t grinder. Subsamples weighing 20 g were extracted Soxhlet extractor with a 1:1 mixture of hexane methylene chloride. Following Florisil column clea samples were analyzed by electron-capture (EC) flame-ionization (FI) GLC and multiple-ion-dete (MID) GLC/MS.

GLC analysis provided measurement of PCBs, H DDE, and ΣDDT, as well as information on the plexity of the residue with respect to other nonp organic chemicals. MID GLC/MS was used to qu tate *cis*- and *trans*-chlordane, *cis*- and *trans*-nonac heptachlor epoxide, and oxychlordane. A proce blank was performed with every fifth sample. Dupl analyses of several samples gave results within 4 pe for both EC GLC and MID GLC/MS. Recovery laboratory-raised fathead minnows spiked with 1 PCB and 50 ppb pesticides was >92 percent for compound.

A second subsample (100 g) of each fish was Sox extracted in a 1:1 mixture of hexane and methy chloride, cleaned by gel-permeation chromatogr (*2*), and qualitatively analyzed by full mass r

watersheds near the Great Lakes, 1978

Sampling Area	Sample Composition	PCB Residues, ppm			DDE, ppm	ΣDDT, ppm	HCB, ppb	Chlordane (cis + trans), ppb	Nonachlor (cis + trans), ppb	Heptachlor, ppb	Heptachlor Epoxide, ppb	Oxychlordane, ppb
		1016/1242	1254	Total								
Wisconsin River, below Nekoosa Dam, Wisc.	5 walleye 2 carp 2 white sucker	0.38	0.86	1.24	0.08	0.14	7	*	*	*	*	*
Fox River, below DePere Dam, Wisc.	4 carp 4 white sucker 5 channel catfish	3.61	6.41	10.0	0.75	1.06	18	*	17	*	*	*
Lake Pepin, Mississippi River, Minn.	3 carp	0.15	4.35	4.50	0.36	1.03	37	*	20	*	*	*
Wabash River, below Terre Haute, Ind.	5 channel catfish	0.31	1.77	2.08	0.08	0.15	<5	45	37	27	5	*
Wabash River, above Terre Haute, Ind.	5 carp	0.18	1.07	1.25	0.13	0.21	<5	21	25	*	*	*
White River, Paragon, Ind.	11 channel catfish	0.51	2.65	3.16	0.15	0.47	7	239	288	*	*	*
St. Joseph River, Berrien Springs Dam, Mich.	4 carp	0.34	2.62	2.96	0.35	0.76	9	*	24	*	*	*
Grand River, Clinton County, Mich.	3 carp	<0.10	4.91	4.91	0.56	0.31	36	2,570	3,070	*	*	*
Tittabawassee River, Smith's Crossing, Mich.	5 channel catfish 2 carp	1.25	1.40	2.65	0.23	0.36	64	*	4	*	*	*
Raisin River, Monroe County, Mich.	4 carp	9.83	4.80	14.6	0.25	0.48	14	*	36	*	*	*
Scioto River, Rosemont, Ohio	1 freshwater drum 2 carp 1 channel catfish 1 quillback	0.32	1.98	2.30	0.12	0.40	7	64	125	*	*	*
Ashtabula River, Ashtabula, Ohio	1 white sucker 1 hog sucker 2 stone rollers 1 carp	9.36	1.52	10.9	0.79	0.92	447	*	*	77	*	*
Huron River, Ohio	1 goldfish 2 freshwater drum 2 carp	<0.10	0.62	0.62	0.17	0.26	<5	*	*	8	*	*
Chagrin River, Ohio	3 freshwater drum 2 carp	0.26	3.57	3.83	0.50	0.82	<5	51	434	*	*	*
Rocky River, Ohio	2 carp 1 goldfish	0.84	4.54	5.38	0.52	0.88	21	2,680	1,820	*	*	167
Conneaut River, Ohio	4 freshwater drum 1 carp	<0.10	0.40	0.40	0.04	0.09	39	*	*	*	*	*
Black River, Ohio	5 channel catfish 1 freshwater drum	0.16	1.62	1.78	0.10	0.31	<5	*	*	*	*	*
Portage River, Ohio	5 carp	0.35	2.66	3.01	0.46	0.72	<5	*	*	*	*	*
Sandusky River, Ohio	5 freshwater drum	<0.10	0.59	0.59	0.08	0.15	<5	*	*	*	*	*
Maumee River, Waterville, Ohio	5 carp	<0.10	0.25	0.25	0.02	0.05	<5	25	25	*	*	*
Maumee River, Collen Park, Ohio	3 carp	1.38	3.38	4.76	0.23	0.53	24	*	*	*	*	*
Great Miami River, Miamisburg, Ohio	2 carp 3 goldfish	2.00	5.18	7.18	0.24	0.45	13	24	16	11	*	*
Great Miami River, Elizabethtown, Ohio	3 carp 1 channel catfish	0.78	8.59	9.37	0.66	1.32	13	43	25	*	*	*
Lake Ontario, near Oswego, N.Y.	2 brown trout	1.79	3.97	5.76	1.00	1.66	87	*	*	2	*	1
Cattaragaus Creek, N.Y.	5 white sucker 2 hog sucker 1 brown trout	<0.10	0.13	0.13	0.01	0.03	<5	*	*	*	*	*
Cattaragaus Creek Mouth, N.Y.	3 coho salmon	0.16	1.59	1.75	0.21	0.40	7	*	*	9	*	3

NOTE: * = Below the detection limit of 0.5 ppb.

(m/z 50–550) scanning GLC/MS. Again, procedural blanks were performed with every fifth sample, and spiking experiments showed >90 percent recovery.

ANALYSES

The GLC/MS analyses were performed on a Finnigan 4000 mass spectrometer interfaced to an INCOS data system. Instrument parameters and operating conditions follow:

Column:	glass, capillary, 30-m long by 0.25-mm (ID), coated with SE-30
Temperature, °C:	column programmed from 100 to 225° at 4°/minute (with a 20-minute hold) ion source 280
Carrier gas:	helium flowing at 30 cm/second
Mass scan:	50–550/2 seconds
Electron energy:	70 eV
Emission:	350 mA

MID GLC/MS analyses were also performed on the above equipment, with the same temperature programming, followed by a 20-minute hold. The mass spectrometer was computer-controlled to monitor six ions for equal time during a 2-second period. The six ions were m/z 373 for chlordane, m/z 409 for nonachlor, m/z 272 for heptachlor, m/z 355 for heptachlor epoxide, m/z 387 for oxychlordane, and m/z 442 for defluorotriphenylphosphene (DFTPP).

DFTPP was used as an internal standard for MID quantification. Each extract was spiked with DFTPP to give a concentration of 10 ng/μl. Two standards of the chlordane components of 5 ng/μl and 20 ng/μl each were used as samples after each set of five fish samples. Quantification was based on a 10-ng/μl solution with standard INCOS software. The quantified standards gave values within 4 percent of expected values. The limit of detectability was 0.50 ppb wet weight.

Ion source was operated as above with an emission of 350 mA.

Results and Discussion

PCBs were found in all 26 samples at concentrations ranging from <0.1 ppm in fish from the upper reaches of Cattaragaus Creek, New York, to 14.6 ppm in fish from the Raisin River, Michigan. Aroclor 1254 constituted over 50 percent of the total PCB residues in the majority of the samples. Aroclor 1016/1242 was found in 20 of the 26 samples at concentrations ranging from <0.1 to 9.83 ppm in Raisin River fish. These results are consistent with the authors' previous study of 58 samples, in which Aroclor 1016/1242 was present in 77 percent of the samples (*6*).

Fish from the Fox River (Wisconsin), Raisin River (Michigan), and Ashtabula and Greater Miami Rivers (Ohio) remain heavily contaminated with PCBs. Twelve other samples contained PCB residues >2 ppm. Although PCB concentration in the edible portion o fish is expected to be lower than that in the whole the present data suggest that 65 percent of the fish ples would pose significant hazards to animals, suc mink, feeding on the fish (*1*).

DDT, once the major organochlorine contamina fish in many U.S. waterways, is a minor contamina the river systems investigated in the present study though DDE was found in all samples, ΣDDT co tration in 81 percent of the samples was below 1.0 the maximum concentration was 1.66 ppm, in Ontario fish.

HCB was the next most prevalent organochlorine f in the present study; 65 percent of the samples tained measurable quantities. Although most sar contained <0.05 ppm HCB, Ashtabula River fish tained 0.447 ppm. The authors' previous work (*6* vealed concentrations of 3.14 ppm HCB in fish fror Ashtabula River in 1976. The apparent decline ma the result of sampling variability or of pollution-a ment measures taken since the 1976 discovery. The that fish analyzed in the present study were coll upstream from the alleged discharge (*3*) into the tabula River may also be significant. An ongoing investigation is a direct result and a primary bene this type of biomonitoring, because areas of highest tamination are identified for more intensive stuc minimum cost.

Chlordane and components of technical chlordane found in 38 percent of the samples. Although fish most of the rivers contained <0.05 ppm chlordane from the Grand River, Michigan, and Rocky R Ohio, contained 2.57 ppm and 2.68 ppm, respect The total nonachlor concentrations in these fish 3.07 ppm and 1.82 ppm, respectively. Heptachlor heptachlor epoxide were found only in fish fron Wabash, Ashtabula, and Huron Rivers and Lake tario. Oxychlordane was present in Rocky River, Ontario, and Lake Erie fish at a maximum conce tion of 167 ppb. The coho salmon caught at the n of the Cattaragaus Creek, New York, are undoub Lake Erie fish, which would account for the oxyc dane residues.

In addition to chemicals quantified by GLC or GLC/MS, the results of exhaustive GLC/MS stud the fish extracts are summarized in Table 2. The fi organic chemicals identified in Table 2 are aliphati aromatic hydrocarbons. Heptadecane, pentadecane related hydrocarbons are natural products of be algae, as well as the results of petroleum contamir from mixtures such as fuel oil. Present methodolog mits only qualitative statements about the sourc these compounds, based on FI GLC chromatog

dinecarboxamide appeared to be as common as adecane in fish from these rivers.

achloroanisole was identified in 15 of the 26 sam- of fish. The authors have observed halogenated oles in effluents of sewage treatment plants receiv- the respective halogenated phenols (*4*). Present in- nation suggests that the anisoles arise from methyla- of the corresponding phenols by bacteria. Studies at Environmental Research Laboratory in Duluth (un- ished data) have shown that fish exposed to halo- ted phenols do not produce the anisoles metaboli- . The presence of pentachloroanisole may therefore from the widespread use of pentachlorophenol as a d preservative. Because the bioconcentration factor he methyl derivative of phenols is several orders of nitude greater than that of the phenol, pentachloro- ole as an environmental contaminant is probably the lt of selective bioaccumulation of a more persistent abolite of pentachlorophenol.

tachloronorbornene and hexachloronorbornadiene found only in the Wabash River fish collected w Terre Haute, Indiana. These two compounds are rmediate chemicals in the production of cyclodiene cides, and their occurrence is linked to manufac- ng sites for these pesticides. These chemicals were uded in Table 2 because they are unique in the abash River, not because of widespread occurrence. se data confirm the authors' studies of fish from the r Wabash (*6*) and suggest a source of contamina- in the vicinity of Terre Haute, Indiana. The only r identification of heptachloronorbornene and hexa- ronorbornadiene in the aquatic environment was rted by the Food and Drug Administration, U.S. artment of Health and Human Services, in fish from Mississippi River below Memphis, Tennessee (*5*).

ex was identified only in Lake Ontario fish. The com- nd was first observed in 1973 and was extensively in- gated by state and federal agencies.

Bs were identified in all samples and, although the -, penta-, and hexachlorobiphenyl homologs were ominant, PCBs containing two or three chlorine ns were found in 19 of the 26 samples.

above-mentioned quantitative and qualitative data ent a reasonably comprehensive description of the nical residues that contaminate fish in some major rs. However, these data fail to illustrate adequately need for improved biomonitoring or analytical meth- development. Fish from many of the rivers contain lue mixtures that are similar to the GLC chromato- n of the Maumee River fish presented in Figure 2. chromatogram was obtained by using a 30-m, wall- ed capillary column and an electron-capture detec- Although there are many chemicals in this extract, s, HCB, and natural products account for all peaks in the chromatogram. Therefore, the residues in this area are comparatively simple to work with, and routine GLC methods should be adequate for any surveillance work.

In contrast, the Ashtabula, Wabash, and Tittabawassee Rivers contain extremely complex mixtures of bioaccumulable chemicals. An electron-capture capillary chromatogram of extract of fish from the Ashtabula River is shown in Figure 3. Chemicals identified include tetra-, penta-, and hexachlorobutadiene; chlorinated benzenes up to hexachlorobenzene; penta- and hexachlorobutylamines; and numerous hexa-, hepta-, and octachlorostyrenes. Despite the identification of almost 100 chemicals in this sample, those identified to date are largely only those in the highest concentrations. A comprehensive study of residues in fish from the Ashtabula and Wabash Rivers is presented elsewhere (*3*).

Even though progress has been made in developing methods for rapid characterization of chemical residues, the long lists of chemicals being published from studies of environmental samples should not lead to the conclusion that present methods are thorough or adequate. In many of the rivers the authors have studied during the past four years, chemicals are present that cannot be identified without improved cleanup methods and instrumental techniques. More important, the number of sample sites studied would have to be increased by an order of magnitude in order to screen even a single sample from industrial areas over the next five years. Major improvements in the current state-of-the-art methods for GLC/MS screening will have to be made before an adequate number of samples can be thoroughly studied.

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TABLE 2. *Chemical contaminants identified by GLC/MS in fish from United States rivers near the Great Lakes*

Chemical Contaminant	Wisconsin River	Fox River	Lake Pepin	Wabash River (above Terre Haute)	Wabash River (below Terre Haute)	White River	St. Joseph River	Grand River	Tittabawassee River	Raisin River	Scioto River	Ashtabula River
Tridecane	1			2						2		
Tetradecane				2						2		
Pentadecane							2					
Hexadecene			1									
Hexadecane	1		1	1								
Heptadecene							2	2				
Heptadecane				1			1	1	1	1	1	
Octadecane				1							1	
Nonadecane								1				
Eicosane								2				
Naphthalene					1		1			1		
Methylnaphthalene					2	2	2	2		2		
Dimethylnaphthalene					2		2	2		2		
Biphenyl						1						
Methylbiphenyl						2		2		2		
C2-Biphenyl						2		2				
Phenanthrene				2	2	2	2	2		2		
Fluoranthene				2	2	2	2	2		2		
Pyrene					2	2	2	2		2		
Fluorene												
Dibenzofuran												
Acenaphthalene												
Methylbenzanthracene												
Dibenzothiophene												
Pyridinecarboxamide	1	1			1			1	1	1	1	
Terphenyl												
Phenylnaphthalene												
Pentachlorobenzene									1		1	1
Hexachlorobenzene	1	1	1			1	1	1	1	1	1	1
Pentachloroanisole						1	1	1			1	1
Pentachlorophenol					1							
Pentachlorobenzyl alcohol					2							
DDE			1		1	1	1	1	1	1		
TDE			1			1	1	1	1	1		
DDMU			1		1	1	1					
DDT			1		1	1	1	1	1	1		
Heptachloronorbornene					2							
Heptachloronorbornadiene					2							
Mirex												
Photomirex												
Endrin					1							
Monochlorobiphenyl										2		
Dichlorobiphenyl	2									2		
Trichlorobiphenyl	2	2	2		2	2	2	2	2	2		
Tetrachlorobiphenyl	2	2	2	2	2	2	2	2	2	2	2	2
Pentachlorobiphenyl	2	2	2	2	2	2	2	2	2	2	2	2
Hexachlorobiphenyl			2	2	2		2	2	2	2	2	2
Heptachlorobiphenyl			2	2	2	2	2	2	2	2	2	2
Octachlorobiphenyl							2	2	2			
Hexachlorostyrene												2
Heptachlorostyrene												2
Octachlorostyrene												1
Chlordane				1	1	1		1			1	
Nonachlor		1	1	1	1	1	1	1	1	1	1	
Heptachlor					1							1
Heptachlor epoxide					1							
Oxychlordane												

NOTE: 1 = Confirmed by GLC and MS retention time data; 2 = confirmed by MS data; 3 = suggested by MS data.

BLE 2 (cont'd.).

ON ER	CHAGRIN RIVER	ROCKY RIVER	CONNEAUT RIVER	BLACK RIVER	PORTAGE RIVER	SAN-DUSKY RIVER	MAUMEE RIVER (WATER-VILLE)	MAUMEE RIVER (COLLEN)	GREAT MIAMI RIVER (MIAMIS-BURG)	GREAT MIAMI RIVER (ELIZA-BETHTOWN)	LAKE ONTARIO	CATTA-RAGAUS CREEK	CATTA-RAGAUS CREEK (MOUTH)
		2			2								
		2			2								
											2		
	2	1	1							1	1	1	1
	1	1	1		1	1	1			1			
			1							1			
			1				1			1			
			2							2			
		2	2	2									
		2	2										
		1		1									
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		2	2	2	2				2				2
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		2	2	2					2	2			
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	1		1	1	1	1	1	1	1	1	1	1	1
				2					2				
		3	3	3									
		1	1					1	1	1	1		
	1		1	1	1	1		1	1	1	1		1
	1		1	1	1				1				1
		1	1		1				1				1
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											1		
											1		
									2	2	2		
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		1											

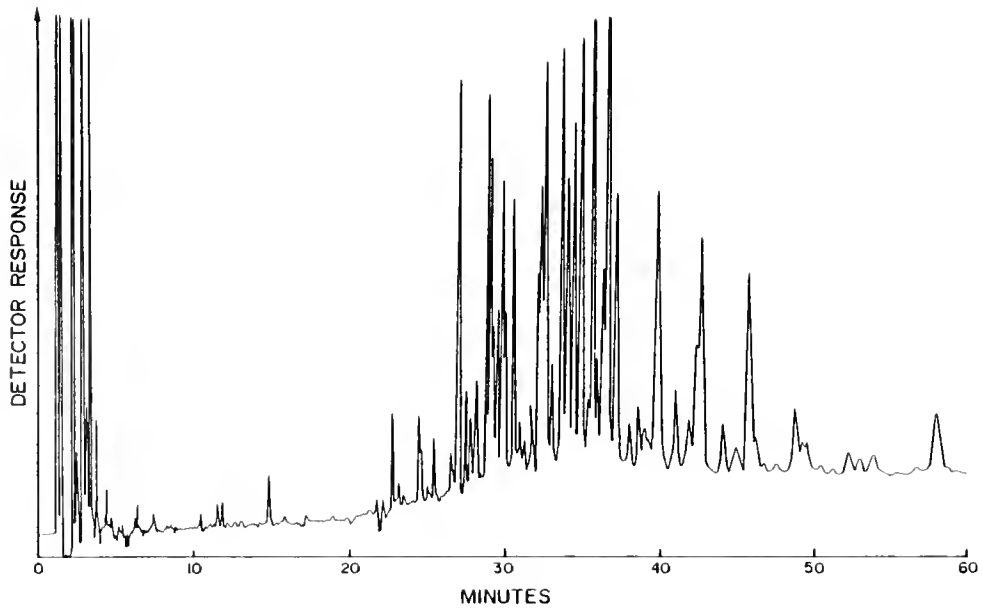

FIGURE 2. *Capillary electron-capture chromatogram of fish extract from Maumee River, Ohio.*

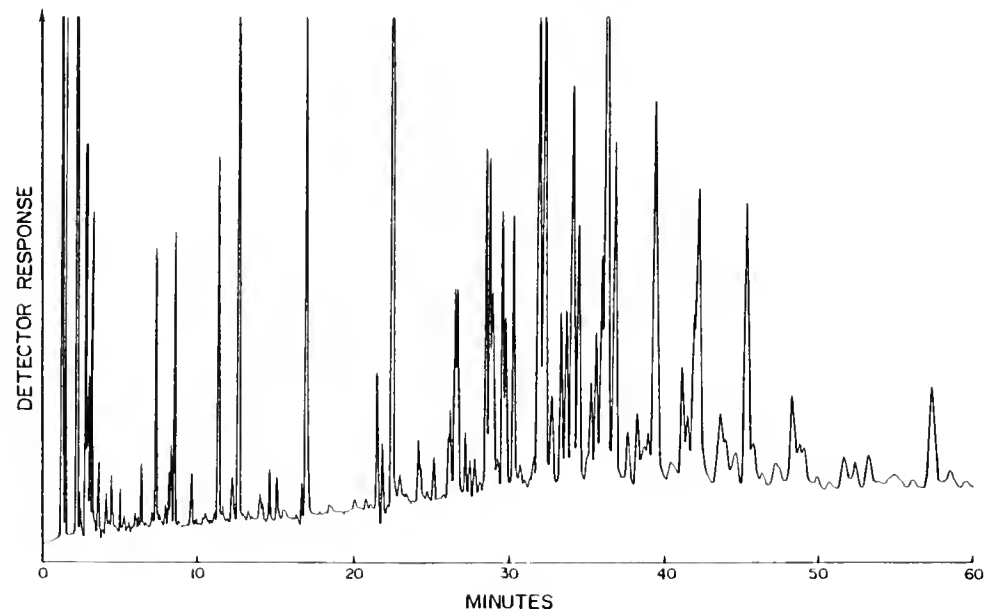

FIGURE 3. *Capillary electron-capture chromatogram of fish extract from Ashtabula River, Ohio.*

Organochlorine Pesticide Residues in Some Indian Wild Birds [1]

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ABSTRACT

sidues of BHC and DDT were estimated by gas-liquid romatographic analysis of the internal body organs, depot , and blood plasma of a few species of Indian wild birds ptured in and around the urban area of Lucknow. Total IC and γ-BHC (lindane) levels were high in breast muscle, er, heart, and lung tissues of pigeon, crow, and vulture, npared with the respective tissues of chicken, cattle egret, l kite. More lindane and total BHC was found in tissues vulture compared with other species. The major part BHC isomers in the brain of birds examined was ac-unted for by α-BHC. Total BHC detected in depot fat of ws was 29.7 ppm; lesser amounts were found in vulture, e, and cattle egret, respectively. Total DDT levels were nparable in the blood plasma of chicken, pigeon, crow, and tle egret, although residues generally showed the follow-order in the tissues examined: chicken < pigeon < cat-egret < crow < kite < vulture. High levels of DDT re detected in depot fat of crow, kite, and vulture (50.8, 0, and 95.3 ppm, respectively). Avian species thus reflect logical magnification of BHC and DDT residues, presum-y due to their food habits.

Introduction

ganochlorine pesticides and related compounds have en detected in significant amounts in the environment l in human body tissues (*8*). Pesticides are dispersed h during their manufacture and by their extensive for controlling vector-borne diseases and crop pests.

vironmental contamination from persistent organo-orines has been recognized as a threat to wildlife for re than two decades. Many residues have been found tissues and eggs of birds in Europe and North Amer- (*7, 20, 23, 24*). Some reports (*10*) of high mortal- of birds have been attributed to poisoning by organo-orines. The bioconcentration of DDT and other or-nochlorine residues is apparently associated with the bitat and dietary habits of different species of birds *4, 9, 17, 23*). For example, earthworms are the prin-al source of DDT for robins (*1*). These pesticides er the bodies of earthworms through soil, which is largest reservoir of pesticide residues.

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Certain species of birds, because of their worldwide distribution, are considered good indicators of environmental pollution by pesticides (*16*). For example, crows have been used by many workers (*11, 15, 18, 21, 22*). The present report deals with DDT and BHC residues in wild pigeon (*Columba livia*), house crow (*Corvus splendens*), common pariah kite (*Milvus migrans*), Bengal vulture (*Gyps bengalensis*), and cattle egret (*Bubulcus ibis*). Farm-bred chickens were taken for comparison.

Materials and Methods

Wild pigeon, crow, kite, vulture, and cattle egret (three birds in each species) were obtained through commercial bird trappers during February and March 1980, from the urban area of Lucknow, a major city located 26°52′ north and 80°56′ east in the Indo-Gangetic plain. It is one of the most populated regions in the world, with a tropical climate. Chickens (average body weight 500 g) were purchased from the State Live Stock Farm, Lucknow. Within 24 hours of capture, birds were sacrificed, blood was collected in heparinized containers, and plasma was separated. Depot fat and internal body organs were excised. The average bird weights were 200, 305, 750, 4200, and 260 g for pigeon, crow, kite, vulture, and cattle egret, respectively.

ANALYSIS FOR ORGANOCHLORINE PESTICIDE RESIDUES

Blood Plasma—One milliliter blood plasma was mixed with 3 ml concentrated formic acid (98 percent pure) and extracted with *n*-hexane by shaking 1 hour. The *n*-hexane extract was washed with glass-distilled water and cleaned by concentrated H_2SO_4 treatment according to Dale et al. (*6*), as modified in the Arrhenius Laboratory, Analytical Chemistry, University of Stockholm, Sweden.

Body Tissues—Minced tissue (2 g) from body organs was thoroughly homogenized with 7 ml formic acid and transferred to a 50-ml conical flask. The homogenizing tube and pestle were washed twice with 5-ml portions of *n*-hexane, and the washings were collected in the flask. The homogenate was shaken in a 40°C water bath for 1 hour and then the solvent layer was withdrawn.

Minced depot fat (0.5 g) was homogenized with 3 ml formic acid and 5 ml *n*-hexane, transferred to a 50-ml conical flask, and treated as above.

The extracts of brain and body fat samples above were partitioned with acetonitrile (saturated with *n*-hexane) to remove fat. Pesticide residues were re-extracted in *n*-hexane. The solvent extract was passed through a column filled with anhydrous Na_2SO_4 and collected in a round-bottomed flask. The column was washed with 10 ml *n*-hexane and the washings were added to the original filtrate. The solvent extract was evaporated to dryness under reduced pressure and then re-dissolved in 5 ml *n-hexane*. Fractions (2 ml) were treated with 2 ml fuming H_2SO_4 and centrifuged, and the solvent layer was withdrawn.

Pesticide residues were determined by gas-liquid chromatography (Varian Aerograph Series 2400), using electron-capture detection (^3H), at the following operating conditions:

Carrier gas:	pure nitrogen passed through silica gel and molecular sieve to remove moisture and oxygen, respectively
Gas pressure:	65 psi
Gas flow:	40 ml/minute
Detector temperature:	200°C
Injector temperature:	190°C
Column temperature:	180°C
Column:	glass spiral column, 6 ft × ⅛ in. ID, coated with 1.5 percent OV-17 + 1.95 percent OV-210

Residue peaks were identified by thin-layer chromatography (TLC) on silica gel G-coated glass plates (*14*) and comparison with reference standards obtained from PolyScience Corp., Niles, Illinois. Further confirmation of the residues was done by chemical methodology and column chromatography (*19*).

Recoveries of BHC isomers, DDT, and DDT metabo (p,p'-DDE and p,p'-TDE) in the fortified sampl liver, brain, muscles, and body fat were between 7(94 percent. Sensitivity of the method was about (ppm for BHC isomers, aldrin, and p,p'-DDE and a 0.002 ppm for p,p'-DDT.

All reagents and chemicals used were high purity were checked for interferences under the experim conditions.

Results and Discussion

The concentrations of BHC and DDT residues in b plasma, brain tissue, and depot fat are summarize Tables 1 and 2. Levels of total BHC, γ-BHC (lind and total DDT in breast muscle, liver, heart, lung, ney, and spleen of birds are shown in Figure 1 values are expressed in terms of whole-tissue wet we results were not corrected for recovery.

DDT and BHC and their residues are widely distrib in the ecological system. Although BHC residues excreted rapidly (*13*), slow accumulation does occ the body tissues and body fat on chronic exposure.] and derivatives are quite stable and are resistar enzymic action; thus, residues accumulate in biolo tissues. The levels of DDT residues present in the are occasionally taken as an index of contaminatio DDT and DDT metabolites of the local environ The general tendency appears to be that the smalle

TABLE 1. *Range and geometric mean values of total BHC and γ-BHC (lindane) residues in blood plasma, brain depot fat of some wild birds and chickens*

	Residues, ppm Whole-Tissue Wet Weight					
	Blood Plasma		Brain Tissue		Depot Fat	
Bird	Total BHC	Lindane	Total BHC	Lindane	Total BHC	Lin
Chicken	0.007 [1]	0.002	0.014	0.001	0.208	0.(
	0.006–0.010 [2]	0.002–0.003	0.008–0.025	0.001–0.002	0.121–0.310	0.075
	(0.008) [3]	(0.002)	(0.016)	(0.002)	(0.253)	(0.(
Pigeon	0.048	0.016	0.316	0.020	—	
	0.045–0.053	0.015–0.019	0.215–0.607	0.014–0.034	—	
	(0.048)	(0.016)	(0.355)	(0.021)	—	
Crow	0.030	0.011	0.246	0.014	21.815	6.
	0.016–0.062	0.006–0.024	0.213–0.266	0.010–0.016	15.532–29.726	3.99
	(0.035)	(0.013)	(0.248)	(0.014)	(22.487)	(6.(
Kite	0.060	0.028	0.093	0.012	5.468	2.
	0.043–0.094	0.020–0.051	0.030–0.168	0.009–0.019	3.328–12.414	1.182
	(0.064)	(0.031)	(0.119)	(0.013)	(6.567)	(3.(
Vulture	0.106	0.066	1.132	0.26	12.628	10.
	0.066–0.143	0.044–0.080	0.759–2.047	0.142–0.683	6.510–19.823	4.951-
	(0.112)	(0.068)	(1.247)	(0.335)	(13.980)	(11.(
Cattle egret	0.004	0.048	0.126	0.053	6.309	4.
	0.056–0.075	0.040–0.057	0.032–0.175	0.042–0.080	5.623–7.239	3.567
	(0.064)	(0.048)	(0.132)	(0.055)	(6.344)	(5.(

[1] Geometric mean.
[2] Range.
[3] Arithmetic mean.

LE 2. *Range and geometric mean values of DDT and DDT metabolites in blood plasma, brain, and depot fat of some wild birds and chickens*

'OUND	Residues, ppm Whole-Tissue Wet Weight					
	Blood Plasma	Brain	Depot Fat	Blood Plasma	Brain	Depot Fat
	CHICKEN			PIGEON		
)DE	0.002	0.002	0.222	0.004	0.012	—
	0.002–0.003	0.001–0.002	0.190–0.250	0.003–0.006	0.005–0.021	—
	(0.002)	(0.002)	(0.226)	(0.004)	(0.014)	—
TDE	0.002	0.001	0.055	0.001	0.001	—
	0.002–0.002	0.001–0.001	0.045–0.083	ND–0.002	ND–0.003	—
	(0.002)	(0.001)	(0.059)	(0.001)	(0.001)	—
)DT	0.003	0.008	0.272	0.003	—	—
	ND–0.007	0.007–0.009	0.236–0.298	0.002–0.007	ND	—
	(0.004)	(0.008)	(0.274)	(0.004)	—	—
DDT	0.009	0.011	0.587	0.009	0.013	—
	0.005–0.012	0.009–0.012	0.550–0.670	0.005–0.014	0.005–0.023	—
	(0.009)	(0.010)	(0.590)	(0.010)	(0.017)	—
	CROW			KITE		
)DE	0.035	0.035	18.595	0.100	0.038	23.108
	0.024–0.044	0.025–0.064	15.081–21.069	0.043–0.192	0.026–0.053	4.652–60.00
	(0.036)	(0.039)	(18.798)	(0.119)	(0.040)	(36.287)
TDE	0.007	0.003	2.107	0.317	0.019	11.275
	0.006–0.010	ND–0.024	1.151–3.530	0.229–0.420	0.014–0.027	2.850–43.886
	(0.007)	(0.011)	(2.327)	(0.327)	(0.020)	(19.391)
)DT	ND	ND	2.107	—	—	—
	—	—	ND–5.024	ND	ND	ND
	ND	ND	(2.289)	—	—	—
)DT	0.018	0.004	12.563	0.044	0.003	4.496
	0.014–0.024	ND–0.030	4.488–63.421	0.027–0.074	ND–0.027	2.454–8.148
	(0.019)	(0.018)	(24.958)	(0.048)	(0.009)	(5.049)
DDT	0.066	0.063	44.486	0.522	0.076	44.986
	0.052–0.080	0.031–0.128	31.197–89.713	0.346–0.655	0.075–0.077	10.310–120.115
	(0.067)	(0.074)	(50.788)	(0.543)	(0.076)	(67.014)
	VULTURE			CATTLE EGRET		
)DE	0.183	0.587	35.070	0.029	0.027	3.014
	0.106–0.245	0.298–1.052	20.297–53.948	0.026–0.033	0.018–0.035	2.131–3.049
	(0.196)	(0.655)	(37.878)	(0.030)	(0.028)	(3.110)
TDE	0.209	0.386	39.543	0.004	0.004	6.991
	0.133–0.317	0.228–1.022	25.197–61.909	0.003–0.006	ND–0.014	2.289–23.478
	(0.222)	(0.499)	(40.736)	(0.005)	(0.006)	(10.710)
)DT	0.039	0.095	6.162	0.003	—	3.979
	0.023–0.060	0.038–0.229	2.477–15.113	ND–0.006	ND	1.418–7.854
	(0.028)	(0.122)	(7.946)	(0.003)	—	(4.976)
DDT	0.479	1.204	87.945	0.041	0.038	17.048
	0.292–0.685	0.644–2.535	53.051–143.92	0.037–0.045	0.035–0.045	8.360–36.267
	(0.509)	(1.416)	(95.353)	(0.042)	(0.039)	(20.323)

al the higher the ratio of food consumption per weight, regardless of food habits. Thus, within the food habit group, smaller individuals are likely to st larger amounts of pesticide residues. Age and size of the species are also important in influencing accumulation of pesticide residues. However, food ts and the food-chain concentration mechanism are important in determining the total body burden of cide residues.

e 1 shows that levels of BHC and lindane present in d plasma, brain tissue, and depot fat of kite and egret are comparable. Relatively high levels of BHC were detected in crow and pigeon brain, as pared with blood plasma levels. Vulture (a carrion-er) contained 1.25 ppm total BHC and 0.34 ppm ne in the brain, which are many times higher than oncentrations present in other species of birds stud- As high as 29.73 ppm total BHC was recorded rage, 22.49 ppm) in crow depot fat.

BHC levels in liver, heart, lung, and kidney were generally high in pigeons and crows (Figure 1). Breast muscles and spleen of vulture exhibited relatively high accumulation of BHC. Kite and cattle egret showed generally low concentrations of these compounds in tissue. Compared with other isomers of BHC, lindane accumulation was high in the tissues of vulture and cattle egret. However, the α-isomer accounted for the major burden of this compound in brain tissue of all birds studied. A single specimen of pigeon ovary examined in the present study contained 1.21 ppm total BHC and 0.31 ppm lindane. Residue levels found in the tissues and blood plasma of chicken were relatively low.

Until 1962 (*8*), carcasses of random samples of birds had been analyzed for aldrin, dieldrin, or DDT. DDE is the primary breakdown product of DDT and is universally distributed; exposure to this compound is essentially a continuous one. Residues of parent compound, DDT, and the metabolite TDE are less frequent. Results of

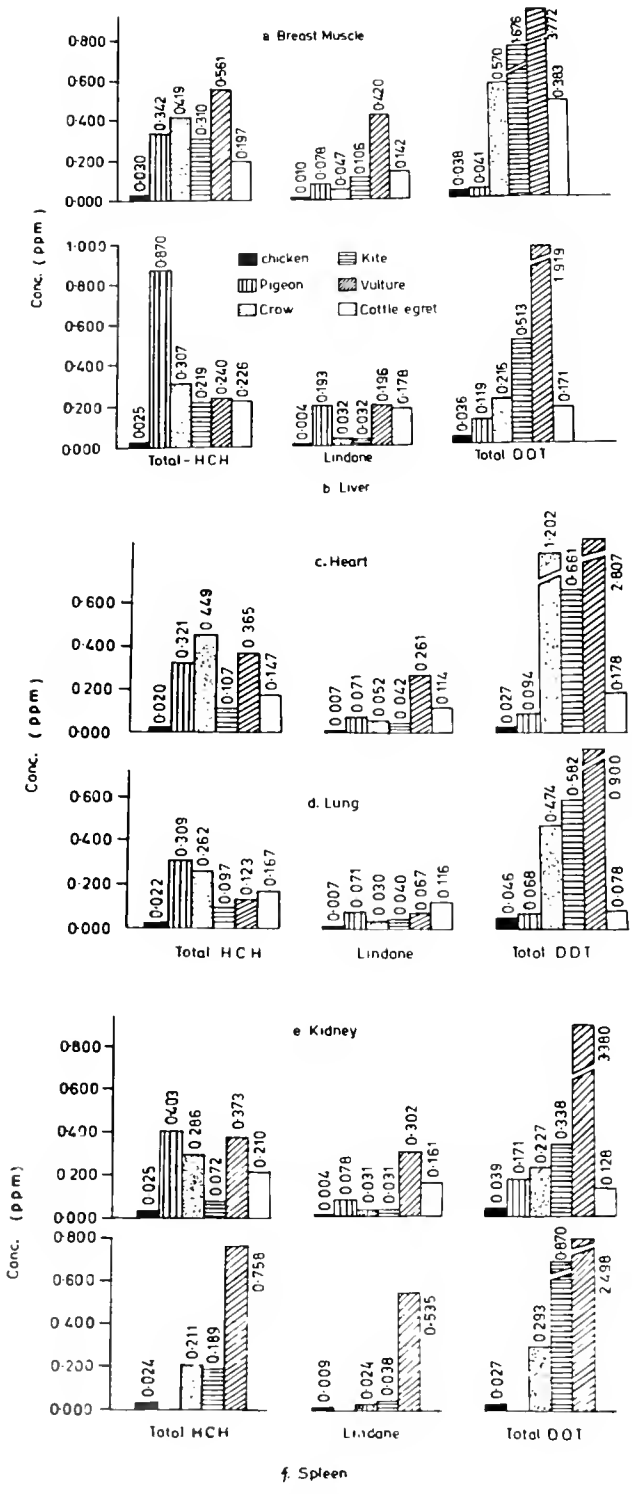

FIGURE 1. *Total BHC, lindane, and total DDT in internal body organs of different species of birds.*

the present study show a positive correlation of D concentration in blood and brain, as well as in bl and depot fat, as suggested by several workers (*2*, Levels of DDT and DDT metabolites in blood plas brain, and depot fat are presented in Table 2, and t DDT levels in the rest of the tissues are given in Figur

Few samples of lungs, spleen, and depot fat of c showed measurable levels of *o,p'*-DDT. *p,p'*-DDT not detected in lung, kidney, and brain tissue of pig and cattle egret. *p,p'*-TDE was not found in the lung these birds. Relatively high levels of *p,p'*-DDE were served in different body organs of cattle egret, compa with those present in other birds examined. More t 70 percent of total DDT was present as *p,p'*-DDE most body organs of pigeon. An equivalent concen tion of *p,p'*-DDT and comparatively low levels of *p* TDE in body organs of crow, and to some ex chicken, indicate that the exposure is rather contin from different environmental sources. Vulture and contained high concentrations of *p,p'*-DDE and *p* TDE, compared with the levels of parent compo (*p,p'*-DDT).

Total DDT levels were 0.59, 20.32, 50.79, 67.10, 95.35 ppm in depot fat of chicken, cattle egret, c kite, and vulture, respectively. In other tissues, total dues of DDT generally occurred in the following or chicken < pigeon < cattle egret < crow < < vulture. Total DDT detected was 0.01, 0.01, 0 0.07, 0.054, and 0.51 ppm in blood plasma and 0 0.02, 0.04, 0.07, 0.08, and 1.42 ppm in brain tissu chicken, pigeon, cattle egret, crow, kite, and vulture spectively. The sample of pigeon ovary analyzed tained 1.01 ppm total DDT.

DDT and its metabolites show a consistent biomagni tion in wild birds, presumably through the food-c concentration mechanism. Flesh-eating birds had sh higher body burdens of DDT than non-flesh-eating c Thus, birds of the upper trophic zone in the food c show higher bioaccumulation of DDT residues. D levels present in birds are perhaps a reflection of the vironmental status of the habitat and food choice particular avian species.

Acknowledgment

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Cadmium, Lead, Mercury, Arsenic, and Selenium Concentrations in Freshwater Fish, 1976–77—National Pesticide Monitoring Program

Thomas W. May [1] and Gerald L. McKinney [2]

ABSTRACT

As part of the National Pesticide Monitoring Program, the Fish and Wildlife Service, U.S. Department of the Interior, collected freshwater fish during 1976–77 from 98 monitoring stations and analyzed them for residues of cadmium, lead, mercury, arsenic, and selenium. Range and geometric mean values in mg/kg wet weight follow: Cd, 0.01–1.04, 0.07; Pb, 0.10–4.92, 0.32; Hg, 0.01–0.84, 0.11; As, 0.05–2.92, 0.27; Se, 0.05–2.87, 0.56. An arbitrary 85th percentile was calculated for concentrations of each element in fish to identify monitoring stations having fish with higher-than-normal concentrations: Cd, 0.11 mg/kg; Pb, 0.44; Hg, 0.19; As, 0.38; Se, 0.82. Log-transformed mean concentrations in fish from 1976–77 monitoring stations are compared with means from the same stations in 1972 (Cd, Hg, Pb, As, Se) and 1973 (Se) to depict temporal trends in whole-body concentrations: Cd, significant decline; Pb, no significant difference; Hg, significant decline; As, significant increase; Se, no significant difference. Because of changes in laboratories and analytical procedures, these conclusions should be used cautiously as trend information. Production, consumption, and disposal of cadmium, lead, mercury, arsenic, and selenium are discussed as potential environmental sources of the elements to the aquatic environment. Specific environmental sources are suggested for monitoring stations having trace element levels exceeding calculated 85th percentiles.

Introduction

The National Pesticide Monitoring Program (NPMP) is a Federal program established to monitor nationwide environmental contaminants in air, soil, water, humans, plants, and animals. United States government agencies participating in NPMP are the U.S. Environmental Protection Agency (EPA); Geological Survey, U.S. Department of the Interior; Food and Drug Administration, U.S. Department of Health and Human Services; U.S. Department of Agriculture; and Fish and Wildlife Service, U.S. Department of the Interior.

The Fish and Wildlife Service (FWS) is responsible for monitoring selected environmental contaminants in freshwater fish. Although primary emphasis has b placed on organic contaminants, selected trace elem have been determined intermittently. In 1969, 3 c posite samples, each of a different species and consis of 3 to 5 whole adult fish, were collected from sampling stations and analyzed for mercury (2 Cadmium, lead, and arsenic were added to the prog in 1971, and selenium was added in 1972. San collections included a replicate for each species in 19 but for only one of three species from each statio 1972. In 1973, all samples were analyzed for seleni but only selected samples were analyzed for merc arsenic, lead, and cadmium. The 1971–73 analyses v conducted by the Denver Wildlife Research Cer FWS (*87*). Samples were collected from 97 station 1974, but no trace elements were analyzed. San collections were suspended during the 1975 samp year to enable a technical and administrative revie fish-monitoring activities. The freshwater fish-monito program was reviewed internally and restructured, responsibility for NPMP in FWS was shifted to Columbia National Fisheries Research Labora (CNFRL).

In 1976, collection stations were increased from 10 117 to include a more extensive coverage of the G Lakes. Collections were then modified to include du cate composite samples of a bottom-dwelling species one composite of a representative predatory specie each station. A list of acceptable bottom-dwellers predator species, listed in order of priority in Tabl was developed. The collections included 146 sam from 52 stations in 1976 and 163 samples from stations in 1977 (Figure 1). The purpose of this re is to present and interpret heavy metals data gath for the NPMP during 1976–77.

Environmental Sources of Heavy Metals

Production, consumption, and disposal processes o result in the transport of trace elements to the aqu environment. The U.S. EPA has established prior for trace element contamination problems and thr to resources by including 13 trace elements on

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BLE 1. *Sequential priority for selection of bottom-ding and predator species of fish, as established by the National Pesticide Monitoring Program* [1]

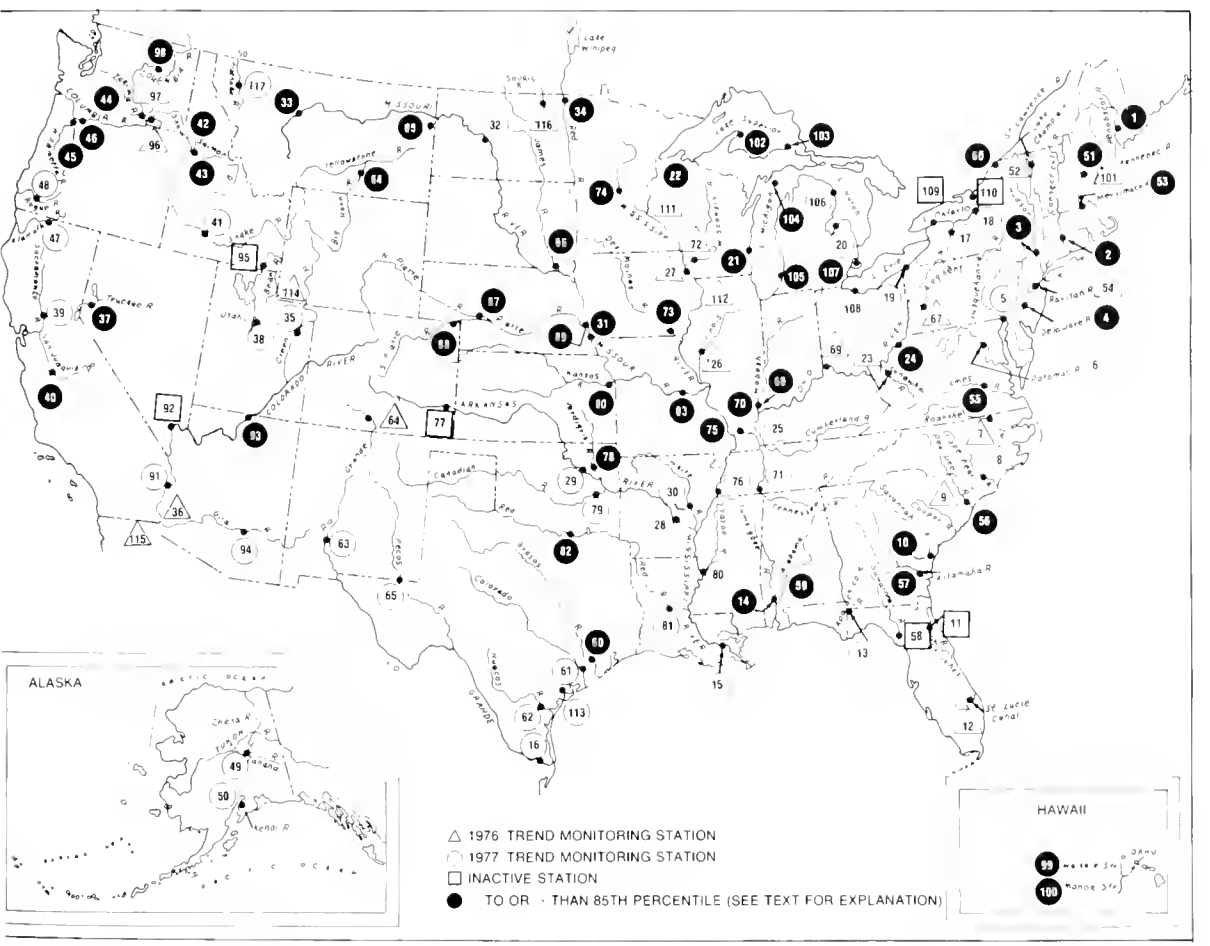
TTOM FEEDERS (commercially or recreationally significant, if ible)
Carp (*Cyprinus carpio*)
Common sucker (*Catostomus commersoni*) or other members of the sucker family
Channel catfish (*Ictalurus punctatus*) or other members of the catfish family
Other, with justification
EDATORS (should be an important sport fish)
Cold water stations: rainbow trout (*Salmo gairdneri*), brown trout (*Salmo trutta*), brook trout (*Salvelinus fontinalis*), lake trout (*Salvelinus namaycush*)
Warm-water stations: largemouth bass (*Micropterus salmoides*), or other member of the sunfish family, such as crappie (*Poxomis* sp.), bluegill (*Lepomis macrochirus*), etc.
Cool-water stations: walleye (*Stizostedion vitreum*) or other members of the perch family
Other, with justification, but must be representative of the drain-age system

om National Pesticide Monitoring Program, Freshwater Fish Col-on Instructions, internal memorandum issued annually to FWS onal Pesticide Specialists.

priority pollutants chemicals list. In this section, authors attempt to link production-consumption practices associated with cadmium, lead, mercury, arsenic, and selenium to environmental sources to clarify the rationale for monitoring concentrations of these trace elements in freshwater fish.

CADMIUM

Cadmium has a close geochemical association with zinc, and natural geochemical sources of cadmium are linked with zinc deposits occurring as massive-sulfide and sulfides in strataform carbonates. Nearly all domestic cadmium is produced as a by-product of zinc concentrates and imported zinc smelter flue dusts (66). The primary domestic producers of cadmium in 1978 were AMAX Zinc Co., Inc., Sauget, Illinois; ASARCO Inc., Corpus Christi, Texas, and Denver, Colorado; Bunker Hill Co., Kellogg, Idaho; National Zinc Co., Bartlesville, Oklahoma; New Jersey Zinc Co., Palmerton, Pennsylvania; and St. Joe Zinc Co., Monaco, Pennsylvania.



URE 1. *Stations sampled for determination of some metals in freshwater fish as part of National Pesticide Monitoring Program, 1976–77.*

Of the domestic consumption of cadmium, 95 percent is divided into five principal uses: plating, pigments, alloys, batteries, and plastic stabilizers. Electrically or mechanically plated hardware used in vehicles and other equipment accounted for 40–45 percent of domestic cadmium consumption in 1978. The production of red, orange, yellow, and maroon pigments consumed 15 percent of the supply, and most of the rest was used in nickel-cadmium batteries, special-purpose alloys, and compounds providing heat and light stability to plastics, particularly polyvinyl chloride (*63*).

In addition to smelter production of cadium metal, primary producers have emphasized production of various cadmium compounds in recent years (*63*). Cadmium is used in the manufacture of pesticides for control of moles and plant diseases affecting residential lawns and golf courses (*63*).

Cadmium is released to the environment primarily from four sources: the electroplating industry; the smelting and refining of zinc, lead, and copper; the application of phosphate fertilizer; and surface mine drainage (*15, 80*). The tendency of cadmium to concentrate in sediments (*15*) may result in a persistent source of the contaminant to various trophic levels in the aquatic environment. Studies indicate that fish accumulate cadmium from the water and through the food chain; both modes of uptake can be toxic (*80*).

The electroplating industry uses cadmium plating for corrosion protection. Wastewater is generated from countercurrent rinses, rinses following chromating, dumping of the chromating solution, and purging of the plating-recovery loop (*82*). Plant outlet pipes often lead to municipal sewage treatment plants, where about 50 percent of the cadmium remains with sewage sludge, and the rest is discharged (*81*). Incineration of sewage sludge volatilizes cadmium, whereas deposition in landfill areas subjects streams and groundwater to contamination. Snowmelt from the roofs and grounds of plating firms can contain more than 1 ppm cadmium, originating as particulate droplets of plating solutions exhausted from the interiors of the firms by fans and accumulating on the roofs or walls or the ground below the discharge point (*55*). Perlmutter and Lieber (*70*), who traced the spread of cadmium from a plating plant, found groundwater containing up to 10 ppm cadmium.

When zinc ores are roasted, cadmium is volatilized and partly collected as fumes or flue dust. The rest is released to the atmosphere and deposited in the area surrounding the smelter (*15*). The soil around a smelter facility that had been operating for 80 years was contaminated with cadmium within a radius of at least 10 miles (*76*). Flue dust returned to the smelter is often stored in waste cinder banks, which are a sou of pollution due to leaching and erosion from r water (*78*). Suspended sediments containing up to percent cadmium have been reported in streams fr high runoff areas near copper and zinc smelters (7 Inland smelters and mills generally have extensive heaps and tailing ponds along streams for waste dispo Estuarine and river refineries generally dispose of wa directly into the water through outfalls.

Phosphate ores used in fertilizer manufacture may c tain from 9 to 130 ppm cadmium (*77*). Runoff fr agricultural areas where phosphate fertilizers are u could result in substantial cadmium loading to aquatic environment.

The primary sources of cadmium contamination du mining are the emission of particulates and the leach of cadmium from the overburden. Ores are enric by flotation techniques to yield a 40–60 percent c mium metal product. Because the cadmium concen tion in a mine is only a few percent, most of original ore mass becomes tailing waste. As much 18–36 percent of the cadmium may be retained in tailings (*15*). Mine waters from sulfide ores can con more than 40 ppm cadmium, but levels of 0.1 to 2 p are more common (*15*). Draining from coal mi areas also poses a threat: Eight bituminous coals f Kentucky and Pennsylvania had 1-2 ppm cadmium (

Low concentrations (< 0.1 ppm) of cadmium in are deceptive, because cadmium is extremely toxic cumulative. Benoit et al. (*6*), who measured cadm levels in various tissues of brook trout exposed to c mium in water for up to 38 weeks, reported that kidney accumulated the highest concentration, follo by the liver and gills. Exposed fish placed in f water lost cadmium rapidly from gill tissue but did lose it from either the kidney or liver. In a similar week exposure of rainbow trout to cadmium, made Kumada et al. (*29*), almost no cadmium was lost f the kidney of exposed fish returned to fresh water.

LEAD

Lead is a major constituent of certain geological for tions, including stratabound deposits, volcanic-sedin tary deposits, replacement deposits, veins, and con metamorphic deposits. Lead ore deposits comm contain the sulfide mineral galena (PbS), which is o associated with sphalerite (ZnS), pyrite (FeS_2), cha pyrite ($CuFeS_2$), and other sulfur salts (*64*).

Most domestic primary lead production (88 perc originates from the limestone or dolomite stratabo deposits of southeastern Missouri (*66*). The silver- vein system of Idaho's Coeur d'Alene District prov 8 percent of domestic primary lead, and the re

vided by replacement deposits in Colorado (3 per-
t) and Utah (1 percent). In 1978, primary lead was
lted and refined at seven U.S. plants (*65*): four
ARCO plants in El Paso, Texas; East Helene, Mon-
a; Omaha, Nebraska; and Glover, Missouri; and
AX in Buick, Missouri; St. Joe Minerals in Hercu-
um, Missouri; and Bunker Hill in Kellogg, Idaho.
ause of the relative ease of reclaiming the metal, old
p lead (secondary lead) accounted for 51 percent
domestic consumption in 1978. More lead is now
duced from secondary sources than from domestic
; (*66*).

transportation industry is the major end user of
l: 51 percent is consumed in storage batteries and
percent in lead alkyl compounds that are used as
oline antiknock additives. The electrical industry (8
cent consumption) has long depended on lead for
le coverings where corrosion or moisture problems
exist. Because of its toxicity, lead is no longer
d in interior paints and has been largely replaced
xterior paints by zinc and titanium pigments. Lead
ments are still the preferred base material for corro-
protection in structural and highway components
percent of total consumption). In the ammunition
ustry, lead remains the major metal in shot and
ll-caliber bullets (4 percent consumption). The con-
ction industry (3 percent consumption) is using
easing amounts of lead as a sound barrier in parti-
s and ceilings, as well as in roofing, piping, flashing,
caulking. Various other industries use lead for many
erent purposes and together account for 13 percent
consumption (*66*).

d enters the environment from several sources. The
or source of lead emissions (88 percent) is the
bustion of leaded gasoline. Although environmental
rictions, initiated in 1972 to control air pollution,
e reversed the growth in use of lead antiknock
itives, unleaded gasoline accounted for only 33 per-
t of the gasoline sold in 1978 (*83*). The average
l content in pooled (leaded and unleaded) gasoline
1972 was 1.2 g/gal. Under cruise conditions, lead
mitted from automobile exhausts in the form of
ll particles, most of which are < 1 μm in mass
lian equivalent diameter (*32*). Such a small par-
size increases the residence time of lead emitted
the atmosphere and, consequently, dispersion from
point of emission. The small size of the particles
tted is generally characteristic of urban lead aero-
, and concentration of lead in ambient air is strongly
elated with automobile traffic density (*39*). Thus,
ospheric fallout and surface runoff of lead into
ams and rivers should be most intense where water-
s flow through metropolitan areas.

Smelting and mining of lead, zinc, and copper have caused marked environmental contamination problems, even though lead emissions from these sources are small relative to vehicle exhausts. Sediments containing up to 17 percent lead by weight have been found below zinc and copper extractive industries, in streams used for irrigation and drinking water (*78*). The pollution hazard is greatest where there is erosion of waste cinder banks, tailings, and slag heaps. Although most large smelters are equipped with efficient dust and fume collection systems that claim 98 percent recovery (*64*), the recovered flue dusts are sometimes stored in unprotected waste cinder banks, where leaching and erosion by rainwater result (*78*). Despite efficient stack collection systems, aerial fallout of lead has resulted in severe local contamination. Leaves of post oak (*Quercus stellata*) and shortleaf pine (*Pinus echinata*) within 0.5 mile of a lead smelter in Missouri contained levels of lead as high as 8,125 and 11,750 ppm (*7*). Samples of various plant species containing normal lead concentrations could be obtained only beyond a 20-mile radius from the smelter-mining-milling complex. The deaths of 20 horses prompted the analyses of samples of forage grass in the vicinity of another Missouri smelter, in which concentrations as high as 14,700 ppm lead were reported (*7*).

Lead mines associated with limestone or dolomite stratabound deposits (Missouri's Old and New Lead Belts) must pump out 5,000–7,000 gal/min of groundwater in order to operate. The relatively clear water is typically cycled through the mill and flotation concentrators and ends up containing mud, organic flotation agents, and other wastes. This effluent is discharged into valleys formed by dams of coarser mill tailings, and the final effluent is the tailing pond outfall. In the New and Old Lead Belt mining-milling areas, tailing pond outfalls have resulted in the deposition of a dark lead-bearing dolomite mud on stream bottoms; the mud in turn is covered by a gray algal-bacterial slime. Benthic fauna were found to be intolerant of the dolomite mud covering (*78*).

Other environmental sources of lead are landfills or dumps, fly ash from coal-burning power stations, coal combustion, sewage sludge, and application of pesticides containing lead (*47*). Small emissions occur from lead oxide manufacturing and fuel oil combustion (*39*). Coal mining could contribute significant quantities of lead to the environment during flood erosion (*78*).

Upon entering natural waters, most lead is precipitated to the sediment bed as carbonates or hydroxides (*80*). Laboratory studies have shown that lead compounds can be transformed to tetraalkyllead, but the exact mechanism is still unclear. Wood et al. (*90*) proposed a Type I microbial methylation reaction for lead, where the high

redox potential of the Pb IV/Pb II redox couple causes Pb IV to act as an attacking electrophile. Subsequent heterolytic cleavage of the Co–C methylcobalamin bond results in the transfer of a carbanion methyl group to the more oxidized form of the element. Jarvie et al. (*25*), however, were unable to achieve methylation of trimethyllead salts and lead nitrate by this microbial pathway and, instead, proposed a chemical mechanism for conversion of the compounds to tetramethyllead in active anaerobic sediments. Other workers (*51*) have demonstrated the methylation of lead(II) compounds to tetramethyllead by microorganisms, which suggests other routes of methylation besides the mentioned microbial and chemical routes. It is not now known whether lead, like mercury, can accumulate through the food chain as an alkylated entity. Because divalent lead is the principal form accumulated by aquatic animals, the possibility of methylation of ionic lead in vivo cannot be disregarded (*80, 53*). Tetraalkyllead compounds have been found in various marine tissues (*53*).

MERCURY

Mercury has an impressive list of uses encompassing many different types of industry and has almost 3,000 distinct applications (*12*). The largest end user in the United States is the electrical apparatus industry, which accounts for 42 percent of total consumption and includes the manufacture of mercury batteries and alkaline energy cells, vapor discharge lamps, rectifiers, and switches. The second greatest use (16 percent) is in the electrolytic preparation of caustic soda and chlorine (chloralkali industry), where the continuous-flow mercury cathode cell still accounts for about 20 percent of total chloralkali-producing capacity (*4*). Mercury consumption in the United States for chloralkali purposes has been reduced sharply since the 1960's for at least three reasons: a decrease in the number of new mercury cell chloralkali plants, modification of existing plants to reduce mercury losses, and conversion of some plants to the diaphragm process. The paint industry consumes 13 percent of the mercury used in the United States, mostly for mildew proofing (*58*). Industries manufacturing industrial control instruments consumed about 8 percent of U.S. mercury supplies in the manufacture of switches, relays, gauges, pump seals, and valves. Other uses, which account for about 15 percent of total mercury consumption, include those in agriculture, dentistry, general laboratory applications, and pharmaceuticals (*4*). Mercury consumption for pesticide use in agriculture is down sharply from the late 1960's, but a relatively small number of mercury pesticide formulations are currently available (*5, 58*). The U.S. paper and pulp industry no longer uses mercury as a slimacide, but still may be consuming mercury at the combined chloralkali-pulping operations (*12*).

There are two primary ways mercury reaches the aqu ic environment: pre-1975 chloralkali operations a pre-1972 paper-pulping operations. Although the int duction of mercury to the environment from these dustries is now relatively small, stream and lake se ments contaminated from discharges 10–15 years a are a persistent mercury source, and methylation anaerobic microbes initiates bioconcentration and fo chain bioaccumulation (*12*). Seepage from some wa disposal areas of closed chloralkali plants continues contaminate streams and reservoirs (*56*). Higher-th background mercury sediment concentrations have b found more than 100 miles downstream from a s thetic fiber operation that stopped using mercury years ago (*3*).

Although U.S. mercury consumption and indust mercury loss have been reduced from early 1970 lev mercury contamination associated with increased c and crude oil production may pose future proble Fossil fuels contain from 10 ppb to several ppm m cury, depending on the coal type (*12*). Inasmuch the United States is preparing for a dramatic intensif tion of coal mining, combustion, and conversion appears likely that an environmental mercury prob will be present for some time to come.

Bacteria present in most natural waterways can con mercury to methylmercury. Ridley et al. propose Type I microbial methylation reaction for mercury is very similar to that already mentioned for lead (*90*). Most of the mercury in fish exists as methyln cury derived largely from food. Some authors h suggested that water, as well as food, is a major sou of methylmercury in fish (*80*).

ARSENIC

Arsenic occurs in association with complex base-m ores, chiefly those of copper, lead, gold, and to a le extent, cobalt and tin (*60, 66*). The element is a mi constituent of those ores and is regarded as a trou some impurity in smelting and refining of base me The recovery of arsenic in residues from fumes, sl mings, and flue dusts involves sophisticated technol and is costly and relatively inefficient. As a result, refinery incentive for arsenic recovery is closely co lated with concurrent economics and market conditi In 1978, all domestic production of arsenic was c fined to the copper smelting-refining complex of American Smelting and Refining Company (ASARC in Tacoma, Washington. Anaconda, another large Nc western copper smelting company located in Bu Montana, has arsenic-refining facilities that have mained unused for the past several years. Bec domestic arsenic production is so limited and availab is so closely tied to prevailing copper prices, the Un

es historically has met most of its requirements for nical compounds by importation (*60*). For example, nestic production supplied only 10.5 percent of total . arsenic demand in 1973 and about 50 percent in 8 (*60, 66*).

nost all arsenic (97 percent) enters end-product nufacturing in the form of white arsenic or As_2O_3. e other 3 percent is in the metallic form and is used an additive in specialized lead and copper alloys. hty-two percent of white arsenic is consumed in the nufacture of agricultural pesticides, such as lead enate, calcium arsenate, sodium arsenite, and organic enicals that are used as insecticides, herbicides, gicides, algicides, desiccants, and defoliants (*60*). ganoarsenical compounds include cacodylic acid, di- ium methanearsonate (DSMA), monosodium meth- arsonate (MSMA), and sodium cacodylate (*5, 60*). e only extensive use of arsenic that is not based on toxicity is in the glass industry, where it is used as a olorizer and as a constituent of opalescent glass and mels. Other small uses (*60*) are in the paint industry gments), pyrotechnics (constituent of fireworks), rmaceuticals (treatment for skin disorders and ping sickness), electronics (diodes, transistors, and rs), and the metals industry (as an additive to rous alloys to increase cast iron strength).

enic enters the aquatic environment by four primary tes: (1) Dissemination by air pollution. Because of complexity, inefficiency, and expense of removing enic from smelter stack gases, the element has be- ne a major air pollution problem in states having elting-refining operations (*60*). Coal combustion is ther important source of arsenic to the air. (2) elter solid waste disposal. Because no domestic tallurgical plants, except ASARCO, process commer- l arsenic, the disposal of fumes, skimmings, and flue sts could constitute a solid waste pollution problem ecting both soil and water. (3) Arsenical pesticides. ntinued use is expected for many years to meet the nand for effective pest control in the face of expand- agricultural production (*60, 66*). (4) Geologic. cause arsenic is found in association with specific logic formations of volcanic origin, ground and sur- e waters in some areas of the western United States e high arsenic levels (*31*).

enic occurs in natural waters primarily in the enate-arsenite forms (*27, 79*). Inorganic forms of enic can be methylated by various microorganisms, luding fungi, methanogenic bacteria, yeasts, and cellular algae (*43*). Evidence suggests that arsenic s in the lower oxidation states perform a free-radical ck (homolytic cleavage) on the Co–C bond of hylcobalamin or nucleophilic attack on *S*-adenosyl- methionine, as well as on methylcobalamin (*49, 90*). Fish apparently can biosynthesize organoarsenic com- pounds within the gastrointestinal tract (*34, 43*). How- ever, the main source of arsenic for fish is primarily organoarsenic compounds that are synthesized at lower stages in the food chain (*34*). Generally, arsenic is not biomagnified in aquatic food chains. Penrose et al. (*44*) suggested that organisms at each trophic level convert inorganic arsenic to a detoxified organic form, organisms at the next higher trophic level then rapidly excrete the ingested organic arsenic, precluding food chain bioaccumulation.

SELENIUM

In 1978, all primary selenium was produced as a by- product from the processing of copper refinery slimes to recover gold, silver, and tellurium. Three copper refineries (AMAX Copper, Inc., Carteret, New Jersey; ASARCO Inc., Amarillo, Texas; and Kennecott Copper Corp., Magna, Utah) accounted for all domestic pro- duction of selenium (*62, 66*). Secondary production, or recycling, was limited; only about 1 percent of the 1978 consumption was recovered from xerographic and rectifier scrap and chemical waste products. Domestic consumption of selenium decreased steadily from 1974 to 1977 and increased slightly in 1978 (*66*). Major end uses of selenium in 1978 (*66*) were in electronic and photocopier components (35 percent), glass manufac- turing (30 percent), and chemicals and pigments (25 percent). The electronics industry used selenium in dry- plate rectifiers for many years, but silicon, germanium, and cadmium have largely replaced it in these applica- tions. The use of metal drums coated with photocon- ducting amorphous selenium in the dry photographic process of xerography has become a major end use of the metal. Selenium has the property of converting light energy directly into electrical energy—a property that has enabled the development of numerous photocell devices, such as photographic exposure meters and solar batteries (*41*).

The glass and ceramics industry adds selenium to glass melt to control final product color. Selenium is used to neutralize green tinting caused by iron impurities, resulting in the manufacture of clear glass. Addition of more selenium to the melt produces a pink-to-ruby red glass. Its use in dark-colored glass in buildings and vehicles to reduce glare and heat transfer is increasing.

A large number of selenium compounds have commer- cial uses, ranging from semiconductor research to anti- dandruff agents in shampoos. Much of the selenium consumed by the chemical industry is used to prepare pigments containing selenium. A major class of pigments is the cadmium sulfoselenide compounds, which have superb resistance to sunlight, heat, and chemical attack (*41*).

The primary sources of selenium in the environment are geologic and industrial. Selenium closely resembles sulfur chemically, and sulfur or sulfide deposits of bismuth, copper, iron, lead, mercury, silver, and zinc sometimes contain as much as 20 percent selenium (*68*). Other sulfate minerals, such as barite and jarosite, contain selenium, and native sulfur can contain more than 0.1 percent selenium. Other geologic formations containing selenium include sandstones, limestones, and shales. Sandstones containing > 100 ppm selenium have been found in Wyoming (*17, 91*). The Niobrara formation, a limestone region of South Dakota, contains > 40 ppm selenium in chalky shales and marls. Phosphate rocks associated with limestone may contain from 1 to 300 ppm selenium, suggesting the occurrence of selenium in phosphate fertilizers. Of the sedimentary rocks, shales have been mainly responsible for cases of selenium poisoning in animals in the United States. For example, vegetation in some areas of the Pierre Formation near the Missouri River in southern South Dakota has potentially toxic selenium concentrations. These shales are considered highly seleniferous and have selenium levels ranging from 1 to > 30 ppm (*41*).

Industry releases selenium to the environment through combustion of coal and fuel oil, nonferrous smelting and refining processes, metal refining, and glass manufacturing. Domestic coal averages 3.2 ppm selenium (*46*). Average selenium concentrations are 1.3 ppm in lignite coal and 2.08 ppm in central and western U.S. coals (*42*). In one study, about 53 percent of the selenium in coal was emitted to the atmosphere during combustion, either as volatilized selenium or in association with fly ash particles too small to be trapped by precipitators (*41*). Coal combustion accounted for 62 percent of the total industrial emission of selenium in 1970 (*41*). EPA found that crude oil contained an average of 0.4 ppm selenium (*41*), and Hashimoto et al. (*19*) reported averages of 0.92 ppm in raw petroleum and about 1.0 ppm in heavy petroleum. Smelting and refining of nonferrous metals produces slag heaps and tailing dumps containing high concentrations of selenium. Thus, solid wastes from metal mining and milling may be a more serious source of selenium pollution than is atmospheric fallout from base metal smelting and refining (*41*). Selenium emissions are high in glass manufacturing, because the high temperature of the glass melt volatilizes selenium (*41*).

Attempts to correlate atmospheric concentrations of selenium with the location of industrial selenium emissions have generally met with only limited success. For example, Traversy et al. (*24*) found the highest selenium concentrations in precipitation samples at or near highly industrialized locations in the Great Lakes region, and Copeland (*10*) showed that selenium concentrations in Lake Michigan zooplankton increased near Chicago. In these two situations, the effects of selenium from ind trial emissions appeared to be localized, and nat sources of selenium may generally be more import than anthropogenic ones (*41*).

Ingestion may be the most important mode of seleni uptake by aquatic biota, but more research is nee to confirm this possibility (*56*). Phillips and Ru (*80*) concluded that the poor survival of stocked in a highly seleniferous Colorado lake was due to accumulation of excess selenium through the f chain. Several species of molds and microorganisms methylate selenium (*41*). Little is known, howe about selenium methylation pathways in the aqu environment.

Methods and Materials

SAMPLE COLLECTION

Fish were collected by FWS biologists, state fish game personnel, and local commercial fishermen, used a variety of nonchemical collecting techniq (e.g., trapping, electrofishing, seining). After the t length and weight of each fish had been determir the sample composites were separately wrapped aluminum foil, frozen, and shipped to CNFRL.

Fish from frozen composites were reduced to ice-c sized blocks with a Hobart Model 5212 food ser band saw. Blocks were passed twice through a l (Hobart 1 hp Model 4822) or small (Hobart ¼ Model 4612) meat grinder, depending on total c posite size and weight. Between sample homogen tions, the band saw and disassembled grinder com nents were washed with hot water or steam and rin with deionized water. About 400-g portions of gro fish were placed in an acid-cleaned glass jar wit Teflon-lined cap and stored in a freezer. In 1976, fro 10-g portions of 83 samples representing 44 stat were sent to the EPA Region VII Laboratory in Kar City for digestion and analysis. All samples colle in 1977 were prepared and analyzed at CNFRL.

DIGESTION AND ANALYSIS OF SAMPLES COLLECTED IN

Arsenic, Cadmium, and Lead—Five grams of tha fish homogenate were placed in 10-in. Technicon dige tubes. Ten milliliters of concentrated HNO_3 was ad to each tube, and the sample–acid mixture was hel room temperature for 1 hr to reduce foaming w heat was applied. Samples were heated on a Techni Model BD-40 block digestor at 150°C for 60 min and at 250°C for 90 minutes. The gradual incr from room temperature to 150°C allowed the sam to dissolve with little foaming; heating to 250°C required to overcome reflux action at the constric of the digestor tube. Samples were heated to dry

lecompose lipid material. If the sample was black n dryness was reached, it was removed from the stor, cooled, treated with an additional 10 ml con- rated HNO_3, and returned to a cold digestion block for 90 minutes at 250°C. Subsequent addition of nl portions of acid was continued until the appear- e of a white residue indicated complete digestion. white residue was dissolved with 10 ml 10 percent O_3 at 90°C. Dilution to 50 ml with deionized water vided a final acid matrix of 2 percent HNO_3. This edure allowed simultaneous preparation of up to tissue samples, with only HNO_3 as the oxidizing . Unfortunately, the recovery of selenium by this hod was incomplete, precluding the use of selenium originating from the 1976 samples.

tissue digestates (2 percent HNO_3) were analyzed a Jarrell-Ash Model 975 Atomcomp inductively pled argon plasma (ICAP) optical emission spectro- tometer. Samples were introduced in a cross-flow ilizer at 1.4 ml/min by a Gilson eight-channel ip. An autosampler maintained sample flow at 30 ples/hr. Other pertinent ICAP parameters follow:

Incident RF power:	1.1 kW
Reflected RF power:	20 W
Observation height:	15 mm above load coil
Sample argon flow rate:	0.5 l/min
Coolant argon flow rate:	18 l/min

ection limits for arsenic, cadmium, and lead were , 0.05, and 0.10 mg/kg, respectively.

cury—One gram of sample was placed on the om of a dry BOD bottle; 1 ml each of concentrated O_4 and HNO_3 was added, and the bottle was placed water bath at 58°C until the tissue was completely olved (30–60 minutes). The bottle was cooled to in an ice bath, and 1 g $KMnO_4$ crystals was added maintain oxidizing conditions. The digestate was ed, loosely capped, and held overnight at room perature (*75*).

cold-vapor atomic absorption method for mercury lysis (*75*) can be summarized as follows: Each state was diluted with distilled water to a final ume of 125 ml, and 6 ml sodium chloride–hydrox- nine sulfate solution was added to reduce excess nanganate. After 30 seconds, 5 ml stannous sulfate tion was added and the bottle was immediately ched to the aeration apparatus. Mercury vapors were pt into a Plexiglass absorption cell and measured a Coleman MAS-50 mercury analyzer system (*26*). ection limit was 0.02 mg/kg.

ESTION AND ANALYSIS OF SAMPLES COLLECTED IN 1977

cury, Cadmium, and Lead—Mercury, cadmium, lead residues in fish were oxidized by acid digestion in heated, enclosed glass bombs (45-ml acylation tubes, Regis Chemical Co.), which allow oxidation and recovery of all three meals with a single digestion. Digestion tubes were cleaned by successive rinsing with concentrated HNO_3, HCl, and ultrapure water (15–18 megohm-cm specific resistivity). Cleaned tubes were oven-dried, cooled, and covered with sheet polyethylene before the sample was introduced. Teflon caps for the tubes were soaked successively for several hours in boiling concentrated HNO_3 and HCl, followed by a final rinsing with ultrapure water.

Approximately 2 g (±0.01 g) thawed fish homogenate was weighed into tared digestion tubes. Sub-boiling-point, distilled concentrated HNO_3 (2 ml) and double-distilled $HClO_4$ (1 ml) were added and the mixture was vortex mixed, capped loosely, and allowed to predigest overnight at room temperature (*1*). The mixture was vortex mixed again, and the bomb was sealed and placed in a heated aluminum block (65°C) for 48 hours. The sample was quantitatively transferred and diluted to a final weight of 50 ± 0.01 g with 1 percent HCl. Diluted digestates were stored in cleaned polypropylene bottles (*38*) for cadmium and lead analyses or borosilicate test tubes for mercury analysis (*14*).

Mercury was determined by flameless atomic absorption spectrophotometry (AAS) (*28*). The analytical system was automated with a Technicon Autosampler IV and Proportioning Pump III, with appropriate pump tubes, pulse suppressors, mixing coils, and locally fabricated phase separator (Figure 2). Atomic absorption measurements were made on a Perkin-Elmer Model 305B spectrophotometer, using the 253.7-nm resonance line from an electrodeless discharge lamp. Scale expansion up to 10× was used when appropriate. The detection limit was about 0.01 mg/kg. The absorption cell was constructed from a Pyrex tube about 100 mm long and 6 mm I.D. with quartz end windows. Side arms of 4-mm-O.D. Pyrex were attached near each end of the cell for vapor passage. The cell was heated to 35–40°C with a high-intensity radiant heat projector (Cole-Parmer Dyna Lume Model 3151–6) to prevent condensation on the end windows.

Lead and cadmium were measured with a Perkin-Elmer Model 305B spectrophotometer equipped with an HGA–2100 graphite furnace and an AS–1 autosampling system. Table 2 specifies the instrument conditions for measuring each element. A four-point additions procedure to correct for chemical and matrix interferences was performed on each diluted digestate:

(1) Digestate + 0.00 ppm Pb; + 0.00 ppm Cd
(2) Digestate + 0.02 ppm Pb; + 0.002 ppm Cd
(3) Digestate + 0.04 ppm Pb; + 0.004 ppm Cd
(4) Digestate + 0.06 ppm Pb; + 0.006 ppm Cd

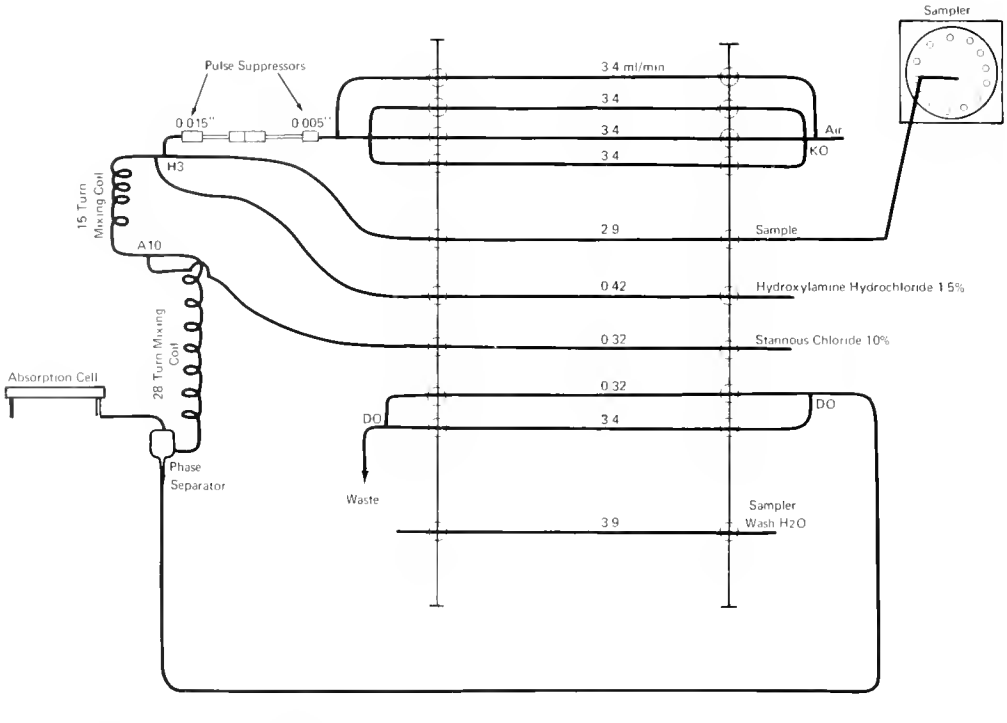


FIGURE 2. *Flow scheme for automated digestion and determination of mercury.*

TABLE 2. *Instrumental conditions for atomic absorption measurement of cadmium, lead, arsenic, and selenium in freshwater fish from the United States, 1977*

Condition	Cadmium	Lead	Arsenic	Selenium
Wavelength, nm	228.8	283.3	193.7	196.0
Spectral band width, nm	0.7	0.7	0.7	2.0
Temperature ramping	no	no	no	no
Drying time, °C (time, seconds)	90(30)	90(30)	—	—
Charring time, °C (time, seconds)	400(20)	400(20)	—	—
Atomization temp., °C (time, seconds)	2200(7)	2300(7)	—	—
Purge gas and flow (ml/minute)	Ar(20)	Ar(20)	Ar	Ar
Gas mode	normal	normal	EDL	—
Source	EDL	EDL	no	EDL
Background correction	D₂Arc	D₂Arc	5 mv	no
Scale expansion	3×	10×	PR I	3×
Recorder full scale	10 mv	10 mv	—	10 mv
AS-1 injection volume	10 µl	10 µl	none	—
Tube type	uncoated	uncoated	—	—
Quartz cell temp., °C	—	—	—	800
Reductant	—	—	1000	$NaBH_4$
Reaction flask volume, ml	—	—	$NaBH_4$	10
Analysis cycle time	—	—	10	PR 11
Detection limit, mg/kg	0.01	0.1	0.05	0.05

The average of two injections was used as one additions point. Correlation coefficients (r) below 0.999 for the line of best fit were rejected, and corresponding digestates were rerun.

Arsenic and Selenium—For arsenic digestions, approximately 2 g (±0.01 g) thawed fish homogenate was weighed into a tared, 100-ml Kjeldahl flask. Sub-boiling-point, distilled concentrated HNO_3 (5 ml) was ad the flask was loosely covered with sheet polyethyl and the mixture was predigested overnight at r temperature. Subboiled HNO_3 (25 ml) and do distilled $HClO_4$ (3 ml) were added, and the flask heated on a micro-Kjeldahl rack to drive off H After digestion had proceeded through the $HClO_4$ f ing and reaction stages, additional heat was applie drive off the acid. When about 0.5 ml $HClO_4$ remai the flasks were removed from the heat, cooled, contents were diluted with 3 percent HCl to volumes of 100 ml. Diluted digestates were store linear polyethylene bottles before analysis.

Predigestion sample preparation for selenium was same as that for arsenic. Following predigestion, 2 subboiled HNO_3 and 1 ml double-distilled $HClO_4$ added and the flask was heated to drive off H Digestion was allowed to proceed through $HClO_4$ f ing and reaction stages. The $HClO_4$ reaction stage characterized by an initial foaming with subseq clearing (decoloration) of the digestate. Care was t to terminate the digestion before $HClO_4$ was driver (*88*). Cooled digestates were diluted to 100 ml wi percent HCl and transferred to linear polyethy bottles.

Arsenic and selenium were analyzed with a Pe Elmer MHS–1 mercury-hydride system in conjunc with a Perkin-Elmer Model 305B spectrophotom

rument conditions for measuring the elements are d in Table 2. On the MHS–1 system, a reaction containing 10 ml diluted digestate was installed a polypropylene manifold. Argon was recycled in osed circuit through the reaction flask and a heated rtz cell. An $NaBH_4$ pellet (Alfa Ventron) was dis- ed into the flask and reacted with the digestate to form hydrogen, which reduced the metals to tile arsine and hydrogen selenide. The gas stream ied the hydrides into the heated quartz cell where were decomposed and measured. Complete analy- from addition of the digestate to readout on the trophotometer, proceeded automatically for each al.

TISTICAL TREATMENT

wo-way analysis of variance (ANOVA) with sta- and years as main effects was used to test two hypotheses: (1) There was no significant difference etal residue concentrations due to location, and (2) e was no effect due to time (1972–73 vs. 1976–77). eneral, stations were confounded by species differ- s across years. The following adjustments were e in the data sets before statistical testing:

a) Absolute values were used for all less than (<) ata.

b) Selenium values for 1972 and 1973 were avail- ble for only 44 of the stations sampled in 1977. herefore, the two-way ANOVA data set for selen- m consisted of 44 stations and 3 years (1972, 1973, nd 1977).

c) The detection limit for cadmium in 1977 sam- es (0.01 ppm) was one-fifth the limit in 1972 and 976 samples (0.05 ppm). Therefore, we adjusted l 1977 cadmium values <0.05 mg/kg to 0.05, to iminate bias due to differences in detection limits. he two-way ANOVA data set consisted of 82 atching stations and two time periods (1972 vs. 976–77).

d) The two-way ANOVA data set for lead and mer- ury also consisted of 82 stations and two time periods 972 vs. 1976–77).

e) Detection limits for arsenic were 0.05 ppm for e 1972 and 1977 samples and 0.25 ppm for 1976 mples. Because most of the 1977 arsenic concentra- ons were <0.25 mg/kg, the results of arsenic residue alyses for the 1976 stations were not included in e two-way ANOVA set; consequently, only 44 atching stations and 2 years (1972 vs. 1977) mained.

error sum of squares to estimate variation within vidual samples was obtained from a preliminary way ANOVA with an unbalanced cell size (*52*). method of weighted squares of means (*52*) was used to make inferences about main effects. All analyses were performed on log-transformed data [$\log_{10}(1 + \text{conc.})$]

Results

The precision and accuracy of the 1976–77 trend-monitoring analyses were determined by duplicate sample sets and samples containing inorganic spikes. A duplicate sample set is defined as two aliquots of tissue from the same sample composite carried through the entire digestion-analytical procedure. The average difference of duplicate sets was within 25 percent for all elements, except for mercury in 1976 samples (37 percent) and lead in 1977 samples (70 percent). Average recoveries from spiked samples were within 10 percent of the added quantity, except for mercury in 1976, for which average recovery was 64 percent (Table 3a). Analyses of reference materials yielded average values within the specified certification ranges for all elements (Table 3b).

TABLE 3. *Quality control results of the 1976–77 trend-monitoring analyses*

a. Recoveries of elements from spiked samples

	1976				1977			
ELEMENT	*n*	CONCN., µG/ML	MEAN RECOVERY, %	S.D.	*n*	CONCN., µG/ML	MEAN RECOVERY, %	S.D.
Cadmium	14	0.1	92	10	7	0.004	106	7
Lead	13	0.1	91	10	8	0.040	102	12
Mercury	6	0.001	64	15	8	0.010	98	12
Arsenic	14	0.1	98	17	17	0.004	94	10
Selenium	—	—	—	—	15	0.004	101	17

b. Reference materials—1977

REFERENCE MATERIAL [1]	ELEMENT	CERTIFIED CONCN. RANGE, µG/G	*n*	MEAN CONCN., µG/G	S.D.
NBS Bovine liver	cadmium	0.27 ± 0.04	11	0.31	0.02
NBS Bovine liver	lead	0.34 ± 0.08	9	0.38	0.05
NBS Bovine liver	mercury	0.016 ± 0.002	12	0.016	0.005
FDA Cod	arsenic	11 ± 2	13	10.5	1.37
NBS Albacore tuna	arsenic	3.3 ± 0.4	18	3.27	0.35
FDA Cod	selenium	1.4 ± 0.4	13	1.36	0.21
NBS Albacore tuna	selenium	3.6 ± 0.4	18	3.68	0.40

NOTE: *n* = number of samples; S.D. = standard deviation; FDA = Food and Drug Administration; NBS = National Bureau of Standards.

Locations, species sampled, average size, and trace element concentrations for 1976–77 trend-monitoring samples are listed in Table 4. Eighty-three samples collected in 1976 were analyzed by the EPA Region VII Laboratory. The 1977 samples (157 samples of 163 collected) were analyzed by CNFRL. The data ranges in mg/kg wet weight were Pb, 0.10–4.92; Hg, 0.01–0.84; Cd, 0.01–1.04; As, 0.05–2.92; and Se, 0.05–

2.87. To examine potential temporal trends of trace element concentrations, 1976–77 data for lead, mercury, cadmium, and arsenic were compared with those reported by Walsh et al. (*87*) for the same stations in 1972. Because selenium concentrations were not ported for the 1976 collections, 1977 selenium con trations were compared with those from the s stations in 1972 and 1973.

TABLE 4. *Concentrations of cadmium, lead, mercury, arsenic, and selenium in whole-fish samples collected for the Nati Pesticide Monitoring Program, 1976–77*

Station Number and Location (Figure 1)	Species [1]	No. of Fish	Average Size		Residues, mg/kg Wet Weight				
			Length, inches	Weight, lb	Cadmium	Lead	Mercury	Arsenic	Sele
ATLANTIC COASTAL STREAMS									
1. Pennobscot River, Old Town, Me.	white perch	5	9.8	0.5	<0.05	0.12	0.23	<0.25	
	white sucker [2]	5	14.3	1.18	—[3]	—	—	—	
		5	14.1	1.16	<0.05	0.13	0.20	<0.25	
51. Kennebec River, Hinckley, Me.	yellow perch	5	9.6	0.36	<0.05	0.13	0.34	<0.25	
	white sucker	5	14.2	1.22	0.06	0.13	0.16	<0.25	
		5	14.5	1.22	—	—	—	—	
52. Lake Champlain, Burlington, Vt.	northern pike	5	17.8	1.48	<0.05	<0.10	0.21	<0.25	
	brown bullhead	5	11.1	0.8	<0.05	0.34	0.04	<0.25	
		5	10.7	0.64	—	—	—	—	
53. Merrimac River, Lowell, Mass	largemouth bass	4	9.7	0.48	<0.05	0.21	—	<0.25	
	white sucker	5	11.8	0.64	0.06	1.23	<0.02	<0.25	
		5	12.6	0.76	—	—	—	—	
2. Connecticut River, Windsor Locks, Conn.	white perch	5	9.2	0.46	0.11	0.40	0.27	<0.25	
	white catfish	5	11.6	0.74	0.25	1.19	0.08	<0.25	
		5	12.1	0.88	0.16	0.79	0.12	<0.25	
3. Hudson River, Poughkeepsie, N.Y.	largemouth bass	5	12.1	0.92	<0.05	0.10	0.09	<0.25	
	goldfish	5	11.3	1.18	0.20	3.07	0.05	<0.25	
		5	11.1	1.08	0.32	3.83	0.06	0.68	
54. Raritan River, Highland Park, N.J.	carp	5	17.3	3.14	<0.05	0.23	0.05	<0.25	
4. Delaware River, Camden, N.J.	white perch	5	7.0	0.2	0.22	1.57	0.14	0.21	1.
	white sucker	5	15.4	1.7	0.20	0.98	0.12	0.10	0.
		5	15.2	1.6	0.16	1.17	0.14	0.10	0.
5. Susquehanna River, Conowingo Dam, Md.	white perch	5	6.3	0.1	0.05	0.44	0.10	0.28	1.
	channel catfish	6	10.7	0.4	0.04	0.19	0.05	<0.05	0.
	carp	5	16.6	1.9	0.02	0.34	0.08	0.11	0.
		5	16.7	1.9	0.05	0.26	0.11	0.11	0.
6. Potomac River, Little Falls, Md.	largemouth bass	5	12.2	1.2	<0.01	0.15	0.20	<0.05	0.
	carp	5	19.0	3.9	0.04	0.78	0.12	0.13	0.
		5	17.5	2.9	0.04	0.33	0.09	0.16	0.
55. James River, Richmond, Va.	smallmouth bass	5	9.2	0.4	0.03	0.14	0.12	0.06	0.
	redhorse	4	16.0	1.8	0.81	0.32	0.25	0.10	0.
		4	17.5	2.2	0.36	0.15	0.18	0.07	0.
7. Roanoke River, Roanoke Rapids, N.C.	white catfish	5	11.1	0.54	<0.05	0.16	0.05	<0.25	
		5	12.2	0.86	—	—	—	—	
8. Cape Fear River, Elizabethtown, N.C.	gizzard shad	5	13.7	1.06	0.08	0.40	0.04	0.26	
		5	13.3	0.96	—	—	—	—	
56. Pee Dee River, Dongola, S.C.	white catfish	4	15.1	1.35	—	—	—	—	
		5	14.7	1.26	<0.05	0.20	0.45	<0.25	
9. Cooper River, Summerton, S.C.	striped bass	2	26.0	7.3	—	—	—	—	
	channel catfish	5	13.3	0.86	<0.05	0.28	<0.02	<0.25	
		5	13.9	0.8	—	—	—	—	
10. Savannah River, Savannah, Ga.	largemouth bass	4	10.9	0.83	<0.05	<0.10	0.12	<0.25	
	channel catfish	3	15.1	1.33	0.08	<0.10	0.06	0.63	
	white catfish	3	13.8	1.63	0.17	<0.10	0.14	1.46	
	carp	4	14.6	1.83	—	—	—	—	
57. Altamaha River, Doctortown, Ga.	brown bullhead	5	14.6	1.56	—	—	—	—	
	channel catfish	3	17.4	1.9	<0.05	0.30	0.14	<0.25	
	largemouth bass	5	15.4	2.1	<0.05	0.18	0.34	<0.25	
11. St. Johns River, Welaka, Fla.	inactive [4]								
12. St. Lucie Canal, Indiantown, Fla.	largemouth bass	5	15.3	2.26	<0.05	<0.10	<0.02	<0.25	
	white catfish	5	13.4	1.24	<0.05	0.14	0.06	<0.50	
	channel catfish	3	19.8	3.03	—	—	—	—	

BLE 4. (cont'd.). *Concentrations of cadmium, lead, mercury, arsenic, and selenium in whole fish samples collected for the National Pesticide Monitoring Program, 1976–77*

TATION NUMBER AND LOCATION (FIGURE 1)	SPECIES [1]	NO. OF FISH	AVERAGE SIZE LENGTH, INCHES	AVERAGE SIZE WEIGHT, LB	RESIDUES, MG/KG WET WEIGHT CADMIUM	LEAD	MERCURY	ARSENIC	SELENIUM
Androscogin River, Lewiston, Me.	yellow perch	5	9.3	0.38	<0.05	0.16	0.20	<0.25	—
	white sucker	5	12.2	0.68	<0.05	0.24	0.11	<0.25	—
		5	12.4	0.38	—	—	—	—	—
			GULF COAST STREAMS						
Suwanee River, Old Town, Fla.	inactive								
Apalachicola River, Jim Woodruff Dam, Ala.	largemouth bass	5	14.1	1.56	0.02	0.18	0.11	0.11	0.23
	spotted sucker	5	17.5	2.38	0.02	<0.10	0.11	<0.05	0.52
		5	18.4	2.82	0.03	0.16	0.17	0.07	0.52
Alabama River, Chrysler, Ala.	mixed species [5]	3	13.5	1.77	0.02	0.19	0.16	0.13	0.34
	largemouth bass	5	15.9	2.3	0.03	<0.10	0.55	0.20	0.31
	freshwater drum	8	10.2	0.66	0.03	0.15	0.07	0.21	0.65
Tombigbee River, McIntosh, Ala.	mixed species [6]	4	13.9	2.3	0.03	0.20	0.18	0.18	0.44
	freshwater drum	5	11.7	0.78	0.04	0.13	0.50	0.09	0.77
Mississippi River, Luling, La.	freshwater drum	5	13.0	1.1	0.03	0.17	0.03	0.26	0.44
		5	14.1	1.58	0.03	0.12	0.10	0.13	0.45
		5	14.3	1.58	0.02	0.17	0.12	0.18	0.67
Brazos River, Richmond, Tex.	alligator gar	3	18.5	1.0	0.02	<0.10	0.31	0.08	0.24
	striped mullet	5	14.1	1.3	0.03	0.48	0.01	1.48	0.40
	striped mullet [2]	5	13.3	1.1	0.02	0.46	0.02	1.40	0.24
	gizzard shad	5	9.9	0.4	0.01	0.65	0.04	0.60	0.26
Colorado River, Wharton, Tex.	largemouth bass	3	9.4	0.4	0.01	0.10	0.12	0.05	0.44
	channel catfish	5	12.4	0.6	0.06	0.14	0.03	<0.05	0.30
		5	13.3	0.8	0.04	<0.10	0.05	0.07	0.29
	gizzard shad	5	12.2	0.8	0.01	0.20	0.01	0.85	0.32
Nueces River, Mathis, Tex.	largemouth bass	5	13.3	1.5	<0.01	<0.10	0.18	0.21	0.29
	gizzard shad	5	11.3	0.6	0.03	0.61	0.02	0.53	0.29
		5	11.3	0.7	0.03	0.56	0.02	0.37	0.47
Rio Grande, Brownsville, Tex.	channel catfish	3	12.6	0.63	—	—	—	—	—
	gizzard shad	5	11.6	0.56	—	—	—	—	—
		5	11.8	0.52	—	—	—	—	—
Rio Grande, Elephant Butte, N.M.	not collected [7]								
Rio Grande, Alamosa, Colo.	brown trout	5	11.18	0.62	—	—	—	—	—
	white sucker	5	10.7	0.52	<0.05	0.39	0.03	<0.25	—
		5	10.8	0.52	<0.05	0.10	0.04	<0.25	
Pecos River, Red Bluff Lake, Tex.	not collected								
San Antonio River, McFaddin, Tex.	channel catfish	3	19.2	4.8	0.02	0.25	0.13	<0.05	0.41
	alligator gar	3	22.9	2.2	0.17	0.11	0.28	0.13	0.17
	smallmouth bass	3	18.3	6.6	0.02	0.71	0.06	0.09	0.66
			GREAT LAKES DRAINAGE						
Genessee River, Scottsville, N.Y.	pumpkinseed	5	5.1	0.2	0.03	0.62	0.09	0.06	0.28
	carp	5	15.9	2.3	0.02	0.35	0.04	0.09	0.19
		5	15.5	2.2	0.03	0.23	0.04	0.14	0.37
St. Lawrence River, Massena, N.Y.	smallmouth bass	5	12.6	1.2	0.01	0.14	0.26	0.67	0.45
	white sucker	5	14.1	1.3	0.03	0.41	0.19	0.16	0.31
Lake Ontario, Port Ontario, N.Y.	rock bass	5	8.6	0.5	0.03	0.20	0.36	0.31	0.36
	channel catfish	5	14.1	0.9	0.02	0.22	0.07	0.10	0.30
		5	14.2	0.9	0.04	0.20	0.07	0.16	0.29
Lake Erie, Erie, Pa.	yellow perch	5	8.6	0.4	0.03	<0.10	0.08	0.11	0.67
	white sucker	5	11.3	0.6	0.05	0.19	0.05	0.17	0.69
		5	11.4	0.7	0.05	0.16	0.05	0.17	0.50
Lake Huron, Bay Port, Mich.	carp	5	18.7	3.72	0.04	0.49	0.23	0.10	0.35
	carp [2]	5	17.1	2.9	0.02	0.22	0.05	0.13	0.64
	yellow perch	5	7.6	0.2	0.02	0.23	0.04	<0.05	0.44
		5	7.5	0.2	0.01	0.23	0.03	<0.05	0.34

TABLE 4. (cont'd.). *Concentrations of cadmium, lead, mercury, arsenic, and selenium in whole fish samples collected the National Pesticide Monitoring Program, 1976–77*

Station Number and Location (Figure 1)	Species [1]	No. of Fish	Average Size		Residues, mg/kg Wet Weight				
			Length, inches	Weight, lb	Cadmium	Lead	Mercury	Arsenic	Sele
21. Lake Michigan, Sheboygan, Wis.	bloater	5	10.1	0.52	0.01	0.15	0.03	2.92	0.
		5	10.0	0.56	0.02	0.15	0.04	2.91	0.
	lake trout	5	27.5	6.6	<0.01	<0.10	0.19	1.20	0.
		4	23.8	4.5	0.02	<0.10	0.19	1.33	0.
22. Lake Superior, Bayfield, Wis.	lake trout	6	24.7	5.0	0.02	<0.10	0.43	0.56	0
	lake whitefish	3	20.3	2.86	0.05	<0.10	0.03	0.47	0
102. Lake Superior, Keeweenaw Point, Mich.	bloater	5	10.4	0.60	0.03	0.12	0.11	1.33	0
		5	10.3	0.60	0.30	<0.10	0.10	1.19	0
	lake trout	4	22.0	4.40	0.02	<0.10	0.10	0.39	0.
103. Lake Superior, Whitefish Point, Mich.	lake trout	4	23.9	5.1	0.02	0.14	0.26	0.43	0
	lake whitefish	5	19.2	3.0	0.04	0.29	0.05	0.41	0
		5	19.8	2.8	0.04	0.11	0.07	0.97	0
104. Lake Michigan, Beaver Island, Mich.	bloater	4	11.3	0.6	0.02	0.12	0.04	2.41	0
	lake trout	5	25.7	5.9	<0.01	<0.10	0.27	0.92	0
105. Lake Michigan, Saugatuck, Mich.	bloater	5	11.4	0.6	—	—	—	—	
		5	11.3	0.6	0.03	0.31	0.05	2.30	0
	lake trout	5	24.7	4.7	0.01	<0.10	0.25	0.94	0.
MISSISSIPPI RIVER SYSTEM									
67. Allegheny River, Natrona, Pa.	walleye	3	12.4	0.63	—	—	—	—	
	silver redhorse	5	10.6	0.48	—	—	—	—	
	golden redhorse	5	13.2	0.94	0.07	0.19	0.07	0.26	
23. Kanawha River, Winfield, W.Va.	black crappie	5	6.3	0.14	—	—	—	—	
	carp	5	14.8	1.44	<0.05	<0.10	<0.02	<0.25	
	brown bullhead	5	9.6	0.46	—	—	—	—	
68. Wabash River, New Harmony, Ind.	largemouth bass	5	10.7	0.72	0.06	0.17	—	<0.25	
	carp	5	16.8	2.7	—	—	—	—	
		5	16.1	2.38	0.18	0.22	0.10	<0.25	
24. Ohio River, Marietta, Ohio	sauger	5	13.9	1.18	<0.05	0.26	0.10	<0.25	
	carp	4	17.2	2.92	0.22	2.49	0.05	<0.25	
69. Ohio River, Cincinnati, Ohio	sauger	5	13.7	1.04	<0.05	0.10	0.10	<0.25	
	channel catfish	5	11.1	0.5	—	—	—	—	
		4	15.5	1.3	<0.05	0.42	0.04	<0.25	
	smallmouth buffalo	5	12.2	1.08	—	—	—	—	
		3	13.7	1.8	—	—	—	—	
70. Ohio River, Metropolis, Ill.	largemouth bass	5	14.2	1.72	<0.05	<0.10	0.30	<0.25	
	carp	5	16.5	2.52	—	—	—	—	
		5	16.2	2.12	0.18	0.25	0.15	<0.25	
25. Cumberland River, Clarksville, Tenn.	largemouth bass	4	9.8	0.52	—	—	—	—	
	carp	5	13.4	1.16	—	—	—	—	
	spotted sucker	4	12.2	0.76	—	—	—	—	
71. Tennessee River, Savannah, Tenn.	not collected								
106. Lake Huron, Alpena, Mich.	lake trout	5	23.4	4.3	<0.01	<0.10	0.23	0.51	0.
	white sucker	5	19.0	2.8	0.04	0.39	0.07	0.11	0
		6	16.3	1.9	0.02	0.28	0.03	0.10	0
		5	12.7	0.9	0.02	0.13	0.02	0.16	0
107. Lake St. Clair, Mt. Clemens, Mich.	walleye	5	20.3	2.7	0.06	0.13	0.84	0.24	0.
	carp	5	20.4	4.5	0.15	1.83	0.60	0.13	0
		5	20.1	4.5	0.16	0.78	0.32	0.09	0
108. Lake Erie, Port Clinton, Ohio	walleye	5	15.9	1.6	<0.01	<0.10	0.09	0.36	0.
	carp	5	15.9	2.5	0.03	0.19	0.03	0.15	0.
		5	16.7	2.4	0.03	0.21	0.04	0.21	0
109. Lake Ontario, Roosevelt Beach, N.Y.	inactive								
110. Lake Ontario, Cape Vincent, N.Y.	inactive								
72. Wisconsin River, Woodsman, Wis.	smallmouth bass	5	12.9	1.12	—	—	—	—	
	carp	5	17.2	2.3	0.07	0.23	0.14	<0.25	
		5	17.7	2.46	—	—	—	—	

LE 4. (cont'd.). *Concentrations of cadmium, lead, mercury, arsenic, and selenium in whole fish samples collected for the National Pesticide Monitoring Program, 1976–77*

ATION NUMBER ND LOCATION (FIGURE 1)	SPECIES [1]	NO. OF FISH	AVERAGE SIZE		RESIDUES, MG/KG WET WEIGHT				
			LENGTH, INCHES	WEIGHT, LB	CADMIUM	LEAD	MERCURY	ARSENIC	SELENIUM
Des Moines River, Keosauqua, Iowa	carp	5	15.6	1.94	0.06	0.27	0.07	<0.25	—
		5	15.4	1.94	1.04	0.41	—	<0.25	—
	walleye	3	16.5	1.53	<0.05	<0.10	0.06	<0.25	—
Illinois River, Beardstown, Ill.	black crappie	5	8.2	0.32	<0.05	0.23	0.09	<0.25	—
	carp	5	14.1	1.22	<0.05	0.32	0.05	<0.25	—
		5	14.2	1.40	—	—	—	—	—
Mississippi River, Little Falls, Minn.	walleye	5	11.1	0.5	—	—	—	—	—
	black bullhead	5	8.2	0.32	0.06	0.10	0.32	<0.25	—
		5	7.9	0.28	—	—	—	—	—
Mississippi River, Guttenberg, Iowa	largemouth bass	5	14.1	1.72	<0.05	0.55	0.05	<0.25	—
	carp	5	19.9	3.56	<0.05	0.30	0.05	<0.25	—
		5	21.3	4.48	—	—	—	—	—
Mississippi River, Cape Girardeau, Mo.	white crappie	5	8.7	0.24	<0.05	0.13	0.17	<0.25	—
	carp	5	14.4	1.26	0.45	0.49	<0.02	0.30	—
		5	15.4	1.68	—	—	—	—	—
Mississippi River, Memphis, Tenn.	smallmouth buffalo	3	17.3	2.63	0.02	<0.10	0.04	0.14	0.25
		3	16.4	2.97	0.03	0.13	0.05	0.11	0.33
Arkansas River, Pine Bluff, Ark.	bluegill	5	6.3	0.1	0.02	0.27	0.05	0.12	0.23
	carp	5	19.8	3.78	0.05	0.18	0.07	0.12	0.33
Arkansas River, Keystone Reservoir, Okla.	largemouth bass	5	13.7	1.8	<0.01	<0.10	0.17	0.20	0.67
	carp	5	17.9	2.1	0.12	0.39	0.15	<0.05	0.54
		5	17.8	2.4	0.09	0.44	0.21	0.07	0.65
Arkansas River, John Martin Reservoir, Colo.	inactive								
Verdigris River, Oologah, Okla.	white bass	5	12.4	0.9	0.02	0.11	0.07	0.55	0.60
	carp	5	17.8	2.5	0.54	0.75	0.09	0.08	0.50
		5	16.1	2.1	0.78	0.82	0.09	0.09	0.44
Canadian River, Eufaula, Okla.	white bass	5	13.9	1.4	<0.01	<0.10	0.34	0.65	0.35
	river carpsucker	5	13.0	1.1	0.02	0.38	0.13	0.08	0.28
		5	12.2	0.7	0.02	0.38	0.06	0.16	0.38
White River, DeValls Bluff, Ark.	white crappie	5	8.5	0.2	0.02	0.15	0.18	0.12	0.24
	bigmouth buffalo	3	15.1	1.87	0.04	0.17	0.13	0.06	0.54
		3	15.5	1.87	0.04	0.24	0.14	0.12	0.41
Yazoo River, Redwood, Miss.	black crappie	5	9.3	0.9	<0.01	0.10	0.14	0.16	0.43
	bigmouth buffalo	5	15.0	2.0	0.02	0.10	0.04	0.10	0.41
		5	15.5	2.2	0.04	0.11	0.06	0.09	0.38
Red River, Alexandria, La.	smallmouth buffalo	5	17.1	2.8	0.01	0.19	0.10	<0.05	0.22
		5	17.3	3.14	0.02	0.12	0.13	0.05	0.32
		5	17.0	2.94	0.01	0.15	0.10	<0.05	0.35
Red River, Lake Texoma, Okla.	largemouth bass	5	10.4	0.6	0.03	0.31	0.12	0.11	0.72
	gizzard shad	5	10.4	0.4	0.05	1.14	0.02	0.55	0.89
		5	9.9	0.3	0.05	1.44	0.02	0.61	0.86
Missouri River, Hermann, Mo.	freshwater drum	5	16.3	2.2	0.03	<0.10	0.24	0.06	0.66
Missouri River, Nebraska City, Neb.	goldeye	5	12.5	0.7	0.03	2.43	0.09	<0.05	0.73
	carp	5	14.8	1.7	0.06	0.75	0.03	0.10	1.28
		5	15.3	1.8	0.06	0.86	0.05	0 13	1.52
Missouri River, Garrison Dam, N.D.	walleye	5	17.3	1.64	<0.01	0.10	0.22	0.18	0.70
	white sucker	5	14.2	1.18	0.03	0.47	0.08	0.32	0.73
		5	14.3	1.18	0.03	0.30	0.07	0.23	0.73
Missouri River, Great Falls, Mont.	goldeye	9	12.7	0.7	0.06	0.13	0.12	0.08	1.36
	longnose sucker	3	16.6	1.97	0.18	0.32	0.06	0.42	0.33
	redhorse sucker	5	17.1	2.36	0.44	0.14	0.15	0.10	0.29
Big Horn River, Hardin, Mont.	goldeye	10	12.4	0.5	0.03	0.11	0.19	0.06	2.87
	white sucker	10	14.2	1.2	0.01	0.10	0.09	0.09	1.71
		10	12.5	0.8	<0.01	<0.10	0.05	0.06	1.07
Yellowstone River, Sidney, Mont.	sauger	5	12.7	0.58	0.02	<0.10	0.22	0.06	1.75
	carp	5	14.8	1.62	0.04	<0.10	0.12	0.16	0.88
		5	20.7	3.82	0.24	0.17	0.15	0.08	0.82
James River, Olivet, S.D.	goldeye	5	14.1	0.9	0.03	0.92	0.23	<0.05	0.82
	carp	5	16.1	2.0	0.05	1.95	0.07	0.06	0.53
		5	16.2	2.0	0.10	1.08	0.09	0.07	0.57
North Platte River, Lake McConaughy, Neb.	walleye	5	17.2	1.6	<0.01	0.42	0.04	0.81	0.73
	carp	5	19.1	3.0	0.09	0.54	0.17	0.13	0.81
		5	20.1	3.8	0.08	0.94	0.10	0.20	0.63
South Platte River, Brule, Neb.	green sunfish	5	5.4	0.1	0.01	1.25	0.06	0.09	2.08
	carp	5	10.1	0.5	0.02	0.49	0.01	0.14	2.05
		5	9.6	0.4	0.02	0.53	0.02	0.05	2.53

TABLE 4. (cont'd.). *Concentrations of cadmium, lead, mercury, arsenic, and selenium in whole fish samples collected the National Pesticide Monitoring Program, 1976–77*

Station Number and Location (Figure 1)	Species [1]	No. of Fish	Average Size		Residues, mg/kg Wet Weight				
			Length, inches	Weight, lb	Cadmium	Lead	Mercury	Arsenic	Selen
89. Platte River, Louisville, Neb.	goldeye	5	12.8	0.7	0.03	0.97	0.10	0.07	1.0
	river carpsucker	5	13.4	1.0	0.06	1.33	0.11	0.13	1.0
		5	14.6	1.4	0.10	1.74	0.12	0.07	1.1
90. Kansas River, Bonner Springs, Kans.	freshwater drum	5	9.3	0.34	0.02	<0.10	0.10	0.08	0.8
	carp	5	19.1	3.5	0.07	0.16	0.13	<0.05	0.8
		5	19.3	3.58	<0.01	0.21	0.12	0.09	1.0
111. Mississippi River, Lake City, Minn.	walleye	5	21.1	3.76	0.06	0.25	0.11	<0.25	-
	white sucker	5	17.8	2.56	0.05	0.25	<0.02	<0.25	-
112. Mississippi River, Dubuque, Iowa	largemouth bass	5	9.6	0.48	<0.05	<0.10	0.05	<0.25	-
	carp	5	18.5	2.98	<0.05	0.14	0.04	<0.25	-
		5	17.9	2.84	—	—	—	—	-
116. Souris River, International Border, N.D.	northern pike	5	19.5	1.66	<0.05	0.37	—	<0.25	-
HUDSON BAY DRAINAGE									
34. Red River, Noyes, Minn.	sauger	5	13.1	0.62	<0.05	<0.10	0.45	<0.25	-
		5	12.4	0.52	—	—	—	—	-
	white sucker	5	13.9	1.14	0.16	<0.10	0.13	<0.25	-
COLORADO RIVER SYSTEM									
35. Green River, Vernal, Utah	channel catfish	5	12.5	0.54	—	—	—	—	-
	carp	5	13.6	1.3	—	—	—	—	-
		5	12.5	1.24	—	—	—	—	-
36. Colorado River, Imperial Reservoir, Ariz	channel catfish	5	16.8	1.34	<0.05	<0.10	<0.02	<0.25	-
	carp	Not collected			--	—	—	—	-
		5	14.8	1.84	<0.05	0.18	<0.02	0.30	-
91. Colorado River, Lake Havasu, Ariz.	channel catfish	4	19.0	2.28	—	—	—	—	-
	carp	4	15.9	1.88	—	—	—	—	-
92. Colorado River, Lake Mead, Nebr.	inactive								
93. Colorado River, Lake Powell, Ariz.	largemouth bass	5	13.8	1.46	<0.05	0.27	0.14	<0.25	-
	carp	5	13.5	1.1	0.21	0.35	0.15	0.26	-
		5	13.5	1.2	0.22	0.16	0.07	<0.25	-
94. Gila River, San Carlos Reservoir, Ariz.	not collected								
114. Bear Creek, Brigham City, Utah	channel catfish	5	13.3	0.9	—	—	—	—	-
	carp	5	11.5	0.96	—	—	—	—	-
		5	14.7	1.68	0.09	<0.10	—	<0.25	-
115. Colorado River, Yuma, Colo.	mullet	5	13.5	0.99	—	—	—	—	-
	carp	4	11.7	0.81	<0.05	0.23	<0.02	<0.25	-
	largemouth bass	5	12.0	1.02	<0.05	0.20	0.03	<0.25	-
INTERIOR BASINS									
37. Truckee River, Fernley, Nebr.	carp	5	16.1	3.02	0.03	0.26	0.37	0.07	0.1
	Tahoe sucker	5	8.8	0.34	0.02	0.14	0.39	0.15	0.2
		5	8.7	0.32	0.02	0.28	0.32	0.19	0.1
38. Utah Lake, Provo, Utah	walleye	5	19.8	3.62	—	—	—	—	-
	carp	5	18.9	3.32	—	—	—	—	-
		5	18.8	3.24	—	—	—	—	-
95. Bear River, Preston, Idaho	inactive								
CALIFORNIA STREAMS									
39. Sacramento River, Sacramento, Calif.	largemouth bass	5	12.5	1.2	0.02	<0.10	0.14	0.19	0.3
	goldfish	4	12.4	1.3	0.11	0.19	0.19	0.23	0.2
		3	10.2	0.7	0.06	0.21	0.09	0.22	0.4
40. San Joaquin River, Los Banos, Calif.	striped bass	5	13.0	0.9	<0.01	<0.10	0.08	0.33	1.0
	Sacramento blackfish	5	12.3	0.8	<0.01	<0.10	0.07	0.12	1.3
		5	11.0	0.6	<0.01	0.12	0.16	0.09	1.0

BLE 4. (cont'd.). *Concentrations of cadmium, lead, mercury, arsenic, and selenium in whole fish samples collected for the National Pesticide Monitoring Program, 1976–77*

Station Number and Location (Figure 1)	Species [1]	No. of Fish	Average Size: Length, inches	Average Size: Weight, lb	Residues, mg/kg Wet Weight: Cadmium	Lead	Mercury	Arsenic	Selenium
COLUMBIA RIVER SYSTEM									
Snake River, Hagerman, Idaho	northern squawfish	5	15.3	1.18	—	—	—	—	—
	largescale sucker	5	13.7	0.92	—	—	—	—	—
		5	13.5	0.94	—	—	—	—	—
	rainbow trout	5	13.8	1.0	—	—	—	—	—
Snake River, Lewiston, Idaho	northern squawfish	5	15.2	1.14	<0.05	0.10	0.31	<0.25	—
	largescale sucker	5	15.4	1.28	0.10	0.12	0.07	0.50	—
		5	15.9	1.36	0.07	0.10	0.11	1.11	
Salmon River, Riggins, Idaho	largescale sucker	5	18.2	1.7	0.12	0.23	0.19	0.50	—
		4	17.9	2.1	—	—	—	—	—
Snake River, Ice Harbor, Wash.	channel catfish	5	13.0	0.54	0.10	0.21	0.10	0.61	—
	largescale sucker	5	14.7	1.14	0.09	0.17	0.04	<0.25	—
		5	14.8	1.12	0.07	0.11	0.05	<0.25	—
Yakima River, Granger, Wash.	black crappie	4	6.0	0.1	0.14	0.19	0.05	0.50	—
	largescale sucker	5	11.6	0.56	—	—	—	—	—
		5	12.1	0.66	<0.05	0.10	0.09	0.61	—
Willamette River, Oregon City, Oreg.	smallmouth bass	3	9.2	0.5	<0.05	0.12	0.13	<0.25	—
	chiselmouth	5	10.2	0.4	0.20	0.85	<0.02	1.15	—
		5	10.8	0.5	—	—	—	—	—
Columbia River, Booneville Dam, Oreg.	northern squawfish	5	13.5	0.9	<0.05	<0.10	0.23	<0.25	—
	largescale sucker	5	14.3	1.08	—	—	—	—	—
		5	12.4	0.82	0.15	<0.10	0.05	0.87	—
Columbia River, Pasco, Wash.	carp	5	11.4	0.66	<0.05	0.34	<0.02	<0.25	—
		5	11.6	0.7	<0.05	0.13	<0.02	0.35	—
Flathead River, Creston, Mont.	northern squawfish	5	13.6	0.74	—	—	—	—	—
	longnose sucker	4	15.2	1.1	—	—	—	—	—
		3	12.8	1.0	—	—	—	—	—
Columbia River, Grand Coulee, Wash.	yellow perch	5	7.9	0.26	<0.05	0.16	0.03	<0.25	—
	largescale sucker	5	16.4	1.58	—	—	—	—	—
		5	17.3	1.74	0.33	2.57	<0.02	0.30	—
PACIFIC COAST STREAMS									
Klamath River, Hornbrook, Calif.	yellow perch	5	9.2	0.4	<0.01	<0.10	0.09	<0.05	0.16
	Klamath sucker	5	12.4	0.7	<0.01	<0.10	0.06	0.11	<0.05
		5	12.5	0.7	0.01	0.10	0.03	0.12	0.08
Rogue River, Gold Ray Dam, Oreg.	black crappie	5	9.1	0.76	<0.01	<0.10	0.16	<0.05	0.11
	Klamath sucker	5	8.7	0.28	0.01	<0.10	0.02	0.11	0.06
		5	9.1	0.32	0.01	<0.10	0.03	0.13	0.12
ALASKAN STREAMS									
Chena River, Fairbanks, Alaska	Artic grayling	5	10.5	0.38	0.02	0.27	0.07	0.05	0.80
	longnose sucker	5	14.6	1.26	0.03	0.13	0.08	0.17	0.32
Kenai River, Soldatna, Alaska	not collected								
HAWAIIAN STREAMS									
Waikele Stream, Waipahu, Hawaii	Cuban limia	28	1.9	<0.10	0.05	0.38	0.04	0.08	0.77
		28	2.4	<0.10	0.05	0.51	0.05	0.10	0.80
Manoa Stream, Honolulu, Hawaii	Chinese catfish	3	6.9	0.2	0.11	0.80	0.12	0.10	0.43
	tilapia	33	6.9	0.23	0.03	2.28	0.02	0.27	0.38
		3	6.3	0.2	—	—	—	—	—
	Cuban limia	36	2.7	<0.10	—	—	—	—	—
		37	2.7	<0.10	0.03	4.93	0.05	0.49	0.12

mmon names for species from the continental United States follow those designated in "A list of common and scientific names of fishes m the United States and Canada", American Fisheries Society Special Publication No. 6, 3rd Edition, 1970.
iere two or more rows of data follow a species name, the data represent replicate samples.
shes (—) = not analyzed (sample not submitted, or inadequate digestion procedure, e.g., 1976 Se data).
ictive = stations so designated have been temporarily deleted fromverse conditions, etc.).
xed species = white catfish, carp, and spotted sucker.
xed species = freshwater drum, spotted sucker, and smallmouth buffalo.
t collected = personnel were unable to obtain fish samples (e.g., ad the NPMP collection station network.

As expected, location effects were highly significant ($P < 0.001$) for all five elements (Table 5). Effects due to time were significant for mercury, arsenic, selenium ($P < 0.001$), and cadmium ($P < 0.05$), but not for lead ($P = 0.213$). Interactions between main effects were not significant.

TABLE 5. *Results of two-way analysis of variance (weighted squares of means) on concentrations of lead, mercury, cadmium, arsenic, and selenium in freshwater fish, United States, 1976–77*

Source	Degrees of Freedom	Sum of Squares	Mean Square	*F*	Significance Level
Lead					
Stations	81	4.536	0.056	5.905	0.001
Years	1	0.014	0.014	1.553	0.213
Interaction	81	0.661	0.008	0.860	0.791
Error	368	3.490	0.009		
Mercury					
Stations	81	0.367	0.004	3.305	0.001
Years	1	0.023	0.023	16.874	0.001
Interaction	81	0.059	0.0007	0.531	0.999
Error	364	0.499	0.001		
Cadmium					
Stations	81	0.432	0.005	2.196	0.001
Years	1	0.015	0.015	6.434	0.011
Interaction	81	0.126	0.001	0.645	0.991
Error	368	0.894	0.002		
Arsenic					
Stations	43	0.804	0.018	7.875	0.001
Years	1	0.051	0.051	21.774	0.001
Interaction	43	0.090	0.002	0.887	0.671
Error	217	0.515	0.002		
Selenium					
Stations	43	2.579	0.60	13.173	0.001
Years	2	0.160	0.080	17.663	0.001
Interaction	86	0.273	0.003	0.698	0.976
Error	352	1.603	0.004		

Significant differences in mercury ($P < 0.001$) and cadmium concentrations ($P < 0.05$) were observed from 1972 to 1976–77 (Table 6); lead concentrations did not decline significantly, but arsenic concentrations increased significantly ($P < 0.001$). The two-way ANOVA indicated an effect for selenium due to time ($P < 0.001$, Table 6). Mean selenium concentrations for 1973 were significantly lower than those for 1972 selenium values (a priori test, $0.001 < P < 0.005$). A posteriori comparison (*54*) of mean selenium levels indicated no significant differences between 1972 and 1977 samples. Because of changes in laboratories, analytical procedures, station, fish species, size and age of fish, etc., these results should be used cautiously as temporal trend information.

Discussion

The average percent difference between duplicates for cadmium, mercury, arsenic, and selenium was considered acceptable, particularly because some duplicates had elemental concentrations near the detection limit. Recoveries from spiked samples, and reference materials, indicated satisfactorily accurate recovery of elements in all years, except for mercury in the spik samples for 1976. The low recovery (64 percent) mercury (Table 3) suggests problems during sam digestion and analysis.

TABLE 6. *Mean concentrations of lead, mercury, c mium, arsenic, and selenium in whole fish* [1]

Element	Mean Concentrations, mg/kg wet weight [2]		Significa (*P*)
	1972	1976–77	
Lead	0.354 (0.322–0.387)	0.338 (0.297–0.380)	>0.05 (N
Mercury	0.153 (0.142–0.164)	0.112 (0.099–0.126)	<0.001
Cadmium	0.112 (0.098–0.126)	0.085 (0.068–0.102)	<0.05
Arsenic	0.127 (0.108–0.146)	0.207 (0.184–0.231)	<0.001
Selenium [3]	0.604 (0.567–0.641)	0.576 (0.534–0.619)	<0.001

[1] Matching stations in years.
[2] Figures in parentheses are 95 percent confidence intervals.
[3] The mean concentration (and 95% CI) for selenium in 1973 0.455 (0.422–0.488) mg/kg. This was the only element having matcl station data in 1973. The *P* value (<0.001) results from the two- ANOVA on all 3 years.

Imprecision in lead-quality control data indicates t measured lead values may not accurately reflect av age levels in fish tissues. The accuracy and precis of lead spike recoveries (91 ± 10 percent and 102 12 percent) and National Bureau of Standards refere material analyses (Table 3) indicate that digestion a analytical techniques were satisfactory. Nonunifo distribution of lead in fish tissue and authors' inabi to achieve complete homogenization were more lik the causes of imprecision. For example, in tuna, lead content of epidermis tissue is several thousand tir that in muscle tissue from the same fish (*9, 59*). M of the lead in the epidermis is associated with mu (*9*). Similarly, rainbow trout (*Salmo gairdneri*) ac mulate lead in mucus and scales (*85, 86*). As a res lead digestate concentrations are difficult to correl with muscle tissue dry weights because of mucosal sli contamination (*89*).

To approximate normal background ranges for wh fish trace element concentrations, station means of l transformed individual data values (Table 4) w calculated for each element and arranged in order increasing concentration. The stations with transforn mean values exceeding the 85th percentile were t identified (Table 7). The antilog of this 85th percen was arbitrarily used to distinguish stations with h metal concentrations. Though the 85th percentile n not be meaningful biologically, it was considered ab background and potentially worth further study. Auth

ABLE 7. *Stations from which fish had trace element concentration equal to or exceeding the 85th percentile for the 1976–77 trend-monitoring collection*

EMENT	85TH PERCENTILE, MG/KG	STATIONS (IN ORDER OF INCREASING CONCENTRATION)
dmium	0.11	70, 68, 43, 107, 45, 24, 93, 2, 98, 3, 4, 33, 75, 73, 55, 78
ad	0.44	99, 78, 87, 53, 88, 2, 107, 82, 98, 24, 4, 31, 86, 89, 3, 100
rcury	0.19	43, 22, 1, 70, 66, 57, 83, 59, 51, 34, 74, 14, 37, 56, 107
senic	0.38	3, 66, 82, 43, 22, 46, 44, 42, 103, 45, 10, 60, 102, 105, 104, 21
enium	0.82	82, 4, 90, 89, 85, 31, 40, 84, 88

empted to suggest sources that could account for the gher values encountered at these stations. It should recognized that relating specific sources of metals to evated concentrations of the elements in freshwater h is speculative. The intent is to provide a metal urce perspective for the drainage basins to help arify elevated metal concentrations in fish from these eas.

DMIUM

dmium concentrations in freshwater fish had a range 0.01–1.04 ppm, a mean of 0.067 ppm, and an 85th rcentile of 0.11 ppm. The decrease in cadmium ncentrations in fish since 1972 (Table 6) parallels dmium metal production and consumption, which clined over the same period (*63*). NPMP stations which fish had cadmium concentrations equal to or ceeding the 85th percentile (Table 7) are discussed low in relation to possible contaminant sources.

lantic Coastal Streams—Fish from four rivers, the nnecticut (station 2), the Hudson (station 3), the elaware (station 4), and the James (station 55), all ntained mean cadmium concentrations exceeding 0.17 m. Each of these river systems lies in a heavily dustrialized area. A zinc smelting company, which is primary cadmium producer, is on the Lehigh River, a butary of the Delaware. Metal fumes from the elter's low stacks have killed trees in the Lehigh lley, and river sediments contained 5.4 ppm cadmium *8*). The James River receives effluents from numerous emical, fertilizer, and other industries (*16*).

reat Lakes Drainage—Like the Atlantic coastal eams, Lake St. Clair (station 107) is surrounded by heavily industrialized area. Cadmium residues in fish m the area ranged from 0.06 to 0.16 ppm, apparently iginating from a number of industrial sources in and ar Detroit.

ississippi River System—The 0.22-ppm cadmium level carp from station 24 at Marietta, Ohio, may result from zinc-smelting activity from a primary cadmium producer located on the Ohio River at Monaco, Pennsylvania. Similarly, a lead-smelting and refining complex at East Helena, Montana may be the primary source of cadmium in fish collected at station 33 (Great Falls, Montana. Miesch and Huffman (*76*) found cadmium contamination in soil 10 miles from a smelter in Helena Valley. It was estimated that 290 tons of cadmium had been added to the soil within a radius of 1–19 km from the smelter stacks. Superphosphate fertilizers are a suspect source at station 73 (Des Moines River), where high cadmium levels may reflect substantial agricultural runoff. High cadmium fluxes have been reported for the Mississippi River as it flows through mineralized areas in Tennessee, Missouri, and Kentucky (*15*). Cadmium levels in carp at Cape Girardeau, Missouri (station 75, Mississippi River), are probably the result of numerous sources. A zinc company at Sauget, Illinois (East St. Louis), has discharged waste on the Mississippi floodplain, forming a black sludge containing 0.1 percent cadmium (*78*). A large lead-smelting facility at Herculaneum, Missouri, has discharged effluent directly into the river. The smelter's slag piles along the banks of the Mississippi contained from 19 to 250 ppm cadmium, and much slag has been bulldozed into the river (*78*). In addition, industrial and municipal sewage effluents from St. Louis and phosphate fertilizer runoff may contribute to the cadmium load at this station.

The highest cadmium mean value was in carp from station 78 on the Verdigris River at Oologah, Oklahoma. A zinc company in Bartlesville, Oklahoma, may supply cadmium to the upper Verdigris River area as a result of particulate fallout from smelter stack emissions (*55*). The 85th percentile value of 0.11 ppm was characteristic of fish from station 70 on the Ohio River and probably reflects the relatively heavy industrialization of the lower river area.

Colorado River System—Southwestern Colorado and north-central Utah contain major deposits of lead and zinc ores, and numerous active mines are located there (*61*). A geologic source of cadmium, as well as mine waste drainage into tributaries of the Colorado River, could account for elevated cadmium levels in fish from Lake Powell, Arizona (station 93).

Columbia River System—Bottom sediments of the Willamette River and its numerous tributaries have cadmium concentrations ranging from 0.5 to 1 ppm (*73*). Concentrations of 2.5 ppm cadmium were found in sediment samples near the river mouth downstream from Portland, Oregon. Uniformity in sediment cadmium concentrations throughout the Williamette River basin suggests a geologic source of the metal. Active lead-zinc-silver mining in the Salmon River basin (station 43) may

account for the elevated concentrations in large-scale suckers (*23, 21*). High cadmium concentrations in fish from Grand Coulee, Washington (station 98), may reflect industrial waste from Spokane and activities of the Bunker Hill smelting complex at Kellogg, Idaho. Water from the South Fork of the Coeur d'Alene River has contained up to 0.45 ppm cadmium, corresponding to a cadmium transport of 240 lb cadmium/day (*22, 37*). The South Fork drains an area where thousands of tons of mine ground tailings of lead-zinc-silver ores were dumped decades ago (*15*). The Bunker Hill and associated smelters have tailing ponds extending for over 4 miles in the flood plain of the South Fork of the Coeur d'Alene River (*78*).

LEAD

Lead concentrations in freshwater fish (Table 4) ranged from 0.10 to 4.93 ppm and averaged 0.32 ppm. The trend in lead concentrations (Table 6) indicated no significant change from 1972 to 1976–77. The NPMP stations having concentration means at or above the 85th percentile of 0.44 ppm are discussed below.

Atlantic Coastal Streams—Segments of the Atlantic coastal streams where stations 2, 3, 4, and 53 are located contain many different types of industry. Industrial sources of lead could include those from metal finishing, brass manufacturing, lead alkyl manufacturing, primary and secondary lead smelting, coal combustion, and lead oxide manufacturing. River mud in the vicinity of a New Jersey zinc company, located on a tributary of the Delaware River, contained 0.13 percent lead (*78*). The St. Lawrence, New York, area contains a geologic source of lead; the Balmat mine, located there, ranks 18th in domestic output (*61*). The headwaters of the Hudson River may receive a lead flux from these ore deposits.

Great Lakes Drainage—Lake St. Clair (station 107), like the Atlantic coastal streams, is bordered by substantial industry and has a well-documented history of pollution (*13*). Lake St. Clair may receive urban lead aerosol fallout from the Detroit area, as well as effluents from numerous Detroit industries.

Mississippi River System—The Missouri-Oklahoma-Kansas vicinity is the location of stratabound deposits characteristically containing lead ores (*64*). Thus, in addition to point industrial sources of lead, the Verdigris River (station 78) and Red River (station 82) may receive lead from geologic origins. Fish residues at station 24 (Ohio River) may be affected by effluents (aerial fallout, tailing erosion, etc.) from a zinc company at Monaca, Pennsylvania. High concentrations at stations 88 and 89 (South Platte River), presumably reflect industrial discharges from Denver. The Pierre Shale of the Great Plains region contains low concentrations of lead and may provide a natural source of lead for statio 31, 86, 87, and 88 (*69*).

Columbia River System—Lead residues from fish Grand Coulee, Washington (station 98), may be fluenced by several lead sources affecting Franklin Roosevelt Lake. These are industrial effluents from Sp kane, lead-zinc mining in Pend Oreille, Washingtc natural stratabound deposits in Metaline Falls, Washir ton; and the mining-smelting complex at the South Fc of the Coeur d'Alene River. The Spokane water supp has had concentrations of copper and zinc above thc allowed by Public Health Drinking Water Standar The source is erosion and leaching of heavy metals fr slag and tailing piles along the South Fork of the Coe d'Alene River (*78*).

Hawaiian Streams—Waikele Stream (station 99) and tributaries total 117 miles in length and drain a 45 square-mile watershed. Diversions for domestic and ag cultural uses and highly permeable soils contribute extreme variations in flows, which ranged from 0.02 13,600 ft^3/second over 24 years. Heavy urban runofl characteristic of the flood flows in the lower reaches the stream. Agricultural and residential use of le arsenate has occurred in the drainage area, and vehi sources of lead are prevalent. The Manoa-Palola stre system (station 100) drains an area of about 9.35 mi characterized by high vehicle density. Air quality d have reflected high levels of lead aerosols and ot vehicle pollutants in the area. Lead arsenate has a been applied in the past for agricultural use and term control (Lenhart, D. J. 1979. Regional Pesticide Spec ist, Fish and Wildlife Service, U.S. Department of Interior, Portland, Oregon, personal communication)

MERCURY

Mercury concentrations in fish in 1976–77 (Table ranged from 0.01 to 0.84 ppm, and averaged 0.11 pp The decline of mercury levels in freshwater fish si 1972 (Table 6) is probably due to an overall reduct of industrial mercury emissions, coupled with a relat decrease in total domestic mercury consumption o the same period (*65*). NPMP monitoring stations hav fish with mercury concentrations exceeding the 85th p centile (0.19 ppm; Table 7) are discussed below.

Atlantic Coastal Streams—The Penobscot and Kenne River stations 1 and 51 have a long history of chloral and paper-pulping operations (Haines, T. A. 1979. F Research Station Leader, Fish and Wildlife Serv Orono, Maine, personal communication). Unfilte water samples from various sites in both rivers had t mercury levels in 1971 that equaled or exceeded the μg/liter recommended by the National Academy of ences Water Quality Criteria (*35, 40*). U.S Geolog Survey water quality data (retrieved through STORI

so substantiated concentrations > 0.2 μg/liter; some lues as high as 0.5 μg/liter were reported from the nobscot River in 1978 (*74*). An old paper industry Hartsville on a tributary to the Pee Dee River (station), most likely discharged mercury that became en- ıpped in sediments years ago. Georgia's Altamaha ver (station 57) was studied intensively in 1970, and ercury residues of 1.0 ppm in largemouth bass were ported by the Georgia Water Control Board (*18*). A ge pulp processing company is just above this sam- ing site (station 57), at Doctortown, Georgia.

ulf Coast Streams—Alabama's Tombigbee River (sta- ın 14) and Alabama River (station 59) both exceeded e 85th percentile of 0.19 ppm, with fish from station having a mean concentration of 0.33 ppm. There ere two chloralkali plants contaminating the Tombig- e in the early 1970's (*12*)—one at McIntosh and the her at river mile 26 (Smith, B. W. 1970. Assistant ief of Fisheries Section, Alabama Game and Fish ommission, personal communication). Mercury con- ntrations have been relatively high in fish from the labama River throughout the NPMP samplings (*20,* '), but the source of mercury has not been identified.

reat Lakes Drainage—The Lake St. Clair (station 07) mercury problem originated from chloralkali op- ations at Sarnia, Ontario, and is well documented (*12,* ?). In 1970, mercury concentrations in fillets from four ecies of Lake St. Clair fish exceeded 1 ppm (*67*). An- her Great Lakes station at which fish had mercury ncentrations greater than 0.19 ppm was station 22 on ake Superior. The Ontario Department of Lands and orests reported mercury concentrations > 0.5 ppm in e muscle of fish from different parts of Lake Superior 1970 (*12*). The source was presumably chloralkali ants at Marathon and Thunder Bay. The St. Lawrence iver (station 66) was listed by FDA as seriously con- minated in 1970. Mercury cell chloralkali plants are ill operating along the river at Cornwall, New York, ıd Beauharnois and Shawinigan, Quebec (*13*).

'ississippi River System—In the Red River (station 4), which drains into Lake Winnipeg in Manitoba rovince, the 0.28-ppm mercury concentration in fish ceeds the 85th percentile. The source of mercury has ot been identified. Station 70 at Metropolis, Illinois, is rectly downstream from the confluence of the Ken- cky and Ohio Rivers. Two mercury cell chloralkali ants are located at Calvert City, Kentucky, near the outh of the Kentucky River (*13*).

terior Basins—Pre-1900 gold and silver milling opera- ns of the Nevada Comstock Lode introduced substan- l amounts of mercury into the Truckee and Carson ver drainage systems; in bottom sediments, total mer- ry concentrations were as high as 20 ppm in 1971 (*48*). Concentrations in fish (0.50–2.72 ppm) were highest in white bass, a piscivorous species from Lahontan Reservoir. Bottom sediments in the Truckee River basin (station 37) contained greater than background mercury concentrations, as a result of ore milling activity in the Washoe Valley (*72*).

Columbia River System—The Columbia River system, including the tributary Yakima, Willamette, Snake, and Salmon Rivers is on the East Pacific Rise, the location of major mercury deposits (cinnabar) in the Western Hemisphere. There are secondary mercury mining operations in Washington and Idaho, as well as gold mining, where mercury was used to recover gold from its ores by amalgamation (*12*). In 77 percent of northern squawfish samples from the Salmon River, the axial musculature contained mercury concentrations higher than 0.5 ppm (*8*).

ARSENIC

Arsenic concentrations in fish (Table 4) ranged from 0.05 to 2.92 ppm and averaged 0.27 ppm. The increase in arsenic in freshwater fish since 1972 (Table 6) may be the result of dissemination by air pollution, smelter solid waste disposal, and continued use of arsenical pesticides. Contamination sources for arsenic are suggested here for the $\geqslant$ 85th percentile ($\geqslant 0.38$ ppm) NPMP stations.

Atlantic Coastal Streams—No specific industrial source for arsenic in the Hudson River (station 3) is known. Extensive industrialization of the river, however, presumably accounts for high arsenic concentrations in fish. In Georgia and South Carolina, substantial numbers of cotton farms (*71*) border the Savannah River and its tributaries (station 10). Arsenicals were used extensively on cotton from the early 1940's through the middle 1960's in Georgia (Winstead, E. E. 1979. Assistant Commissioner, Georgia Department of Agriculture, Atlanta, personal communication). Agricultural runoff of applied arsenicals would provide a persistent source of arsenic to sediment beds.

Gulf Coast Streams—In 1976, the Southern Plains states had more than 5 million acres planted in cotton, compared with slightly over 3 million for the Delta states (*57*). The highest concentration of cotton farms in the Southern Plains occurs along the Rio Grande Valley and western Texas Panhandle. Stations 82 and 60 are located on the Red and Brazos River systems, respectively, that drain these cotton-growing areas. Arsenic acid was the most heavily applied arsenical in 1976 in the Southern Plains, followed by sodium cacodylate and DSMA (*57*).

Great Lakes Drainage—Relatively high arsenic levels have been reported in many areas of Lake Michigan. In the southern portion (stations 21 and 105), sediment

concentrations have reached values as high as 30 ppm (*50*). In the northern portion (station 104), arsenic has accumulated in ferromanganese nodules that exist in the Green Bay area (*50*). One of the more striking cases of arsenic pollution involves the Ansul Co. of Marinette, Wisconsin (located close to the Menominee River, which empties into Green Bay). That company was a major manufacturer of methanearsonic acid (MAA) and cacodylic acid (CA), both arsenical herbicides (*2*). The company stored arsenic-contaminated sodium chloride and sodium sulfate manufacturing by-products in unprotected salt piles on the bank of the river. Precipitation runoff from the piles produced levels of > 200 ppm arsenic in river sediments. Groundwater below the piles had total arsenic concentrations in excess of 6,000 ppm. Sediment levels adjacent to the salt piles were 2 percent arsenic by weight. As a result, the Menominee River is responsible for contributing 30–50 tons of arsenic per year to Lake Michigan (*2*). Marsh (*36*) concluded that there was a definite accumulation of lead and arsenic in and around Grand Traverse Bay in northeast Lake Michigan. Lead arsenate pesticides, used as orchard spray, accounted for all of the arsenic and about half of the lead buildup.

In contrast to Lake Michigan, specific sources of arsenic in Lake Superior (stations 22, 102, and 103) and the St. Lawrence River (station 66) were not readily apparent. A nonpoint source affecting all of the Great Lakes was mentioned by Traversy et al. (*24*), who reported that arsenic levels in precipitation were higher than those in water from the Great Lakes and surrounding rivers. The elevated arsenic precipitation levels were especially prevalent at or near highly industrialized locations such as Toronto, Sarnia, and Hamilton.

A mine and copper smelting facility at White Pine, Michigan, is on the Mineral River, which drains into southern Lake Superior. Wash water and smelter runoff flow into Mineral River, as well as uncontrolled erosion from slag piles and tailing pond outfalls (*78*). Any of these effluents could contain substantial amounts of arsenic.

Arsenic concentrations in whole fish from the Great Lakes have been reported by Lucas et al. (*33*) and Traversy et al. (*24*) for the period from 1968 to 1971. Lucas et al., who analyzed 19 fish of 3 species, found a mean of 0.16 ppm arsenic, whereas Traversy et al., who analyzed 43 whole fish samples of 15 species, reported a mean of 0.063 ppm. The present authors report a mean arsenic concentration level of 0.72 ppm for fish from Great Lakes stations, including data from 33 sample composites of 10 different species. Although species, location, and methodology differences cannot be ruled out, the mean differences suggest a significant increase in arsenic concentrations in Great Lakes fish from 1970 to 1977. The arsenic levels in the present repo are similar to those found by the Upper Lakes Referen Group (*84*). At stations where arsenic seems to l higher than background levels—i.e., greater than t 85th percentile (0.38 ppm)—concentrations in bloate (*Coregonus* spp.) tended to be about double those lake trout (stations 21, 102, 104, and 105). The ten ency of bloaters to concentrate arsenic is apparent fro other work (*11, 84*) and may be related to a prima diet of zooplankton, which has been shown to bioco centrate arsenic (*80*).

Columbia River System—Stations 42–46 had mean a senic residues above the calculated 85th percent (Table 7). Such a preponderance of "high" stations a relatively small geographical area gives credence the following four possible sources of arsenic pollution

1. Volcanic eruptions in the central Cascade area duri the Eocene epoch resulted in a large accumulation volcanic deposits referred to as the Fisher formation. some instances, arsenic and perhaps boron were a p of the pyroclastic debris that formed the so-called Fish rocks. Arsenic released from Fisher rocks by percolati subsurface water has resulted in arsenic groundwa contamination in some areas of the southern Willame Valley (*31*). This geologic source of arsenic may present in other areas of the Columbia River system.

2. A copper-smelting facility at Tacoma, Washingt and the lead-smelting refineries located at Kellogg, Ida (Bunker Hill), and East Helena, Montana, may prov airborne sources of arsenic to the Columbia River s tem. Soil and water pollution are possible through sm er solid waste disposal (*78*).

3. Active mining of copper, lead, and gold may pres mine water and mine tailing disposal problems, beca arsenic is found in association with these base-m ores.

4. In the headwater regions of the Yakima, monosodi methanearsonate (MSMA) and cacodylic acid are c rently used for thinning in forestry (Gregory, S. 1979. Field Station Leader, Columbia National Fishe Research Laboratory, Fish and Wildlife Service, C vallis, Oregon, personal communication).

SELENIUM

Concentrations of selenium in fish ranged from 0.0 2.87 ppm and averaged 0.56 ppm. Stations having m concentration levels exceeding the 85th percentile ((ppm) are discussed below.

Atlantic Coastal Streams—Fish from station 4 on Delaware River at Camden, New Jersey, had con trations exceeding the 85th percentile, not only

enium (0.82 ppm), but also for cadmium and lead. e elevated trace element concentrations in these fish obably reflect the highly industrialized character of Delaware River.

ssissippi River System—The Big Horn (station 84) d Yellowstone (station 85) River tributaries of the ssouri River are closely associated with Montana's rt Union coal formation and outcroppings of phos-ate beds in Montana and Wyoming (*45, 71*). Sele-um concentrations in fish from these rivers may result m a geologic source of the element. Selenium sources the aquatic environment at the South Platte River ar Denver (station 88) may be industrial effluents or posits of coal, barite, and sulfur ore (*71*). Phosphate d outcroppings are located along the Kansas-Missouri rder close to station 90 on the Kansas River (*71*). enium concentrations in fish from stations 80 and 31 y also reflect a geologic source of the element, pri-rily sedimentary rocks associated with the Pierre mation.

lifornia Streams—The source of selenium in fish at tion 40 on the San Joaquin River is unknown. Selo-e, a selenium-containing pesticide, was registered for on citrus in California in the 1960's (*41*). This terial may have been applied in the San Joaquin ver valley and, if so, could still be a source of sele-m to the aquatic environment.

Summary

mary sources of the trace elements to the aquatic vironment follow:

dmium: electroplating industry, zinc-lead-copper elting and refining, phosphate fertilizers, sulfide ore-ning activities.

ad: combustion of gasoline, lead-zinc-copper smelt-operations, sulfide ore-mining activities, coal com-stion.

ercury: pre-1975 chloralkali industry, pre-1972 paper-ping operations, synthetic fiber industries, coal com-stion.

senic: copper-lead-gold smelting and refining, coal nbustion, smelter solid waste disposal, arsenical pesti-es, geologic.

enium: geologic, industrial.

ce in the environment, there is evidence that all five ce elements may undergo biologically mediated trans-mation reactions that yield organometallic compounds t are routed through the food chain.

Trace element concentrations (mg/kg wet weight) in whole fish in 1976–77 follow:

Metal	Range	Geometric Mean	Median	85th Percentile
Cadmium	0.01–1.04	0.07	0.05	0.11
Lead	0.10–4.92	0.32	0.19	0.44
Mercury	0.01–0.84	0.11	0.09	0.19
Arsenic	0.05–2.92	0.27	0.25	0.38
Selenium	0.05–2.87	0.56	0.50	0.82

Temporal trends in whole-fish trace element concentrations (mg/kg wet weight) from 1972 to 1976–77 were as follows: cadmium, significant decline; lead, no significant difference; mercury, significant decline; arsenic, significant increase; and selenium, no significant difference (1972 vs. 1977).

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FOOD AND FEED

Pesticide, Heavy Metal, and Other Chemical Residues in Infant and Toddler Total Diet Samples—(II)—August 1975–July 1976 [1]

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ABSTRACT

Food and Drug Administration, U.S. Department of lth and Human Services, initiated the Total Diet Study 964 to monitor residues of pesticides and other chemi- ingested in the average diet of the United States' hearti- ater, the young adult male. In August 1974, one-third ie adult market baskets were replaced with infant and ler market baskets. Averages and ranges of residues for second in a series of infant and toddler baskets, for ist 1975–July 1976, are reported. Included are results of minations for zinc, cadmium, lead, selenium, arsenic, mercury. Results of recovery studies conducted with pounds of each residue type are also presented.

Introduction

Food and Drug Administration (FDA), U.S. De- ment of Health and Human Services (formerly U.S. artment of Health, Education, and Welfare), has monitoring the United States' total diet since 1964 *, 11–17*). The program began with surveillance of s for fission products from atmospheric tests of nonuclear weapons. Later, the emphasis was di- d toward pesticide residues in foods. For several s the program focused on the total diet of the 16- 9-year-old male, statistically the United States' tiest eater. In August 1974, 10 of the 30 market ets were replaced with the total diet of 6-month-old nts and 2-year-old toddlers. The 10 market baskets collected in 10 cities that ranged in population fewer than 50,000 to one million or more.

ds in each of 11 broad classes, as listed in Table 1, prepared separately, composited into a slurry, and yzed for organochlorine and organophosphorus pes- es, carbaryl, herbicides, metals, and a few industrial nicals. Methodologies included atomic absorption roscopy, fluorometry, gas chromatography, thin-layer chromatography, mass spectroscopy, and established extraction and cleanup techniques (*7, 8, 10, 18, 19*). Except for the water composite (*9*), quantitation limits and instrumental conditions were the same as those described for the adult market baskets.

TABLE 1. *Commodity classes of infant and toddler foods analyzed for pesticides, metals, and other chemical residues, August 1975–July 1976*

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] Because of similarity between infant and toddler diets, single determinations for certain classes of food are made and reported for both.
[2] No infant composite for western region.
[3] No infant composite from the north-central, western, and southern regions.
[4] No infant composite from north-central region.

Results

The infant composites of the present series contained 301 residues of 31 compounds, with 51 residues at the trace level. In comparison, the first infant composites reported last year contained 306 residues of 28 compounds; 121 were reported at the trace level.

Toddler composites of the present series showed 473 residues of 38 compounds; 76 were present in trace amounts. The first toddler series last year reported 468 residues of 30 compounds with 179 at the trace level.

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The chemical compounds found, the number of findings, and the range for each are listed in Table 2. The frequency of occurrence of each compound by food class is presented in Table 3. Table 4 shows the level of every residue found within each food class. The averages given in Table 4 are based on the total number of composites examined for that food class. Trace values were treated as zero in calculating these averages. Table 5 shows the intake of pesticide and industrial chemical residues in terms of μg/kg body weight/day, and Table 6 shows the intake of six metals in terms of μg/day (mg/day for zinc). For comparison, the findings for the 1975 fiscal year are also shown. The most common residues and their average levels are discussed below for each of the 11 food classes. No findings have been corrected for recoveries.

DRINKING WATER

Infant and Toddler—Tap water samples analyzed were taken from the same location as the market basket. The result of a single analysis is that reported for both infant and toddler composites. The water was used to prepare other market basket items requiring dilution or addition of water. Only two metal residues were found: four samples contained zinc averaging 0.170 ppm for the series, and one sample contained cadmium, averaging 0.002 ppm.

WHOLE MILK, FRESH

Infant and Toddler—This composite was common to both diets. Averages for chlorinated pesticide residues included 0.001 ppm *p,p'*-DDE; trace α-BHC (hexachlorocyclohexane); trace dieldrin; and a trace of heptachlor epoxide. Averages for the three metals found were 6.80 ppm zinc; 0.007 ppm cadmium; and 0.002 ppm selenium. A trace of PCP was detected in one composite.

OTHER DAIRY AND SUBSTITUTIONS

Infant—The variation in infants' and toddlers' diets becomes apparent with these composites. Dieldrin was found in four composites averaging trace for the series. Averages of other organochlorines were traces of α-BHC, heptachlor epoxide, methoxychlor, and *p,p'*-DDE. A trace of PCP was found in one composite. Averages for metal residues were 5.38 ppm zinc, 0.004 ppm cadmium, and 0.013 ppm lead.

Toddler—All 10 composites contained dieldrin, averaging 0.003 ppm, and α-BHC, averaging 0.002 ppm. Averages of other pesticide residues included 0.004 ppm *p,p'*-DDE, 0.001 ppm heptachlor epoxide, and traces of octachlor epoxide, methoxychlor, HCB, and lindane. A trace of PCP was found in one composite. Averages of metal residues included 5.94 ppm zinc, 0.016 ppm selenium, 0.013 ppm cadmium, 0.006 ppm lead, and a trace of mercury.

TABLE 2. *Chemical and metal residues found in inf and toddler food composites from 10 United States citie August 1975–July 1976*

Chemical Found	No. of Composites With Residues	No. of Positive Composites With Residues Reported as Trace [1]	Range,
INFANT			
Zinc	85	0	0.100–36
Cadmium	59	0	0.005–0.
Lead	35	0	0.050–0.
Selenium	21	0	0.020–0.
p,p'-DDE [2]	17	8	0.001–0.
Dieldrin	15	7	0.001–0.
Malathion	12	0	0.003–0.
α-BHC	9	7	0.0006–0.
Heptachlor epoxide	6	6	T
Mercury	4	0	0.002–0.
PCP	4	4	T
CIPC	3	0	0.023–0.
Arsenic	3	0	0.040–0.
Dichloran	3	0	0.006–0.
Endosulfan [3]	3	2	0.
HCB	3	3	T
Endrin	2	1	0.
Lindane	2	0	0.
Toxaphene	2	2	T
Octachlor epoxide	2	2	T
TCNB	1	0	0.
p,p'-DDT [2]	1	1	T
Chlordane	1	1	T
Diazinon	1	0	0.
Methoxychlor	1	1	T
Parathion	1	1	T
Ethion	1	1	T
Fonofos	1	1	T
Carbaryl	1	1	T
TCTA	1	1	T
Perthane	1	1	T
TODDLER			
Zinc	100	0	0.100–34
Cadmium	77	0	0.005–0.
Lead	35	0	0.050–0.
Dieldrin	31	6	0.001–0.
α-BHC	29	12	0.0006–0.
Selenium	27	0	0.020–0.
p,p'-DDE [2]	26	4	0.001–0.
Heptachlor epoxide	20	13	0.001–0.
Malathion	16	0	0.005–0.
Lindane	15	3	0.001–0.
HCB	14	8	0.0007–0.
Arsenic	11	0	0.030–0.
Octachlor epoxide	10	9	0.
Mercury	7	0	0.002–0.
PCP	6	5	0.
CIPC	5	0	0.023–0.
PCA	4	0	0.002–0.
Pentachlorobenzene	4	1	0.001–0.
Toxaphene	4	3	0.
Dichloran	3	0	0.012–0.
PCNB	3	0	0.001–0.
Diazinon	3	1	0.001–0.
Chlordane	3	2	0.
Parathion	3	3	T
p,p'-DDT [2]	2	1	0.
p,p'-TDE [2]	2	1	0.
Fonofos	2	0	0.001–0.
Ronnel	1	0	0.
Endrin	1	0	0.
2,4-D	1	0	0.
TCNB	1	0	0.
trans-Nonachlor	1	0	0.
PCTA	1	0	0.
TCTA	1	1	T
Ethion	1	1	T
o-Phenylphenol	1	1	T
Methoxychlor	1	1	T
PCP methyl ether	1	0	0.

[1] Chemicals detected by the specific analytical methodology below limit of quantitation were confirmed qualitatively and reported trace (T). The limits of quantitation vary with residues and classes.
[2] Other isomers also included in reporting.
[3] Reportings include isomers I and II and sulfate.

LE 3. *Frequency of occurrence of chemical and metal ues, by food class, in infant and toddler food composites rom 10 United States cities—August 1975–July 1976*

ICAL	Food Class [1] I	II	III	IV	V	VI	VII	VIII	IX	X	XI
NUMBER OF OCCURRENCES IN INFANT FOODS											
	4	10	10	10	10	8	10	9	2	7	5
ium	1	4	4	7	10	8	10	6	2	6	1
	0	0	1	8	6	6	8	5	0	0	1
um	0	1	0	10	10	0	0	0	0	0	0
DE	0	3	4	5	0	3	2	0	0	0	0
in	0	2	4	6	0	2	0	0	1	0	0
hion	0	0	0	0	10	0	0	0	2	0	0
:	0	3	5	1	0	0	0	0	0	0	0
chlor epoxide	0	1	3	0	0	0	0	0	2	0	0
ry	0	0	0	2	0	0	1	0	0	1	0
	0	1	1	0	1	0	0	1	0	0	0
	0	0	0	0	0	3	0	0	0	0	0
c	0	0	0	0	3	0	0	0	0	0	0
ran	0	0	0	0	0	1	0	2	0	0	0
ulfan	0	0	0	0	0	1	1	1	0	0	0
	0	0	0	2	0	1	0	0	0	0	0
	0	0	0	0	0	0	0	0	2	0	0
ne	0	0	0	0	2	0	0	0	0	0	0
hene	0	0	0	0	0	0	0	0	2	0	0
lor epoxide	0	0	0	2	0	0	0	0	0	0	0
	0	0	0	0	0	1	0	0	0	0	0
DT	0	0	0	0	0	0	1	0	0	0	0
lane	0	0	0	0	0	0	0	0	1	0	0
on	0	0	0	0	1	0	0	0	0	0	0
xychlor	0	0	1	0	0	0	0	0	0	0	0
ion	0	0	0	0	0	0	1	0	0	0	0
	0	0	0	0	0	0	0	1	0	0	0
os	0	0	0	0	0	0	0	0	1	0	0
yl	0	0	0	0	0	0	0	1	0	0	0
	0	0	0	0	0	1	0	0	0	0	0
ne	0	0	0	0	0	0	0	1	0	0	0
NUMBER OF OCCURRENCES IN TODDLER FOODS											
	4	10	10	10	10	10	10	9	10	10	7
um	1	4	7	9	10	10	10	4	10	10	2
	0	0	1	3	5	6	6	5	6	2	1
in	0	2	10	10	0	2	2	0	5	0	0
:	0	3	10	8	0	0	2	0	0	6	0
um	0	1	4	9	10	0	0	0	2	1	0
DE	0	3	8	10	0	3	1	0	1	0	0
chlor epoxide	0	1	8	9	0	0	0	0	2	0	0
hion	0	0	0	0	10	0	0	0	6	0	0
ne	0	0	1	4	0	1	3	0	0	6	0
	0	0	5	4	0	1	0	0	4	0	0
c	0	0	0	7	2	0	0	0	1	1	0
lor epoxide	0	0	6	4	0	0	0	0	0	0	0
ry	0	0	1	6	0	0	0	0	0	0	0
	0	1	1	0	1	0	1	1	0	1	0
	0	0	0	0	0	5	0	0	0	0	0
	0	0	0	0	0	0	0	0	4	0	0
hlorobenzene	0	0	0	0	0	0	0	0	4	0	0
nene	0	0	0	0	0	0	0	0	4	0	0
ran	0	0	0	0	0	0	0	3	0	0	0
	0	0	0	0	0	0	0	0	3	0	0
on	0	0	0	0	3	0	0	0	0	0	0
ane	0	0	0	0	0	0	0	0	3	0	0
ion	0	0	0	0	0	0	1	0	2	0	0
DT	0	0	0	2	0	0	0	0	0	0	0
DE	0	0	0	2	0	0	0	0	0	0	0
os	0	0	0	0	0	0	0	0	2	0	0
l	0	0	0	1	0	0	0	0	0	0	0
	0	0	0	0	0	0	0	0	1	0	0
	0	0	0	0	0	0	0	0	0	1	0
	0	0	0	0	0	1	0	0	0	0	0
lonachlor	0	0	0	1	0	0	0	0	0	0	0
	0	0	0	0	0	0	0	0	1	0	0
	0	0	0	0	0	1	0	0	0	0	0
	0	0	0	0	0	0	0	1	0	0	0
ylphenol	0	0	0	0	0	0	0	1	0	0	0
ychlor	0	0	1	0	0	0	0	0	0	0	0
ethyl ether	0	0	0	0	0	0	0	0	1	0	0

able 1 for key to food classes.

MEAT, FISH, AND POULTRY

Infant—These infant composites contained among the highest number of residues. Metals dominated 37 of the 53 residues, with averages of 16.8 ppm zinc, 0.094 ppm selenium, 0.087 ppm lead, 0.023 ppm cadmium, and 0.002 ppm mercury. Of the 16 nonmetals, dieldrin was found in six composites averaging a trace for the series; *p,p'*-DDE, averaging 0.003 ppm for the series, was found in five composites; HCB, octachlor epoxide, and α-BHC averaged a trace.

Toddler—Ninety-nine residues were found. All 10 composites contained residues of *p,p'*-DDE, ranging from 0.002 to 0.016 ppm, and dieldrin, ranging from 0.001 to 0.003 ppm. Heptachlor epoxide, *p,p'*-TDE, *p,p'*-DDT, hexachlorobenzene (HCB), α-BHC, lindane, octachlor epoxide, ronnel, and *trans*-nonachlor averaged a trace for the series. Average metal residues included 27.5 ppm zinc and 0.180 ppm selenium. Lesser amounts of arsenic, lead, cadmium, and mercury, averaging 0.092, 0.030, 0.010, and 0.006 ppm, respectively, were also found.

GRAIN AND CEREAL PRODUCTS

Infant—All 10 composites contained malathion, ranging from 0.003 to 0.049 ppm and averaging 0.020 ppm. There was one report of diazinon at the 0.010 ppm level, and only traces of lindane and PCP were found. Averages for the metals were 14.6 ppm zinc, 0.189 ppm selenium, 0.046 ppm lead, 0.027 ppm cadmium, and 0.018 ppm arsenic.

Toddler—Like the infant composites, these toddler composites all contained malathion residues, ranging from 0.006 to 0.025 ppm and averaging 0.012 ppm. Diazinon, averaging trace amounts, was found in three composites. Averages for the metals found were 10.3 ppm zinc, 0.179 ppm selenium, 0.065 ppm lead, 0.026 ppm cadmium, and 0.008 ppm arsenic.

POTATOES

Infant—The chlorinated herbicide CIPC was found in three composites, ranging from 0.023 to 0.469 ppm and averaging 0.073 ppm for the series. TCNB averaged 0.003 ppm for the series. Other organochlorine pesticides averaging trace amounts included *p,p'*-DDE, dieldrin, dichloran, endosulfan, TCTA, and HCB. Of the metals found, zinc averaged 2.72 ppm, lead averaged 0.061 ppm, and cadmium averaged 0.048 ppm.

Toddler—The chlorinated herbicide CIPC was found in five composites, ranging from 0.023 to 0.469 ppm and averaging 0.156 ppm for the series. TCNB was found in one composite at 0.026 ppm, and dieldrin, lindane, *p,p'*-DDE, TCTA, and HCB averaged a trace. The metals zinc and cadmium averaged 3.92

TABLE 4. *Levels of chemical and metal residues, by food class, in infant and toddler food composites from 10 Un States cities—August 1975–July 1976*

Chemical	Residue, ppm	
	Infant	Toddler
I. WATER		
ZINC		
Average	0.170	0.170
Positive composites		
Total number	4	4
Number reported as trace	0	0
Range	0.200–0.600	0.200–0.600
CADMIUM		
Average	0.002	0.002
Positive composites		
Total number	1	1
Number reported as trace	0	0
Range	0.02	0.020
II. WHOLE MILK, FRESH		
ZINC		
Average	6.80	6.80
Positive composites		
Total number	10	10
Number reported as trace	0	0
Range	3.30–28.8	3.30–28.8
α-BHC		
Average	T	T
Positive composites		
Total number	3	3
Number reported as trace	2	2
Range	0.0006	0.0006
p,p'-DDE		
Average	0.001	0.001
Positive composites		
Total number	3	3
Number reported as trace	1	1
Range	0.002–0.005	0.002–0.005
DIELDRIN		
Average	T	T
Positive composites		
Total number	2	2
Number reported as trace	0	0
Range	0.001	0.001
CADMIUM		
Average	0.007	0.007
Positive composites		
Total number	4	4
Number reported as trace	0	0
Range	0.005–0.040	0.005–0.040
PCP		
Average	T	T
Positive composites		
Total number	1	1
Number reported as trace	1	1
Range	T	T
HEPTACHLOR EPOXIDE		
Average	T	T
Positive composites		
Total number	1	1
Number reported as trace	1	1
Range	T	T
SELENIUM		
Average	0.002	0.002
Positive composites		
Total number	1	1
Number reported as trace	0	0
Range	0.02	0.020
III. OTHER DAIRY AND SUBSTITUTIONS		
ZINC		
Average	5.38	5.94
Positive composites		
Total number	10	10
Number reported as trace	0	0
Range	2.90–8.50	1.60–14.6
HEPTACHLOR EPOXIDE		
Average	T	0.001
Positive composites		
Total number	3	8
Number reported as trace	3	3
Range	T	0.001–0.003
DIELDRIN		
Average	T	0.003
Positive composites		
Total number	4	10
Number reported as trace	2	0
Range	0.001	0.001–0.0
METHOXYCHLOR		
Average	T	T
Positive composites		
Total number	1	1
Number reported as trace	1	1
Range	T	T
CADMIUM		
Average	0.004	0.013
Positive composites		
Total number	4	7
Number reported as trace	0	0
Range	0.005–0.020	0.006–0.0
α-BHC		
Average	T	0.002
Positive composites		
Total number	5	10
Number reported as trace	4	0
Range	0.001	0.001–0.0
p,p'-DDE		
Average	T	0.004
Positive composites		
Total number	4	8
Number reported as trace	4	1
Range	T	0.001–0.0
LEAD		
Average	0.013	0.006
Positive composites		
Total number	1	1
Number reported as trace	0	0
Range	0.130	0.060
PCP		
Average	T	T
Positive composites		
Total number	1	1
Number reported as trace	1	1
Range	T	T
SELENIUM		
Average		0.016
Positive composites		
Total		4
Number reported as trace		0
Range		0.030–0.0
OCTACHLOR EPOXIDE		
Average		T
Positive composites		
Total number		6
Number reported as trace		6
Range		T
MERCURY		
Average		T
Positive composites		
Total number		1
Number reported as trace		0
Range		0.002
HCB		
Average		T
Positive composites		
Total number		5
Number reported as trace		4
Range		0.0007
LINDANE		
Average		T
Positive composites		
Total number		1
Number reported as trace		0
Range		0.002
IV. MEAT, FISH, AND POULTRY		
ZINC		
Average	16.84	27.52
Positive composites		
Total number	10	10
Number reported as trace	0	0
Range	8.90–36.3	11.3–34.

LE 4 (cont'd.). *Levels of chemical and metal residues, by food class, in infant and toddler food composites from 10 United States cities—August 1975–July 1976*

Chemical	Residue, ppm	
	Infant	Toddler
NIUM		
age	0.094	0.180
ive composites		
tal number	10	9
mber reported as trace	0	0
nge	0.040–0.220	0.110–0.300
age	0.087	0.030
ive composites		
tal number	8	3
mber reported as trace	0	0
nge	0.050–0.180	0.050–0.190
IIUM		
age	0.023	0.010
ive composites		
tal number	7	9
mber reported as trace	0	0
nge	0.010–0.100	0.008–0.020
URY		
age	0.002	0.006
ive composites		
tal number	2	6
mber reported as trace	0	0
nge	0.004–0.016	0.005–0.020
RIN		
age	T	0.002
ive composites		
tal number	6	10
mber reported as trace	4	1
nge	0.002–0.003	0.001–0.003
age	T	T
ive composites		
tal number	2	4
mber reported as trace	2	2
nge	T	0.0007–0.0009
age	T	T
ve composites		
al number	1	8
mber reported as trace	1	7
nge	T	0.0007
DE		
age	0.003	0.005
ve composites		
al number	5	10
mber reported as trace	2	0
nge	0.002–0.019	0.002–0.016
CHLOR EPOXIDE		
age	T	T
ve composites		
al number	2	4
mber reported as trace	2	3
nge	T	0.004
IC		
age		0.092
ve composites		
al number		7
mber reported as trace		0
nge		0.060–0.290
CHLOR EPOXIDE		
age		T
ve composites		
al number		9
mber reported as trace		8
nge		0.002
E		
age		T
ve composites		
al number		2
mber reported as trace		1
nge		0.002
T		
age		T
ve composites		
al number		2
mber reported as trace		1
nge		0.005

Chemical	Residue, ppm	
	Infant	Toddler
LINDANE		
Average		T
Positive composites		
Total number		4
Number reported as trace		3
Range		0.003
RONNEL		
Average		T
Positive composites		
Total number		1
Number reported as trace		0
Range		0.002
trans-NONACHLOR		
Average		T
Positive composites		
Total number		1
Number reported as trace		0
Range		0.006

V. GRAIN AND CEREAL PRODUCTS

ZINC		
Average	14.6	10.29
Positive composites		
Total number	10	10
Number reported as trace	0	0
Range	6.8–20.3	6.30–18.9
SELENIUM		
Average	0.189	0.179
Positive composites		
Total number	10	10
Number reported as trace	0	0
Range	0.140–0.250	0.080–0.290
CADMIUM		
Average	0.027	0.026
Positive composites		
Total number	10	10
Number reported as trace	0	0
Range	0.020–0.050	0.018–0.040
ARSENIC		
Average	0.018	0.008
Positive composites		
Total number	3	2
Number reported as trace	0	0
Range	0.040–0.090	0.030–0.050
MALATHION		
Average	0.020	0.012
Positive composites		
Total number	10	10
Number reported as trace	0	0
Range	0.003–0.049	0.006–0.025
LEAD		
Average	0.046	0.065
Positive composites		
Total number	6	5
Number reported as trace	0	0
Range	0.050–0.100	0.060–0.210
PCP		
Average	T	T
Positive composites		
Total number	1	1
Number reported as trace	1	1
Range	T	T
LINDANE		
Average	T	
Positive composites		
Total number	2	
Number reported as trace	0	
Range	0.004	
DIAZINON		
Average	0.001	T
Positive composites		
Total number	1	3
Number reported as trace	0	1
Range	0.010	0.001–0.003

TABLE 4 (cont'd.). *Levels of chemical and metal residues, by food class, in infant and toddler food composites fro United States cities—August 1975–July 1976*

Chemical	Residue, ppm	
	Infant	Toddler
VI. POTATOES		
ZINC		
Average	2.72	3.92
Positive composites		
Total number	8	10
Number reported as trace	0	0
Range	0.30–4.30	0.300–8.20
LEAD		
Average	0.061	0.078
Positive composites		
Total number	6	6
Number reported as trace	0	0
Range	0.050–0.120	0.050–0.350
CADMIUM		
Average	0.048	0.045
Positive composites		
Total number	8	10
Number reported as trace	0	0
Range	0.020–0.130	0.010–0.120
DIELDRIN		
Average	T	T
Positive composites		
Total number	2	2
Number reported as trace	1	1
Range	0.002	0.002
LINDANE		
Average		T
Positive composites		
Total number		1
Number reported as trace		0
Range		0.007
p,p'-DDE		
Average	T	T
Positive composites		
Total number	3	3
Number reported as trace	1	1
Range	0.001–0.002	0.002
DICHLORAN		
Average	T	
Positive composites		
Total number	1	
Number reported as trace	0	
Range	0.006	
ENDOSULFAN		
Average	T	
Positive composites		
Total number	1	
Number reported as trace	1	
Range	T	
CIPC		
Average	0.073	0.156
Positive composites		
Total number	3	5
Number reported as trace	0	0
Range	0.023–0.469	0.023–0.469
TCNB		
Average	0.003	0.003
Positive composites		
Total number	1	1
Number reported as trace	0	0
Range	0.026	0.026
TCTA		
Average	T	T
Positive composites		
Total number	1	1
Number reported as trace	1	1
Range	T	T
HCB		
Average	T	T
Positive composites		
Total number	1	1
Number reported as trace	1	1
Range	T	T

Chemical	Residue, ppm	
	Infant	Toddle
VII. VEGETABLES		
ZINC		
Average	3.66	3.49
Positive composites		
Total number	10	10
Number reported as trace	0	0
Range	1.80–6.40	0.600–4
LEAD		
Average	0.078	0.081
Positive composites		
Total number	8	6
Number reported as trace	0	0
Range	0.060–0.240	0.070–0
CADMIUM		
Average	0.043	0.026
Positive composites		
Total number	10	10
Number reported as trace	0	0
Range	0.010–0.120	0.017–0
MERCURY		
Average	T	
Positive composites		
Total number	1	
Number reported as trace	0	
Range	0.002	
PARATHION		
Average	T	T
Positive composites		
Total number	1	1
Number reported as trace	1	1
Range	T	T
p,p'-DDE		
Average	T	T
Positive composites		
Total number	2	1
Number reported as trace	0	0
Range	0.002–0.004	0.002
p,p'-DDT		
Average	T	
Positive composites		
Total number	1	
Number reported as trace	1	
Range	T	
ENDOSULFAN		
Average	0.004	
Positive composites		
Total number	1	
Number reported as trace	0	
Range	0.037	
PCP		
Average		T
Positive composites		
Total number		1
Number reported as trace		1
Range		T
LINDANE		
Average		T
Positive composites		
Total number		3
Number reported as trace		0
Range		0.001–0
DIELDRIN		
Average		T
Positive composites		
Total number		2
Number reported as trace		1
Range		0.005
α-BHC		
Average		T
Positive composites		
Total number		2
Number reported as trace		0
Range		0.002

LE 4 (cont'd.). *Levels of chemical and metal residues, by food class, in infant and toddler food composites from 10 United States cities—August 1975–July 1976*

Chemical	Residue, ppm	
	Infant	Toddler
VIII. FRUITS AND FRUIT JUICES		
rage	0.610	0.870
tive composites		
otal number	9	9
umber reported as trace	0	0
ange	0.300–1.00	0.200–2.40
rage	0.066	0.062
tive composites		
otal number	5	5
umber reported as trace	0	0
ange	0.070–0.290	0.080–0.240
OSULFAN		
rage	T	
tive composites		
otal number	1	
umber reported as trace	1	
ange	T	
HANE		
rage	T	
tive composites		
otal number	1	
umber reported as trace	1	
ange	T	
LORAN		
rage	0.001	0.005
tive composites		
otal number	2	3
umber reported as trace	0	0
ange	0.006–0.007	0.012–0.026
IIUM		
rage	0.007	0.005
tive composites		
otal number	6	4
umber reported as trace	0	0
ange	0.010–0.017	0.010–0.020
ARYL		
age	T	
tive composites		
otal number	1	
umber reported as trace	1	
ange	T	
rage	T	T
tive composites		
otal number	1	1
umber reported as trace	1	1
ange	T	T
ON		
age	T	T
tive composites		
otal number	1	1
umber reported as trace	1	1
ange	T	T
NYLPHENOL		
rage		T
tive composites		
otal number		1
umber reported as trace		1
ange		T
IX. OILS AND FATS		
age	20.3	14.43
ive composites		
tal number	2	10
umber reported as trace	0	0
nge	20.2–20.4	10.6–19.2
1UM		
age	0.074	0.062
ive composites		
tal number	2	10
mber reported as trace	0	0
nge	0.067–0.080	0.040–0.110

Chemical	Residue, ppm	
	Infant	Toddler
MALATHION		
Average	0.025	0.041
Positive composites		
Total number	2	6
Number reported as trace	0	0
Range	0.015–0.035	0.005–0.187
TOXAPHENE		
Average	T	0.007
Positive composites		
Total number	2	4
Number reported as trace	2	3
Range	T	0.075
DIELDRIN		
Average	0.001	0.001
Positive composites		
Total number	1	5
Number reported as trace	0	3
Range	0.002	0.002–0.007
ENDRIN		
Average	0.006	0.001
Positive composites		
Total number	2	1
Number reported as trace	1	0
Range	0.011	0.009
HEPTACHLOR EPOXIDE		
Average	T	0.001
Positive composites		
Total number	2	2
Number reported as trace	2	1
Range	T	0.007
FONOFOS		
Average	T	T
Positive composites		
Total number	1	2
Number reported as trace	1	0
Range	T	0.001–0.002
CHLORDANE		
Average	T	0.014
Positive composites		
Total number	1	3
Number reported as trace	1	2
Range	T	0.137
p,p'-DDE		
Average		T
Positive composites		
Total number		1
Number reported as trace		1
Range		T
LEAD		
Average		0.050
Positive composites		
Total number		6
Number reported as trace		0
Range		0.060–0.120
HCB		
Average		0.002
Positive composites		
Total number		4
Number reported as trace		1
Range		0.001–0.016
PCNB		
Average		0.001
Positive composites		
Total number		3
Number reported as trace		0
Range		0.001–0.005
PCA		
Average		0.005
Positive composites		
Total number		4
Number reported as trace		0
Range		0.002–0.044
PENTACHLOROBENZENE		
Average		0.001
Positive composites		
Total number		4
Number reported as trace		1
Range		0.001–0.009

TABLE 4 (cont'd.). *Levels of chemical and metal residues, by food class, in infant and toddler food composites fro United States cities—August 1975–July 1976*

Chemical	Residue, ppm	
	Infant	Toddler
SELENIUM		
Average		0.011
Positive composites		
Total number		2
Number reported as trace		0
Range		0.050–0.060
PARATHION		
Average		T
Positive composites		
Total number		2
Number reported as trace		2
Range		T
ARSENIC		
Average		0.003
Positive composites		
Total number		1
Number reported as trace		0
Range		0.030
PCTA		
Average		T
Positive composites		
Total number		1
Number reported as trace		0
Range		0.003
PCP METHYL ETHER		
Average		T
Positive composites		
Total number		1
Number reported as trace		0
Range		0.002
X. SUGAR AND ADJUNCTS		
ZINC		
Average	2.73	5.51
Positive composites		
Total number	7	10
Number reported as trace	0	0
Range	0.20–20.7	1.50–12.5
CADMIUM		
Average	0.005	0.015
Positive composites		
Total number	6	10
Number reported as trace	0	0
Range	0.007–0.010	0.010–0.020
MERCURY		
Average	0.0006	
Positive composites		
Total number	1	
Number reported as trace	0	
Range	0.006	
SELENIUM		
Average		0.004
Positive composites		
Total number		1
Number reported as trace		0
Range		0.040
PCP		
Average		0.007
Positive composites		
Total number		1
Number reported as trace		0
Range		0.070
LINDANE		
Average		0.001
Positive composites		
Total number		6
Number reported as trace		0
Range		0.001–0.003
α-BHC		
Average		T
Positive composites		
Total number		6
Number reported as trace		3
Range		0.001–0.002
LEAD		
Average		0.028
Positive composites		
Total number		2
Number reported as trace		0
Range		0.090–0.190
ARSENIC		
Average		0.004
Positive composites		
Total number		1
Number reported as trace		0
Range		0.040
2,4-D		
Average		0.002
Positive composites		
Total number		1
Number reported as trace		0
Range		0.025
XI. BEVERAGES		
ZINC		
Average	0.314	0.180
Positive composites		
Total number	5	7
Number reported as trace	0	0
Range	0.100–1.00	0.100–0
CADMIUM		
Average	0.007	0.002
Positive composites		
Total number	1	2
Number reported as trace	0	0
Range	0.012	0.010
LEAD		
Average	0.011	0.007
Positive composites		
Total number	1	1
Number reported as trace	0	0
Range	0.080	0.070

NOTE: Average residues are based upon the total number of co ites examined; trace values were treated as zero. It is quite p that average values reported as T can be well below the detection of the method for that composite.

ppm and 0.045 ppm, respectively, and were four all 10 composites; lead was found in six compo averaging 0.078 ppm for the series.

VEGETABLES

Infant—The highest level for a chlorinated pes was 0.037 ppm endosulfan found in one comp There were two reports of *p,p'*-DDE, 0.002 ppm 0.004 ppm, and trace findings of parathion and DDT. Average residues of metals included 3.66 zinc, 0.078 ppm lead, 0.043 ppm cadmium, and a of mercury.

Toddler—Trace averages were reported for parat dieldrin, lindane, PCP, *p,p'*-DDE and α-BHC. lead, and cadmium accounted for 26 of the tot residues and averaged 3.49, 0.081, and 0.026 respectively.

FRUITS AND FRUIT JUICES

Infant—The chlorinated pesticide Perthane® an carbamate pesticide carbaryl were found only i food group, in one composite at the trace level.

LE 5. *Intake of pesticide and industrial chemical sidues by infants and toddlers, market basket surveys FY 1975 vs FY 1976*

	Residue, µg/kg Body Wt/Day			
	Infant		Toddler	
ound	FY 75	FY 76	FY 75	FY 76
	ND	ND	ND	ND
in	0.0153	0.0249	0.0502	0.0412
L	0.0153	0.0249	0.0502	0.0412
	0.1276	0.0682	0.1598	0.0985
	T	T	0.0064	0.0046
	T	ND	0.0037	0.0018
L	0.1276	0.0682	0.1699	0.1049
chlor epoxide	0.0097	0.0001	0.0057	0.0057
hlor	ND	ND	ND	ND
L	0.0097	0.0001	0.0057	0.0057
ulfan I	ND	0.0011	ND	ND
ulfan II	ND	0.0045	ND	ND
ulfan sulfate	ND	0.0368	0.0078	ND
L	ND	0.0424	0.0078	ND
	0.0228	0.0055	0.0211	0.0132
n	ND	ND	ND	ND
yl	T	T	0.0047	ND
lane	ND	T	ND	0.0100
	0.0020	0.0321	0.0458	0.3942
	ND	ND	ND	0.0058
	ND	ND	ND	ND
on	T	0.0053	0.0067	0.0030
ran	0.0383	0.0230	0.0506	0.0342
l	ND	ND	ND	ND
	ND	T	ND	ND
	ND	ND	ND	0.0007
s	ND	T	ND	0.0002
	0.0044	0.0009	0.0064	0.0042
hos	ND	ND	0.0033	ND
e	0.0133	0.0049	0.0341	0.0096
ion	0.2028	0.0865	0.1374	0.1488
xychlor	T	T	ND	T
parathion	ND	ND	ND	ND
ylphenol	ND	ND	ND	T
ordane	T	0.0008	T	T
ion	T	T	ND	0.0013
	0.0053	ND	0.0058	0.0064
hloroanisole	ND	ND	ND	0.0003
hlorobenzene	0.0005	ND	0.0007	0.0013
	0.0073	ND	0.0024	0.0007
	0.0154	T	0.0214	0.0162
tachlorothioanisole)	ND	ND	ND	0.0004
ne	ND	T	ND	ND
ne	ND	ND	ND	ND
	T	T	T	ND
	ND	ND	T	0.0022
ene	0.2573	T	0.0467	0.0127
fonachlor	ND	ND	ND	0.0050
	ND	0.0019	T	0.0074
henothion	ND	ND	ND	ND

: ND = not detected; T = Trace (below the limits of quantita- etected and verified, but not quantifiable).

ides reported at the trace level included endo- n, PCP, and ethion. Dichloran was found in two osites and averaged 0.001 ppm for the series. Low- metal residues included zinc, lead, and cadmium, ging 0.610, 0.066, and 0.007 ppm, respectively.

ler—Dichloran, found in three composites, ranged 0.012 to 0.026 ppm for a series average of 0.005 Traces of PCP, ethion, and the fungicide *o*-

TABLE 6. *Dietary intakes of metals by infants and toddlers, FY 1975 vs FY 1976*

	Residue, µg/day			
	Infant		Toddler	
Metal	FY 75	FY 76	FY 75	FY 76
Lead	20.79	26.94	25.61	30.12
Cadmium	5.16	12.33	10.72	14.19
Zinc [1]	5.33	8.15	8.26	9.46
Arsenic [2]	2.76	0.42	11.10	12.28
Selenium	21.63	10.81	58.38	44.99
Mercury	0.03	0.56	0.94	0.81

[1] Values are mg/day.
[2] Values calculated as arsenic trioxide (As_2O_3).

phenylphenol were also reported. Zinc, lead, and cadmium all averaged below 1.0 ppm.

OILS AND FATS

Infant—Only two of the 10 market baskets included a separate composite of oils and fats for the infant. Malathion, endrin, and dieldrin averaged 0.025, 0.006, and and 0.001 ppm, respectively. Trace averages were reported for toxaphene, heptachlor epoxide, and chlordane.

Fonofos, an organophosphorus pesticide, was found only in this food group, at the trace level. Both composites had residues of zinc, 20.2 ppm and 20.4 ppm, and cadmium, 0.067 ppm and 0.080 ppm.

Toddler—A total of 71 residues was reported for these 10 composites. The metals accounted for 29 residues and included zinc (average 14.43 ppm), cadmium (average 0.062 ppm), lead, selenium, and arsenic. Three organophosphorus pesticides were reported: malathion in six composites, ranging from 0.005 to 0.187 ppm and averaging 0.041 ppm for the series; parathion traces in two composites; and fonofos in two composites, ranging from 0.001 to 0.002 ppm and averaging trace for the series. Malathion residues averaged highest of the nonmetals and appeared in the most composites. Among the organochlorine compounds, toxaphene averaged 0.007 ppm and was reported in four composites. Other organochlorine residues included PCA, dieldrin, pentachlorobenzene, chlordane (average 0.014 ppm), HCB, heptachlor epoxide, PCNB, *p,p'*-DDE, PCTA, and PCP methyl ether.

SUGAR AND ADJUNCTS

Infant—Only three metal residues were reported for these infant composites. Zinc was found in seven composites, ranging from 0.20 to 20.7 ppm, for a series average of 2.73 ppm. Cadmium was found in six com-

posites, ranging from 0.007 to 0.010 ppm and averaging 0.005 ppm for the series. One residue of mercury was reported at 0.006 ppm for a series average of 0.0006 ppm.

Toddler—In contrast, the toddler composites had 38 residues of nine different compounds: five metals, two chlorinated herbicides, and two organochlorine pesticides. Averages of the metals included 5.51 ppm zinc, 0.015 ppm cadmium, 0.028 ppm lead, and 0.004 ppm each for arsenic and selenium. Two composites contained herbicides: PCP at 0.07 ppm and 2,4-D at 0.025 ppm. Six residues were reported for each of the chlorinated pesticides, lindane and α-BHC, with ranges 0.001 to 0.003 ppm and 0.001 to 0.002 ppm, respectively.

BEVERAGES

Infant—Only three metal residues were reported for these composites. Zinc was found in five composites, ranging 0.100 to 1.00 ppm, and averaging 0.314 ppm for the series; 0.012 ppm cadmium and 0.080 ppm lead were reported for one composite.

Toddler—The metal residues found in these toddler composites were the same as those found in the infant composites. Zinc was found in seven composites, ranging from 0.100 to 0.500 ppm, and averaging 0.180 ppm for the series. Cadmium was reported twice at the 0.01 ppm level, and lead was reported once at 0.070 ppm.

Discussion

INFANT

The infant composites contained a total of 301 residues: 207, or 68.7 percent, were metals; 86, or 28.6 percent, were pesticides; and the remaining 2.7 percent included seven herbicide residues and one fungicide residue. In comparison, a total of 306 residues was reported for the first infant composite series: 199 (65 percent) metals, 99 (32.3 percent) pesticides, five fungicides, one herbicide, and two industrial chemicals.

Of the metal residues, zinc, occurring most frequently, was found in 85 composites with the highest level, 36.3 ppm, occurring in the meat-fish-poultry composite. Although 59 cadmium residues were reported, the 35 lead residues, ranging from 0.050 to 0.290 ppm, might be of greater significance. The highest level of lead residues was found in the fruit and fruit juice composites. All but one of the 21 selenium residues were found in the meat-fish-poultry composites. Arsenic was reported at low levels in three grain-cereal composites. Sixteen chlorinated pesticide compounds were reported in 69 residues; 43 were found at the trace level. Of these, the most frequently occurring residues were dieldrin and *p,p'*-DDE, found mostly in the dairy composites and the meat composites. Endosulfan, found in one table composite at 0.037 ppm, was the chlori pesticide occurring at the highest level.

Malathion, an organophosphorus pesticide, was f in each of the 10 grain and cereal composites, w high value of 0.049 ppm. In addition to 0.010 diazinon found in one composite, single trace am of three other organophosphorus pesticides wer ported: parathion, ethion, and fonofos. A single of carbaryl, the only carbamate pesticide screened found once in the fruit-fruit juice composite.

Only two herbicides were found in the composites. chlorinated herbicide CIPC, which is usually fou potatoes, was reported for three potato compc ranging from 0.023 to 0.469 ppm, and trace amou PCP were found in four composites. The fun TCNB was reported in one potato composite at ppm.

TODDLER

A total of 473 residues was found in the toddler composites. Of these, the six metals accounted fo residues, or 54.3 percent of the total, the 17 chlori pesticides accounted for 164, or 34.6 percent, an six organophosphorus pesticides were reporte times for 5.4 percent of the total. The remainin percent included four chlorinated herbicides four times, three chlorinated fungicides found eight t one industrial chemical found four times, an phenylphenol found once.

Zinc, ranging from 0.100 to 34.0 ppm, was fou almost every composite. Cadmium was the second frequently occurring residue, but the range, 0.0(0.120 ppm, was much lower. Most of the lead dues, with a range of 0.050 to 0.350 ppm, were in the grain, potato, vegetable, and fruit compc All 10 grain composites and nine meat comp contained selenium residues. The meat-fish-pc composites contained seven of the 11 arsenic res and six of the seven mercury residues, which have traced to the seafood portion of the composite.

Seventeen chlorinated pesticides accounted for or 34.6 percent, of all the residues; these were predominantly in the dairy and meat-fish-poultry posites. The most frequently detected chlorinated cide was dieldrin, found in every dairy and meat poultry composite. α-BHC and DDE were also several times in those two composites.

The most prevalent organophosphorus pesticide malathion, found in all 10 grain-cereal composite in six oil-fat composites. Other reportable organo phorus pesticides were diazinon, parathion, for and ronnel, each residue found in either the cereal or the oil-fat composites. The herbicides

icides represented a small number of residues. four chlorinated herbicides were reported: CIPC ues, found in five potato composites, ranged from 3 to 0.469 ppm; PCP, 2,4-D, and PCP methyl were scattered throughout the other food groups. of the eight residues of the three chlorinated icides detected were found in the fat-oil composite.

achlorobenzene, an industrial chemical, was present e toddler diet but was not found in the infant diet; as detected in four oil-fat composites and ranged 0.001 to 0.009 ppm. The fruit-fruit juice com- es contained one residue of the fungicide *o*- ylphenol at the trace level.

e 7 shows the number of occurrences of each ue type as found in each food class.

very studies were done for many of the more non residues. In each case, simultaneous determi- ns were made on an unfortified composite and on mposite fortified with a known level of residue. e 8 lists the contributions from the unfortified com- e, and the total amount of residue recovered gh the method. A single determination was made ach reported recovery. In some cases only a few posites were fortified with a particular compound; are presented for information only. In other cases, tempt was made to investigate the recovery of the frequently found residues from a variety of prod- natrices and to provide a basis for a meaningful ation of the methods. The data are presented in e 8.

Acknowledgments

ors acknowledge the contributions of all staff bers assigned to the Total Diet Section, Food and Administration, Kansas City District Laboratory.

LE 7. *Types and number of residues, by food class, und in infant and toddler total diet samples from 10 United States cities—August 1975–July 1976*

F E	Food Class [1] I	II	III	IV	V	VI	VII	VIII	IX	X	XI
INFANT											
	2	3	3	5	5	3	4	3	2	3	3
des	—	4	5	5	3	6	4	5	7	—	—
ides	—	—	—	—	—	2	—	—	—	—	—
rial chemicals	—	—	—	—	—	—	—	—	—	—	—
ides	—	1	1	—	1	—	—	1	—	—	—
TODDLER											
	2	3	5	6	5	3	3	3	5	5	3
les	—	4	8	11	2	5	5	2	11	2	—
ides	—	—	—	—	—	2	—	1	2	—	—
ial chemicals	—	—	—	—	—	—	—	—	1	—	—
ides	—	1	1	—	1	—	1	1	1	2	—

ey in Table 1.

TABLE 8. *Recovery data on residues found in infant and toddler total diet samples from 10 United States cities—August 1975–July 1976*

Residue	Type of Food Composite	Spike Level, ppm	Range of Unfortified Composite, ppm [1]	Range of Total Residue Found, ppm [1,2]	Number of Recovery Studies
NONMETALS					
Oxychlordane	Fatty	0.003		0.0027–0.0039	2
	Nonfatty	0.003		0.0026	1
Heptachlor epoxide	Fatty	0.003		0.0027–0.0031	2
	Nonfatty	0.003		0.0027	1
Ethion	Fatty	0.010		0 –trace	2
	Nonfatty	0.010		0.010	1
DCPA	Fatty	0.005	0–0.001	0.0046–0.007	4
	Nonfatty	0.005		0.00043–0.0064 (0.0043)	8
Methyl parathion	Fatty	0.005		0.0011–0.003	2
	Nonfatty	0.005		0.0014–0.0053	4
Perthane	Fatty	0.010		0.005–0.0094	3
	Nonfatty	0.010		0.0009–0.0131 (0.0087)	8
Tetradifon	Fatty	0.100		0.065–0.090	2
	Fatty	0.020		0.019	1
	Nonfatty	0.100		0.048–0.109	4
	Nonfatty	0.020		0.016–0.024	2
Endosulfan sulfate	Fatty	0.010		0.006–0.008	2
	Nonfatty	0.010		0.004–0.013	4
Malathion	Fatty	0.005		0.0025–0.0049	2
	Nonfatty	0.005		0.0043–0.0056	3
Phosalone	Fatty	0.02		0.018	1
	Nonfatty	0.02		0.009–0.015	2
Leptofos	Fatty	0.05		0.039–0.049	2
	Nonfatty	0.05		0.004–0.046	4
PCP	Fatty	0.02	0–0.010	0.0007–0.018	4
	Fatty	0.04		0.020–0.024	3
	Nonfatty	0.02	0–0.003 (0.0012)	0.003–0.016 (0.0096)	6
	Nonfatty	0.04	0–0.004	0.025–0.032	3
Picloram	Fatty	0.10		0–0.075	2
	Nonfatty	0.10		0.033	1
2,4-D	Fatty	0.04		0–0.042	3
	Nonfatty	0.04		0.026–0.039	5
Silvex	Fatty	0.04		0.008–0.022	2
	Nonfatty	0.04		0.023–0.039	2
MCP	Fatty	0.020		0.009–0.011	2
2-methyl-4-chlorophenoxyacetic acid	Nonfatty	0.020		0.009–0.013	3
	Nonfatty	0.040		0.029–0.036	2
2,4-DB	Fatty	0.02		0.014	1
	Nonfatty	0.02		0.012–0.017	2
	Nonfatty	0.04		0–0.026	2
2,4,5-T	Fatty	0.02	0–0.002	0.004–0.022	2
	Fatty	0.04		0.016	1
	Nonfatty	0.02		0.007–0.0196	4
	Nonfatty	0.04		0.025–0.029	2
Carbaryl	Nonfatty	0.20		0.02–0.20 (0.18)	17
o-Phenylphenol	Nonfatty	0.40		0.08–0.40 (0.30)	16
Fonofos	Fatty	0.01		0.002–0.004	2
	Nonfatty	0.01		0.006–0.008 (0.007)	5
Toxaphene	Fatty	0.20		0.201–0.240	2
	Nonfatty	0.20		0.125–0.204 (0.170)	4
METALS					
Arsenic	Fatty	0.30		0.25–0.30	3
	Fatty	0.40	0–0.10	0.34–0.535 (0.462)	5
	Nonfatty	0.30		0.17–0.32	3
	Nonfatty	0.40	0–0.03	0.24–0.385 (0.313)	12
Cadmium	Fatty	0.10	0.002–0.086 (0.030)	0.095–0.162 (0.116)	11
	Nonfatty	0.10	0–0.371 (0.0195)	0.090–0.162 (0.116)	19
Lead	Fatty	0.20	0–0.119 (0.039)	0.099–0.260 (0.187)	11
	Nonfatty	0.20	0–0.072 (0.031)	0.084–0.345 (0.196)	19

TABLE 8 (cont'd.). *Recovery data on residues found in infant and toddler total diet samples from 10 Unted States cities—August 1975–July 1976*

Residue	Type of Food Composite	Spike Level, ppm	Range of Unfortified Composite, ppm [1]	Range of Total Residue Found, ppm [1, 2]	Number of Recovery Studies
Mercury	Fatty	0.06	0–0.019 (0.005)	0.047–0.089 (0.069)	7
	Nonfatty	0.04	0–0.003 (0.001)	0.045–0.056 (0.052)	4
	Nonfatty	0.06	0–0.002 (0.0002)	0.065–0.136 (0.079)	13
Selenium	Fatty	0.20	0–0.20 (0.07)	0.19–0.45 (0.30)	6
	Fatty	0.40	0–0.20 (0.03)	0.26–0.50 (0.39)	5
	Nonfatty	0.20	0–0.29 (0.04)	0.18–0.56 (0.25)	11
	Nonfatty	0.40	0–0.15 (0.034)	0.25–0.54 (0.36)	6
Zinc	Fatty	5.0	1.62–19.2 (7.33)	5.95–24.0 (12.2)	6
	Fatty	25.0	5.0–30.2 (17.9)	28.5–52.6 (41.7)	5
	Nonfatty	10.0	6.3–7.4 (7.0)	14.8–18.2 (16.8)	3
	Nonfatty	5.0	0–7.55 (2.67)	4.55–12.6 (7.37)	14

[1] Numbers in parentheses represent average residue levels.
[2] Values are uncorrected for background.

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Organochlorine Pesticides and PCBs in Cod-Liver Oil of Baltic Origin, 1971–80

Jerzy Falandysz [1]

ABSTRACT

nochlorine pesticides and polychlorinated biphenyls Bs) in cod-liver oil of Baltic origin were monitored dur-1971–80. Residues of DDT and its metabolites, PCBs, hexachlorobenzene were present in all samples. Gen-y, ΣDDT residues declined, but the reason for the ne is unknown.

Introduction

of technical DDT as an insecticide in countries sur-ding the Baltic has been prohibited since 1971. The nochlorine pesticides presently used for agricultural oses in Poland are toxaphene, methoxychlor, endo-n, and lindane. DDT was widely used in agriculture has been detected at high levels in tissues of Baltic ne mammals, fish, and birds (*7*). The prohibition ne agricultural use of DDT in Poland was reflected ie nearly tenfold reduction of ΣDDT residue levels dipose fat of slaughtered animals during the last de (A. Niewiadowska, Veterinary Institute, Pulawy,), personal communication). However, so far there been no reports showing a decline of ΣDDT residue s in animals of the Baltic Sea. Another class of or-chlorine compounds, polychlorinated biphenyls Bs), occurs throughout the Baltic environment. , polychlorinated terphenyls (PCTs) have been d recently in Baltic marine organisms (*2, 13, 15*). rmation on production and industrial use of PCBs PCTS in countries surrounding the Baltic remains ure. Some quantities of PCBs are produced and able in Poland under the trade name Chlorofen *12*). PCBs have also been produced in West nany as Clophen, in the Soviet Union as Sovol, in Czechoslovakia as Delor. This paper presents the ts of analyses of cod-liver oil of Baltic origin for ues of hexachlorobenzene (HCB), ΣDDT, and s.

Analytical Methods

ples of cod-liver oil were obtained from a factory dynia. The procedures for isolation and determination of the organochlorines have been presented elsewhere (*4*). Two cleanup processes were used. The oil sample was dissolved in *n*-hexane; 1 ml *n*-hexane was used for every 20 mg fat extracted. Twenty mg fat was cleaned with 1 ml of a 1:1 mixture of fuming 20–25 percent sulfur dioxide and concentrated sulfuric acid in a screw-capped, Teflon-lined test tube (*2, 4, 8*). The colorless hexane layer was injected directly into the gas chromatograph. In addition, a 4-ml aliquot of cleaned sample was subjected to alcoholic potassium hydroxide hydrolysis in a screw-capped, Teflon-lined test tube. The test tube was immersed for 15 minutes in the water bath at 50°C. After cooling, the mixture was shaken with 4 ml distilled water. Following separation, the upper hexane layer was injected into the gas chromatograph. The residues were quantitated by electron-capture gas chromatography. Instrument parameters and operating conditions follow:

Chromatograph:	PYE 104
Detector:	^{63}Ni
Column:	glass, 150 cm long by 4 mm ID packed with a 2:1 mixture of 8 percent QF-1 and 4 percent SF-96 on 100–120 mesh Gas-Chrom Q
Temperatures, °C:	detector 210 column oven 195
Carrier gas:	argon flowing at ml/min

PCBs were quantified by comparing sample peaks with that of PCB standard Clophen A 50, which appeared on the gas chromatogram after *p,p'*-DDE. DDE content was calculated from the total height of the peak with retention time equal to that of standard *p,p'*-DDE. *p,p'*-DDT and *p,p'*-TDE were calculated from the difference in height of peaks with retention times equal to those of *p,p'*-DDT and *p,p'*-TDE before and after hydrolysis with alcoholic potassium hydroxide. In recovery experiments, the calculated values and standard deviations, in ppm, were as follows: HCB, 0.27 ± 0.015; DDE, 5.8 ± 0.25; TDE, 5.1 ± 0.39; DDT, 1.3 ± 0.14; and PCBs, 11 ± 0.84 (*4*).

Results and Discussion

The levels of organochlorine residues in cod-liver oil are presented in Table 1. DDT and its metabolites were present in all samples. DDE levels ranged from 1.1 to

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TABLE 1. *Mean and range (ppm) of chlorinated hydrocarbons in cod-liver oil of Baltic origin, 1971–80*

Year	*n*	HCB		*p,p'*-DDE		*p,p'*-TDE		*p,p'*-DDT		ΣDDT		PCBs	
		Mean	Range	Mean	Range	Mean	Range	Mean	Range	Mean	Range	Mean	Range
1971	1	0.24		4.6		2.3		6.6		13		4.8	
1972	1	0.36		4.2		4.6		8.4		17		9.5	
1973	3	0.28	0.20–0.32	7.2	4.1–9.3	3.7	2.2–4.5	10	8.4–12	22	15–26	5.7	4.3–7.0
1974	8	0.23	0.10–0.37	5.5	1.3–9.8	2.9	0.69–4.8	5.7	2.1–9.4	14	4.0–22	5.9	2.2–9.0
1975	5	0.23	0.12–0.34	8.3	2.9–17	3.5	1.4–5.4	5.0	2.2–8.5	17	8.9–28	8.6	4.6–13
1976	11	0.30	0.16–0.44	8.3	1.1–24	3.5	1.0–6.5	4.6	1.1–8.9	16	3.3–38	8.6	3.1–16
1977	9	0.35	0.26–0.54	5.3	3.1–9.3	3.9	3.0–5.0	3.9	3.2–5.9	13	9.8–20	9.6	4.9–16
1978	4	0.32	0.28–0.41	4.1	4.1–4.2	2.9	2.7–3.1	2.2	1.3–3.0	9.2	8.2–9.8	7.1	5.5–8.5
1979	1	0.24		4.2		5.2		2.1		11		4.3	
1980	2	0.29	0.28–0.30	3.4	3.0–3.8	1.9	1.3–2.5	1.2	0.59–1.8	6.5	4.9–8.1	5.1	4.7–5.6

NOTE: Mean is arithmetic mean.

24 ppm, TDE from 0.69 to 6.5 ppm, and DDT from 0.59 to 12 ppm; ΣDDT levels ranged from 3.3 to 38 ppm. PCBs, resembling Clophen A 50, and HCB were also detected in all samples, at levels ranging from 2.2 to 16 ppm and from 0.10 to 0.54 ppm, respectively. All samples contained at least trace amounts of α- and γ-BHC. Because the residues of these isomers were negligible by comparison, they were excluded from the table.

Many papers have been published on organochlorine residues in the liver of cod from the Baltic (*1, 5, 6, 8, 10, 11, 13, 14, 16-18*), but only several for cod-liver oil (*1, 3, 10*). The cod-liver oil of Baltic origin is unfit for medical purposes because of its high contamination with DDT and PCBs.The main Polish catches of cod are taken in the southern Baltic (Figure 1, regions 25 and 26) (*9*). The cod-liver oil produced in the factory in Gdynia, Poland, is manufactured from fresh cod livers. The crude cod-liver oil produced on board the fishing vessels operating in the southern Baltic is also delivered to the factory in Gdynia. After clarification, the crude cod-liver oil is usually mixed with that produced from the previous catch and is stored in a large-capacity tank. For the present study, all samples were taken from oil dispatched from the factory. Those particular lots of oil were taken from the day-by-day production or from the storage tank, mainly mixed oil. The annual production of cod-liver oil in 1975, 1976, and 1977 was 280, 316, and 220 tons, respectively. Table 1 shows that ΣDDT may have declined, but that decline cannot be verified because the mean values for organochlorines must be at least corrected by the quantity of oil in the particular lot analyzed—information that was not available to authors. Also, it has been shown (*11, 16, 17*) that the organochlorine residues in livers of cod from the western Baltic can be correlated to the length of the fish. The lengths of the cod from which livers were obtained for processing in the present study were not uniform. Cod caught in the southern Baltic generally range from 25 to 120 cm long. In 1970, the cod were predominantly 39 to 44 cm long, and in 1971, 45 to 50 cm long (*9*).

It should be pointed out that much higher level organochlorines than those noted in Table 1 have found in the livers of some specimens of cod from Baltic. For example, the livers of cod taken from Kattegat in 1973 contained PCBs ranging from 4 t ppm and averaging 13 ppm wet weight; livers of taken from the Rivo Fiord in 1975 contained P ranging from 29 to 57 ppm and averaging 38 ppm weight (*13, 14*).

The following extreme ranges for ΣDDT have been noted: Levels in cod taken from the sout Baltic in 1970–71 ranged from 14 to 57 ppm averaged 26 ppm wet weight and 66 ppm lipid w (*6*); levels in cod taken from the Sund during ranged from 1.4 to 53 ppm and averaged 8.7 ppm weight and 29 ppm lipid weight (*13*).

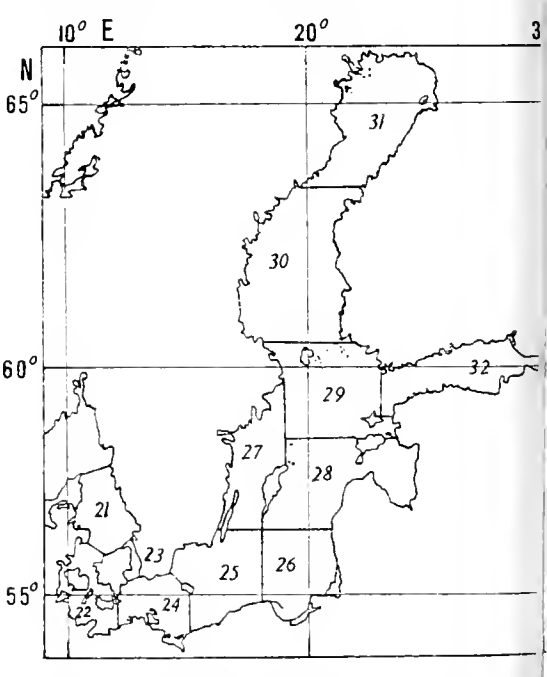

FIGURE 1. *Baltic Sea, with division of the sampling according to International Council for the Exploration Sea*

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Pesticide, Metal, and Other Chemical Residues in Adult Total Diet Samples—(XII)—August 1975–July 1976 [1]

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ABSTRACT

This report is the twelfth in the series on the presence of pesticide and other chemical residues in the average diet of the United States' heartiest eater, the young adult male. Twenty market baskets were collected in 20 U.S. cities that ranged in population from < 50,000 to 1 million or more. Composites of 12 food classes were analyzed. Averages and ranges of residues found are reported for August 1975 through July 1976, by food class. In addition to the pesticide and chemical residues, data for lead, cadmium, selenium, mercury, arsenic, and zinc are included. The individual items making up the dairy and meat composites in four market baskets were analyzed separately for pesticide residues, and the results are included. Results of recovery studies of pesticides and chemicals within various food classes are also presented.

Introduction

In 1964, the Food and Drug Administration (FDA), U.S. Department of Health and Human Services (formerly U.S. Department of Health, Education, and Welfare), initiated a Total Diet Program (*7*), sometimes called the Market Basket study. Its purpose was to monitor the atmosphere for fission products from atmospheric tests of thermonuclear weapons in May 1961. Later, the program was expanded to include pesticide residues and certain nutrients.

At its inception, the program was primarily concerned with the adult diet, which was defined as a market basket of food representing the basic two-week diet of a 16-to-19-year-old male, statistically the United States' heartiest eater. Beginning in August 1974, 10 of the 30 market baskets collected per year were changed to represent the basic two-week diet of infants (6-month-old) and toddlers (2-year-old) (*13*).

The market baskets were collected in four different geographic areas, with the specific diet of the particular region determining the composition of the market basket. Foods were prepared for normal home consumption, and every food item was then placed into one of the 12 composite classes listed in Table 1. For e food class, 20 composites, one from each market bas were prepared. Each composite, containing foods similar characteristics, was analyzed for certain me residues of organochlorine, organophosphorus, carbamate pesticides, herbicides, and industrial ch cals. Methodologies included atomic absorption spec copy, fluorometry, polarography, gas chromatogra thin-layer chromatography, mass spectroscopy, and e lished extraction and cleanup techniques (*8–10, 18,* Amounts and types of residues found from June through July 1975 have been tabulated in earlie ports (*1–5, 11–17*). This report covers the results tained from August 1975 through July 1976 for market baskets collected in 20 different cities. Re for the 10 infant and toddler market baskets colle during the same period are presented in a sep report.

Results

During this reporting period, 1,039 residues of 47 ferent compounds were found in the 240 compc examined. In the previous reporting period, 959 resi of 42 different compounds were found in the same ber of composites. The 47 compounds are listed i creasing order of frequency in Table 2. Table 3 sl the frequency of occurrence of each compound by class, and Table 4 shows the levels of every re found within each food class. The average value in T

TABLE 1. *Classes of adult food composites analyze pesticides, metals, and other chemical residues, A 1975–July 1976*

Key	Food Class
I	Dairy products
II	Meat, fish, and poultry
III	Grain and cereal products
IV	Potatoes
V	Leafy vegetables
VI	Legume vegetables
VII	Root vegetables
VIII	Garden fruits
IX	Fruits
X	Oils, fats, and shortening
XI	Sugar and adjuncts
XII	Beverages (including drinking water)

[1] Food and Drug Administration, Kansas City District Office Laboratory, 1009 Cherry St., Kansas City, MO 64106

BLE 2. *Chemical and metal residues found in adult composites from 20 United States cities—August 1975–July 1976*

ICAL ND	No. of Composites with Residues	No. of Positive Composites with Residues Reported as Trace [1]	Range, ppm
	239	0	0.100 –76.0
ium	170	0	0.010 – 0.100
	85	0	0.040 – 0.820
rin	60	16	0.001 – 0.086
ium	57	0	0.010 – 0.340
DDE [2]	52	16	0.001 – 0.048
C	46	31	0.0003– 0.007
ic	31	0	0.030 – 0.460
chlor epoxide	30	19	0.001 – 0.003
thion	29	3	0.004 – 0.096
ary	24	0	0.006 – 0.080
ne	24	11	0.0006– 0.004
	19	12	0.0002– 0.0060
hlor epoxide	17	15	0.0020
DDT	16	9	0.0030– 0.010
sulfan sulfate	13	5	0.003 – 0.030
sulfan I	12	1	0.0010– 0.0110
sulfan II	11	5	0.002 – 0.0120
oran	10	1	0.002 – 0.163
non	10	2	0.001 – 0.004
B	8	0	0.002 – 0.114
DE	7	6	0.004
n	6	2	0.005 – 0.050
hion	5	0	0.002 – 0.006
	5	0	0.010 – 0.229
al®	5	1	0.002 – 0.014
B	5	2	0.002 – 0.003
ryl	5	4	0.050
ol	4	0	0.007 – 0.028
choloroaniline	4	1	0.007 – 0.018
ane	3	0	0.014 – 0.044
oxychlor	3	2	0.013
	3	3	T
n	2	0	0.026 – 0.040
	2	0	0.026 – 0.060
chlorobenzene	2	0	0.004 – 0.005
	2	0	0.002 – 0.005
el	2	0	0.002 – 0.006
phos	2	1	0.009
dane	2	2	T
C	1	0	0.008
Methyl ether	1	0	0.002
Nonachlor	1	0	0.002
phenothion	1	0	0.195
lone	1	0	0.008
nylphenol	1	1	T
hene	1	1	T

nicals capable of being detected by the specific analytical methgy may be confirmed qualitatively but are not quantifiable when are present at concentrations below the limit of quantitation. of quantitation varies with residue and food class.

TABLE 3. *Frequency of occurrence, by food class, of pesticides, metals, and other chemical residues in adult food composites from 20 United States cities—August 1975–July 1976*

Chemical	Food Class [1]											
	I	II	III	IV	V	VI	VII	VIII	IX	X	XI	XII
	Number of Occurrences											
Zinc	20	20	20	20	20	20	20	20	20	20	20	19
Cadmium	3	17	20	20	19	14	19	18	5	18	14	3
Lead	0	5	12	5	2	17	8	14	11	6	3	2
Dieldrin	15	19	1	4	2	0	1	13	2	3	0	0
Selenium	4	20	20	3	1	5	2	0	0	2	0	0
p,p'-DDE	14	20	0	3	8	1	3	2	0	1	0	0
α-BHC	17	19	0	0	0	0	0	3	1	1	5	0
Arsenic	1	17	8	0	0	1	1	1	0	1	0	1
Heptachlor epoxide	13	15	0	2	0	0	0	0	0	0	0	0
Malathion	0	0	19	0	0	0	0	0	0	7	3	0
Mercury	0	18	1	0	0	0	0	0	1	1	1	2
Lindane	2	7	1	0	1	0	0	5	0	1	7	0
HCB	5	11	0	0	0	0	0	0	0	3	0	0
Octachlor epoxide	5	12	0	0	0	0	0	0	0	0	0	0
p,p'-DDT	0	15	0	0	1	0	0	0	0	0	0	0
Endosulfan sulfate	0	0	0	2	6	0	0	3	2	0	0	0
Endosulfan I	0	0	0	0	5	0	0	6	1	0	0	0
Endosulfan II	0	0	0	0	5	0	0	4	2	0	0	0
Dichloran	0	0	0	0	4	1	0	0	4	0	1	0
Diazinon	0	0	5	0	2	0	0	2	1	0	0	0
TCNB	0	0	1	6	0	0	0	1	0	0	0	0
p,p'-TDE	0	7	0	0	0	0	0	0	0	0	0	0
Ethion	0	1	0	0	0	0	1	1	3	0	0	0
Parathion	0	0	0	0	1	2	1	1	0	0	0	0
CIPC	0	0	0	5	0	0	0	0	0	0	0	0
DCPA	0	0	0	0	3	0	2	0	0	0	0	0
PCNB	0	0	0	0	0	0	0	0	0	5	0	0
Carbaryl	0	0	0	0	0	0	0	2	3	0	0	0
Dicofol	0	0	0	0	0	0	0	0	4	0	0	0
Pentachloroaniline	0	0	0	0	0	0	0	0	0	4	0	0
Perthane	0	0	0	0	2	0	0	0	1	0	0	0
Methoxychlor	3	0	0	0	0	0	0	0	0	0	0	0
PCB	1	2	0	0	0	0	0	0	0	0	0	0
Captan	0	0	0	0	0	0	0	0	2	0	0	0
PCP	0	0	0	0	0	0	0	0	0	0	1	1
Pentachlorobenzene	0	0	0	0	0	0	0	0	0	2	0	0
PCTA	0	0	0	0	0	0	0	0	0	2	0	0
Ronnel	0	1	1	0	0	0	0	0	0	0	0	0
Leptophos	0	0	0	0	0	0	0	2	0	0	0	0
Chlordane	0	0	1	1	0	0	0	0	0	0	0	0
β-BHC	0	0	0	0	1	0	0	0	0	0	0	0
PCP Methyl ether	0	0	0	0	0	0	0	0	0	1	0	0
trans-Nonachlor	0	1	0	0	0	0	0	0	0	0	0	0
Carbophenothion	0	0	0	0	0	0	0	1	0	0	0	0
Phosalone	0	0	0	0	0	0	0	0	1	0	0	0
o-Phenylphenol	0	0	0	0	0	0	0	0	0	0	1	0
Toxaphene	0	0	0	0	1	0	0	0	0	0	0	0

[1] See Table 1 for key to food classes.

based on the 20 composites examined; trace resi-, if present, were treated as zero in calculating the ages. For this reason, an average value reported as can be well below the detection limits of the ods for that compound.

gan et al. reported the human dietary intake of cides and industrial chemicals detected in mg/kg weight/day, for the period July 1969 through 1976 (*6*). Comparative values for fiscal years –75 are also given (*6*). Because Duggan et al. do report dietary intakes for metals determined in the l Diet studies, they are shown here in Table 5 for 76. The daily intakes in μg/day (mg/day for zinc) are listed in Table 5 by food group, together with the percentage of the total daily intake contributed by each.

The most common residues and their maximum levels for each of the 12 food classes are discussed below. No findings have been corrected for recovery.

DAIRY PRODUCTS

Metal residues were found most frequently and at the highest levels in dairy products. Averages were 4.92 ppm zinc, 0.004 ppm selenium, 0.004 ppm arsenic, and 0.002 ppm cadmium. Of the organochlorine residues, *p,p'*-DDE levels, ranging from 0.001 to 0.010 ppm and averaging 0.002 ppm for the series, were the highest. Other

TABLE 4. *Levels of chemical and metal residues, by food class, in adult food composites from 20 United States ci August 1975–July 1976*

CHEMICAL	RESIDUES, PPM	CHEMICAL	RESIDUES
I. DAIRY PRODUCTS			
ZINC		α–BHC	
Average	4.92	Average	T
Positive composites		Positive composites	
Total number	20	Total number	17
Number reported as trace	0	Number reported as trace	8
Range	3.50–5.90	Range	0.0003–
p,p'–DDE		METHOXYCHLOR	
Average	0.002	Average	T
Positive composites		Positive composites	
Total number	14	Total number	3
Number reported as trace	6	Number reported as trace	2
Range	0.0010–0.0100	Range	0
DIELDRIN		HCB	
Average	T	Average	T
Positive composites		Positive composites	
Total number	15	Total number	5
Number reported as trace	7	Number reported as trace	4
Range	0.001–0.003	Range	0
HEPTACHLOR EPOXIDE		LINDANE	
Average	T	Average	T
Positive composites		Positive composites	
Total number	13	Total number	2
Number reported as trace	10	Number reported as trace	2
Range	0.001	Range	T
SELENIUM		CADMIUM	
Average	0.004	Average	(
Positive composites		Positive composites	
Total number	4	Total number	3
Number reported as trace	0	Number reported as trace	(
Range	0.02–0.03	Range	0.01–
OCTACHLOR EPOXIDE		ARSENIC	
Average	T	Average	(
Positive composites		Positive composites	
Total number	5	Total number	1
Number reported as trace	5	Number reported as trace	(
Range	T	Range	(
PCB			
Average	T		
Positive composites			
Total number	1		
Number reported as trace	1		
Range	T		
II. MEAT, FISH, AND POULTRY			
ZINC		SELENIUM	
Average	32.2	Average	
Positive composites		Positive composites	
Total number	20	Total number	2
Number reported as trace	0	Number reported as trace	
Range	25.3–76.0	Range	0.09
MERCURY		LEAD	
Average	0.02	Average	
Positive composites		Positive composites	
Total number	18	Total number	
Number reported as trace	0	Number reported as trace	
Range	0.007–0.08	Range	0.05
CADMIUM		ARSENIC	
Average	0.01	Average	
Positive composites		Positive composites	
Total number	17	Total number	1
Number reported as trace	0	Number reported as trace	
Range	0.01–0.03	Range	0.03
p,p'–DDE		*p,p'*–TDE	
Average	0.010	Average	
Positive composites		Positive composites	
Total number	20	Total number	
Number reported as trace	1	Number reported as trace	
Range	0.002–0.048	Range	

LE 4. (cont'd.). *Levels of chemical and metal residues, by food class, in adult food composites from 20 United States cities—August 1975–July 1976*

CAL	RESIDUES, PPM	CHEMICAL	RESIDUES, PPM
DT		DIELDRIN	
age	0.002	Average	0.007
ive composites		Positive composites	
tal number	15	Total number	19
mber reported as trace	9	Number reported as trace	1
nge	0.003–0.01	Range	0.001–0.086
		HCB	
age	T	Average	T
ive composites		Positive composites	
tal number	19	Total number	11
mber reported as trace	17	Number reported as trace	8
nge	0.001	Range	0.0002–0.002
CHLOR EPOXIDE		HEPTACHLOR EPOXIDE	
age	T	Average	T
ive composites		Positive composites	
tal number	12	Total number	15
mber reported as trace	10	Number reported as trace	9
nge	0.002	Range	0.001–0.002
EL		PCB	
age	T	Average	T
ive composites		Positive composites	
tal number	1	Total number	2
mber reported as trace	0	Number reported as trace	2
nge	0.006	Range	T
NE		*trans*-NONACHLOR	T
age	T	Average	
ive composites		Positive composites	
tal number	7	Total number	1
mber reported as trace	3	Number reported as trace	0
nge	0.0006–0.003	Range	0.002
N			
age	T		
ive composites			
tal number	1		
mber reported as trace	1		
nge	T		

III. GRAIN AND CEREAL PRODUCTS

		SELENIUM	
age	9.0	Average	0.19
ive composites		Positive composites	
tal number	20	Total number	20
mber reported as trace	0	Number reported as trace	0
nge	5.5–15.5	Range	0.04–0.34
		CADMIUM	
age	0.05	Average	0.03
ive composites		Positive composites	
al number	12	Total number	20
mber reported as trace	0	Number reported as trace	0
nge	0.04–0.14	Range	0.02–0.05
THION		DIELDRIN	
age	0.02	Average	T
ve composites		Positive composites	
al number	19	Total number	1
mber reported as trace	0	Number reported as trace	0
ge	0.004–0.096	Range	0.003
DANE		ARSENIC	
ge	T	Average	0.02
ve composites		Positive composites	
al number	1	Total number	8
nber reported as trace	1	Number reported as trace	0
ge	T	Range	0.0303–0.10
JRY		DIAZINON	
ge	T	Average	T
ve composites		Positive composites	
al number	1	Total number	5
nber reported as trace	0	Number reported as trace	0
ge	0.01	Range	0.001–0.004

TABLE 4. (cont'd.). *Levels of chemical and metal residues, by food class, in adult food composites from 20 United S cities—August 1975–July 1976*

Chemical	Residues, ppm	Chemical	Residues
TCNB		LINDANE	
Average	T	Average	T
Positive composites		Positive composites	
Total number	1	Total number	1
Number reported as trace	0	Number reported as trace	1
Range	0.002	Range	T
RONNEL			
Average	T		
Positive composites			
Total number	1		
Number reported as trace	0		
Range	0.002		
IV. POTATOES			
ZINC		CADMIUM	
Average	5.18	Average	0
Positive composites		Positive composites	
Total number	20	Total number	20
Number reported as trace	0	Number reported as trace	0
Range	2.6–14.5	Range	0.02–
TCNB		LEAD	
Average	0.007	Average	0
Positive composites		Positive composites	
Total number	6	Total number	5
Number reported as trace	0	Number reported as trace	0
Range	0.002–0.114	Range	0.06–
HEPTACHLOR EPOXIDE		DIELDRIN	
Average	T	Average	T
Positive composites		Positive composites	
Total number	2	Total number	4
Number reported as trace	0	Number reported as trace	2
Range	0.001–0.002	Range	0.001–
ENDOSULFAN SULFATE		SELENIUM	
Average	T	Average	(
Positive composites		Positive composites	
Total number	2	Total number	3
Number reported as trace	0	Number reported as trace	(
Range	0.003–0.012	Range	0.02–
CIPC		CHLORDANE	
Average	0.04	Average	T
Positive composites		Positive composites	
Total number	5	Total number	
Number reported as trace	0	Number reported as trace	
Range	0.01–0.23	Range	T
p,p'–DDE			
Average	T		
Positive composites			
Total number	3		
Number reported as trace	2		
Range	0.003		
V. LEAFY VEGETABLES			
ZINC		CADMIUM	
Average	2.67	Average	
Positive composites		Positive composites	
Total number	20	Total number	1
Number reported as trace	0	Number reported as trace	
Range	1.7–7.0	Range	0.02
ENDOSULFAN I		ENDOSULFAN II	
Average	0.001	Average	
Positive composites		Positive composites	
Total number	5	Total number	
Number reported as trace	0	Number reported as trace	
Range	0.001–0.011	Range	0.002
ENDOSULFAN SULFATE		LINDANE	
Average	0.004	Average	
Positive composites		Positive composites	
Total number	6	Total number	
Positive composites	2	Number reported as trace	
Range	0.008–0.030	Range	

E 4. (cont'd.). *Levels of chemical and metal residues, by food class, in adult food composites from 20 United States cities—August 1975–July 1976*

AL	RESIDUES, PPM	CHEMICAL	RESIDUES, PPM
THION		DIAZINON	
ge	T	Average	T
ve Composites		Positive composites	
al number	1	Total number	2
mber reported as trace	0	Number reported as trace	1
nge	0.004	Range	0.003
PHENE		*p,p'*-DDE	
ge	T	Average	0.003
ve composites		Positive composites	
al number	1	Total number	8
mber reported as trace	1	Number reported as trace	3
nge	T	Range	0.001–0.023
		p,p'-DDT	
ge	0.007	Average	T
ve composites		Positive composites	
al number	2	Total number	1
mber reported as trace	0	Number reported as trace	0
nge	0.06–0.09	Range	0.005
ORAN		DIELDRIN	
ge	0.002	Average	T
ve composites		Positive composites	
al number	4	Total number	2
mber reported as trace	1	Number reported as trace	1
nge	0.002–0.025	Range	0.002
ANE		SELENIUM	
ge	0.003	Average	T
ve composites		Positive composites	
al number	2	Total number	1
mber reported as trace	0	Number reported as trace	0
nge	0.024–0.044	Range	0.010
		β-BHC	
ge	0.001	Average	T
ve composites		Positive composites	
al number	3	Total number	1
mber reported as trace	0	Number reported as trace	0
nge	0.002–0.014	Range	0.008

VI. LEGUME VEGETABLES

		LEAD	
ge	7.62	Average	0.26
ve composites		Positive composites	
al number	20	Total number	17
mber reported as trace	0	Number reported as trace	0
nge	5.30–12.0	Range	0.08–0.82
UM		ARSENIC	
ge	0.01	Average	0.004
ve composites		Positive composites	
al number	14	Total number	1
mber reported as trace	0	Number reported as trace	0
nge	0.01–0.07	Range	0.07
IUM		PARATHION	
ge	0.008	Average	T
ve composites		Positive composites	
al number	5	Total number	2
mber reported as trace	0	Number reported as trace	0
nge	0.02–0.05	Range	0.002–0.003
DE		DICHLORAN	
ge	T	Average	0.001
ve composites		Positive composites	
al number	1	Total number	1
mber reported as trace	0	Number reported as trace	0
ge	0.001	Range	0.027

VII. ROOT VEGETABLES

		LEAD	
ge	2.32	Average	0.036
ve composites		Positive composites	
al number	20	Total number	8
mber reported as trace	0	Number reported as trace	0
ge	1.30–4.60	Range	0.06–0.14

TABLE 4. (cont'd.). *Levels of chemical and metal residues, by food class, in adult food composites from 20 United S cities—August 1975–July 1976*

Chemical	Residues, ppm	Chemical	Residues
CADMIUM		ARSENIC	
Average	0.027	Average	0
Positive composites		Positive composites	
Total number	19	Total number	1
Number reported as trace	0	Number reported as trace	0
Range	0.01–0.08	Range	0
SELENIUM		PARATHION	
Average	0.002	Average	T
Positive composites		Positive composites	
Total number	2	Total number	1
Number reported as trace	0	Number reported as trace	0
Range	0.020	Range	0
DIELDRIN		*p,p'*-DDE	
Average	T	Average	T
Positive composites		Positive composites	
Total number	1	Total number	3
Number reported as trace	1	Number reported as trace	1
Range	T	Range	0.004–
DCPA		ETHION	
Average	T	Average	T
Positive composites		Positive composites	
Total number	2	Total number	1
Number reported as trace	1	Number reported as trace	1
Range	0.004	Range	T
VIII. GARDEN FRUITS			
ZINC		LEAD	
Average	2.08	Average	(
Positive composites		Positive composites	
Total number	20	Total number	14
Number reported as trace	0	Number reported as trace	(
Range	1.20–3.50	Range	0.06–
CADMIUM		ARSENIC	
Average	0.02	Average	(
Positive composites		Positive composites	
Total number	18	Total number	
Number reported as trace	0	Number reported as trace	(
Range	0.01–0.04	Range	(
DIELDRIN		LEPTOPHOS	
Average	0.002	Average	T
Positive composites		Positive composites	
Total number	13	Total number	
Number reported as trace	2	Number reported as trace	
Range	0.002–0.009	Range	
ENDOSULFAN I		ENDOSULFAN II	
Average	T	Average	T
Positive composites		Positive composites	
Total number	6	Total number	
Number reported as trace	1	Number reported as trace	
Range	0.002–0.004	Range	0.004
ENDOSULFAN SULFATE		CARBARYL	
Average	T	Average	
Positive composites		Positive composites	
Total number	3	Total number	
Number reported as trace	2	Number reported as trace	
Range	0.005	Range	
DIAZINON		LINDANE	
Average	T	Average	
Positive composites		Positive composites	
Total number	2	Total number	
Number reported as trace	1	Number reported as trace	
Range	0.002	Range	0.001
p,p'-DDE		PARATHION	
Average	T	Average	
Positive composites		Positive composites	
Total number	2	Total number	
Number reported as trace	2	Number reported as trace	
Range	T	Range	
α-BHC		ETHION	
Average	T	Average	
Positive composites		Positive composites	
Total number	3	Total number	
Number reported as trace	0	Number reported as trace	
Range	0.004–0.007	Range	

E 4. (cont'd.). *Levels of chemical and metal residues, by food class, in adult food composites from 20 United States cities—August 1975–July 1976*

CAL	RESIDUES, PPM	CHEMICAL	RESIDUES, PPM
OFENOTHION		TCNB	
age	0.010	Average	T
ive composites		Positive composites	
tal number	1	Total number	1
mber reported as trace	0	Number reported as trace	0
nge	0.195	Range	0.002
	IX. FRUITS		
		LEAD	
age	2.44	Average	0.041
ive composites		Positive composites	
tal number	20	Total number	11
mber reported as trace	0	Number reported as trace	0
nge	0.10–19.0	Range	0.05–0.11
LORAN		CARBARYL	
age	0.009	Average	T
ive composites		Positive composites	
tal number	4	Total number	3
mber reported as trace	0	Number reported as trace	3
nge	0.006–0.163	Range	T
IANE		DICOFOL	
age	T	Average	0.003
ve composites		Positive composites	4
tal number	1	Number reported as trace	0
mber reported as trace	0	Range	0.007–0.028
nge	0.014		
SULFAN I		ENDOSULFAN II	
age	T	Average	T
ve composites		Positive composites	
al number	1	Total number	2
mber reported as trace	0	Number reported as trace	1
nge	0.007	Range	0.012
SULFAN SULFATE		CADMIUM	
age	T	Average	0.003
ve composites		Positive composites	
al number	2	Total number	5
muber reported as trace	1	Number reported as trace	0
nge	0.005	Range	0.01–0.02
LONE		ETHION	
age	T	Average	T
ve composites		Positive composites	
al number	1	Total number	3
mber reported as trace	0	Number reported as trace	0
nge	0.008	Range	0.005–0.006
RIN		DIAZINON	
age	T	Average	T
ve composites		Positive composites	
al number	2	Total number	1
mber reported as trace	0	Number reported as trace	0
nge	0.001	Range	0.004
		CAPTAN	
age	T	Average	0.003
ve composites		Positive composites	
al number	1	Total number	2
mber reported as trace	0	Number reported as trace	0
nge	0.001	Range	0.026–0.040
URY			
age	T		
ve composites			
al number	1		
mber reported as trace	0		
nge	0.015		
	X. OILS, FATS, AND SHORTENING		
		CADMIUM	
ge	4.14	Average	0.016
ve composites		Positive composites	
al number	20	Total number	18
nber reported as trace	0	Number reported as trace	0
ige	0.20–6.20	Range	0.01–0.03

TABLE 4. (cont'd.). *Levels of chemical and metal residues, by food class, in adult food composites from 20 United S cities—August 1975–July 1976*

Chemical	Residues, ppm	Chemical	Residue
MALATHION		*p,p'*–DDE	
Average	0.003	Average	T
Positive composites		Positive composites	
Total number	7	Total number	1
Number reported as trace	2	Number reported as trace	1
Range	0.005–0.03	Range	T
DIELDRIN		MERCURY	
Average	T	Average	T
Positive composites		Positive composites	
Total number	3	Total number	1
Number reported as trace	2	Number reported as trace	(
Range	0.002	Range	(
ARSENIC		HCB	
Average	0.002	Average	T
Positive composites		Positive composites	
Total number	1	Total number	3
Number reported as trace	0	Number reported as trace	(
Range	0.04	Range	0.001
PCNB		PENTACHLOROANILINE	
Average	T	Average	
Positive composites		Positive composites	
Total number	5	Total number	
Number reported as trace	2	Number reported as trace	
Range	0.002–0.003	Range	0.007
α–BHC		LINDANE	
Average	T	Average	
Positive composites		Positive composites	
Total number	1	Total number	
Number reported as trace	1	Number reported as trace	
Range	T	Range	
LEAD		SELENIUM	
Average	0.028	Average	
Positive composites		Positive composites	
Total number	6	Total number	
Number reported as trace	0	Number reported as trace	
Range	0.05–0.14	Range	0.04
PENTACHLOROBENZENE		PCTA	
Average	T	Average	
Positive composites		Positive composites	
Total number	2	Total number	
Number reported as trace	0	Number reported as trace	
Range	0.004–0.005	Range	0.002
PCP METHYL ETHER			
Average	T		
Positive composites			
Total number	1		
Number reported as trace	0		
Range	0.002		

XI. SUGAR AND ADJUNCTS

ZINC		PCP	
Average	2.95	Average	)
Positive composites		Positive composites	
Total number	20	Total number	1
Number reported as trace	0	Number reported as trace	)
Range	0.10–16.0	Range	)
CADMIUM		*o*-PHENYLPHENOL	
Average	0.011	Average	T
Positive composites		Positive composites	
Total number	14	Total number	1
Number reported as trace	0	Number reported as trace	1
Range	0.01–0.03	Range	T
LINDANE		α-BHC	
Average	T	Average	T
Positive composites		Positive composites	
Total number	7	Total number	5
Number reported as trace	3	Number reported as trace	5
Range	0.001–0.003	Range	T

E 4. (cont'd.). *Levels of chemical and metal residues, by food class, in adult food composites from 20 United States cities—August 1975–July 1976*

AL	RESIDUES, PPM	CHEMICAL	RESIDUES, PPM
THION		LEAD	
ge	T	Average	0.015
ve composites		Positive composites	
al number	3	Total number	3
mber reported as trace	1	Number reported as trace	0
ge	0.005–0.008	Range	0.06–0.14
ORAN		MERCURY	
ge	T	Average	T
ve composites		Positive composites	
al number	1	Total number	1
mber reported as trace	0	Number reported as trace	0
ge	0.005	Range	0.012
		XII. BEVERAGES	
		LEAD	
ge	0.46	Average	0.004
ve composites		Positive composites	
al number	19	Total number	2
mber reported as trace	0	Number reported as trace	0
ge	0.20–1.90	Range	0.04–0.05
IC		CADMIUM	
ge	0.008	Average	0.002
ve composites		Positive composites	
al number	1	Total number	3
mber reported as trace	0	Number reported as trace	0
ge	0.15	Range	0.01
		MERCURY	
ge	0.001	Average	0.001
ve composites		Positive composites	
al number	1	Total number	2
mber reported as trace	0	Number reported as trace	0
ge	0.026	Range	0.006–0.018

Average values are based on 20 composites examined; trace residues, if present, were treated as zero in calculating averages. Thus, an value of "T" can be well below detection limits of the methods for that compound.

TABLE 5. *FY 76 daily intakes, by food group, of metals in the diet of United States adults*

FOOD GROUP	LEAD		CADMIUM		ZINC		ARSENIC [1]		SELENIUM		MERCURY	
	µG/DAY	% TOTAL INTAKE	µG/DAY	% TOTAL INTAKE	MG/DAY	% TOTAL INTAKE	µG/DAY	% TOTAL INTAKE	µG/DAY	% TOTAL INTAKE	µG/DAY	% TOTAL INTAKE
Dairy products	0.00	0.0	1.63	5.0	3.72	19.4	3.17	4.8	3.26	2.4	0.00	0.0
Meat, fish, and poultry	3.67	5.2	2.63	8.0	8.44	44.1	49.46	74.4	52.52	38.7	5.29	81.3
Grains and cereal products	19.90	28.0	11.97	36.4	3.81	19.9	7.56	11.4	78.41	57.8	0.21	3.2
Potatoes	5.15	7.2	7.46	22.7	0.82	4.3	0.00	0.0	0.59	0.4	0.00	0.0
Leafy vegetables	0.38	0.5	2.43	7.4	0.15	0.8	0.00	0.0	0.03	0.02	0.00	0.0
Legume vegetables	18.98	26.7	0.82	2.5	0.56	2.9	0.28	0.4	0.61	0.4	0.00	0.0
Root vegetables	1.27	1.8	0.87	2.6	0.08	0.4	0.10	0.1	0.06	0.04	0.00	0.0
Garden fruits	6.07	8.5	1.42	4.3	0.15	0.8	0.36	0.5	0.00	0.0	0.00	0.0
Fruits	9.07	12.8	0.66	2.0	0.54	2.8	0.00	0.0	0.00	0.0	0.10	1.5
Oils, fats, and shortening	2.04	2.9	1.11	3.4	0.30	1.6	0.00	0.0	0.16	0.1	0.02	0.3
Sugar and adjuncts	1.24	1.7	0.87	2.6	0.24	1.3	0.00	0.0	0.00	0.0	0.04	0.6
Beverages (including drinking water)	3.31	4.7	1.02	3.1	0.32	1.7	5.57	8.4	0.00	0.0	0.85	13.1
Total intake	71.08	100.0	32.89	100.0	19.13	100.0	66.50	100.0	135.64	99.9[2]	6.51	100.0

calculated as arsenic trioxide (As_2O_3).
ot total 100 because of rounding error.

chlorine compounds present at low levels included
(hexachlorocyclohexane), dieldrin, heptachlor
e, octachlor epoxide, methoxychlor, HCB (hexa-
benzene), and lindane. A trace of an industrial
al, a PCB (polychlorinated biphenyl), was found
of the composites. No organophosphorus com-
were found.

MEAT, FISH, AND POULTRY

Metal residues dominated this food class, with the following series averages: 32.2 ppm zinc (range 25.3–76.0 ppm), 0.20 ppm selenium, 0.19 ppm arsenic, 0.02 ppm mercury, 0.014 ppm lead, and 0.01 ppm cadmium. Of the organochlorine residues, *p,p'*-DDE, ranging from 0.002 to 0.048 ppm and averaging 0.010 ppm for the

series, was found in all 20 composites; dieldrin, averaging 0.007 ppm, was reported in 19 composites; and *p,p'*-DDT averaged 0.002 ppm with positive findings in 15 composites. Trace averages were reported for *p,p'*-TDE, α-BHC, HCB, octachlor epoxide, heptachlor epoxide, ronnel, lindane, and *trans*-nonachlor. Traces of ethion, an organophosphorus pesticide, and a PCB also were found in one and two composites, respectively.

GRAIN AND CEREAL PRODUCTS

All 20 composites contained zinc, selenium, and cadmium residues, averaging 9.0, 0.19, and 0.03 ppm, respectively. Twelve composites had lead residues, averaging 0.05 ppm for the series, and eight composites had arsenic residues, for a series average of 0.02 ppm. Malathion, one of two organophosphorus pesticides, was reported in 19 composites and averaged 0.02 ppm for the series; the other, ronnel, occurred as a trace amount in one composite. Also reported were traces of dieldrin, chlordane, TCNB, lindane, diazinon, and mercury.

POTATOES

Zinc, ranging from 2.6 to 14.5 ppm, and cadmium, ranging from 0.02 to 0.09 ppm, were reported for all 20 composites, with averages of 5.18 and 0.05 ppm, respectively. Lead, averaging 0.03 ppm for the series, was found in five composites, and selenium, ranging from 0.02 to 0.05 ppm in three composites, averaged 0.006 ppm for the 20-composite series. CIPC, ranging from 0.01 to 0.23 ppm in five composites, averaged 0.04 ppm for the series. TCNB averaged 0.007 ppm for the series with a range of 0.002–0.114 ppm in six composites. Traces of heptachlor epoxide, dieldrin, endosulfan sulfate, *p,p'*-DDE, and chlordane were also found.

LEAFY VEGETABLES

Only zinc, ranging from 1.7 to 7.0 ppm and averaging 2.67 ppm, was reported for all 20 composites. Cadmium ranged from 0.02 to 0.10 ppm in 19 composites and averaged 0.04 ppm for the series. The most frequently reported pesticide was *p,p'*-DDE, averaging 0.003 ppm for the series, with eight reported findings. Endosulfan I, ranging from 0.001 to 0.011 ppm, and endosulfan II, ranging from 0.002 to 0.004 ppm, were each reported for five composites; endosulfan sulfate, ranging from 0.008 to 0.030 ppm, was reported for six composites. Other reportable residues and their averages included dichloran, 0.002 ppm; DCPA, 0.001 ppm; Perthane®, 0.003 ppm; and lead, 0.007 ppm. Traces of lindane, diazinon, parathion, toxaphene, dieldrin, *p,p'*-DDT, selenium, and β-BHC were also found.

LEGUME VEGETABLES

Legume vegetables exhibited high metal residues. Zinc, reported in all 20 composites, ranged from 5.30 to 12.0 ppm and averaged 7.62 ppm. Lead ranged from 0.08 to 0.82 ppm and averaged 0.26 ppm for the series. Cadmium, ranging from 0.01 to 0.07 ppm, averaged ppm for the series. Arsenic and selenium occurre frequently. The pesticides parathion, *p,p'*-DDE, dichloran were found at low levels.

ROOT VEGETABLES

Zinc ranged from 1.30 to 4.60 ppm and averaged ppm for the 20 composites. Cadmium, ranging 0.01 to 0.08 ppm in 19 composites, averaged 0.027 overall. Lesser amounts of lead, arsenic, and sele averaging 0.036, 0.004, and 0.002 ppm, respect were also reported. Only traces of parathion, die *p,p'*-DDE, DCPA, and ethion were found.

GARDEN FRUITS

Four metals were reported in this food class: ranging from 1.20 to 3.50 ppm in 20 composite averaging 2.08 ppm; cadmium, ranging from 0.(0.04 ppm in 18 composites and averaging 0.02 ppı the 20-composite series; lead, ranging from 0.06 tc ppm in 14 composites and averaging 0.081 ppm fc series; and arsenic, reported in one composite at ppm. The most significant pesticide residue, die ranged from 0.002 to 0.009 ppm in 13 composite averaged 0.002 ppm for the series. Carbophenothio found in one composite at 0.195 ppm, with a average of 0.01 ppm. The following trace average were reported: leptophos; endosulfan I, II, and su carbaryl; diazinon; lindane; *p,p'*-DDE; para α-BHC; ethion; and TCNB.

FRUITS

The two most prevalent residues in this food class zinc, reported for all 20 composites, ranging from to 19.0 ppm and averaging 2.44 ppm, and lead, ra from 0.05 to 0.11 ppm in 11 composites and aver 0.041 ppm for the series. Cadmium, ranging from to 0.02 ppm in five composites, averaged 0.003 pp the series. Both dichloran and dicofol were fou four composites and averaged 0.009 ppm and ppm, respectively, for the series. Ethion ranged 0.005 to 0.006 ppm for three composites but ave trace for the series. Less frequently occurring re were carbaryl, averaging a trace for the series; c endosulfan I, II, and sulfate; Perthane; phosalone; non; dieldrin; and α-BHC. Mercury, 0.015 ppm reported for one composite.

OILS, FATS, AND SHORTENING

High zinc levels, ranging from 0.20 to 6.20 ppr averaging 4.14 ppm, were reported for 20 comp Cadmium, ranging from 0.01 to 0.03 ppm in 18 posites, averaged 0.016 ppm for the series. Seven posites contained malathion residues, ranging from to 0.03 ppm; series average was 0.003. Lead, ave 0.028 ppm for the series, ranged from 0.05 to 0.1

LE 6. *Pesticide residues in individual commodities of dairy composite of four market basket samples—August 1975–July 1976*

E FOUND	COMMODITY [1,2]								
	WHOLE MILK (4)	EVAPORATED MILK (4)	ICE CREAM (4)	COTTAGE CHEESE (4)	PROCESSED CHEESE (4)	NATURAL CHEESE (4)	BUTTER (4)	SKIM MILK (4)	ICE MILK (2)
s found	1	4	4	3	4	4	4		2
ge, ppm	T	T–0.002	T–0.002	T	0.002–0.005	0.001–0.008	0.008–0.011		T–0.001
DE									
s found	2	4	3	2	4	3	4		2
ge, ppm	0.002–0.003	T–0.020	0.002–0.010	0.003–0.009	0.002–0.016	T–0.004	0.004–0.132		0.002–0.006
s found	1	2	3	1	3	3	4	1	1
ge, ppm	T	T	T	0.001	T–0.001	T–0.002	T–0.004	T	T
hlor epoxide									
s found		2	2	1	3	4	4		
ge, ppm		T	T	T	0.002–0.005	T–0.004	0.004–0.019		
n									
s found		4	4	2	4	4	4		
ge, ppm		T–0.002	T–0.002	T	0.005–0.010	0.003–0.010	0.017–0.053		
ychlor									
s found		1	1	1		1	1		
ge, ppm		0.016	T	T		T	0.141		
e									
s found			2		1		2		
ge, ppm			T		0.001		T–0.002		
lor epoxide									
s found			1		3	3	3		
ge, ppm			T		T–0.002	T	0.004–0.008		
DT									
s found					2	1			
ge, ppm					T	T			
DE									
s found						1			
e, ppm						T			

T = trace.
milk and nonfat dry milk not included because no residues were found
ers in parentheses indicate number of times that commodity was analyzed.

composites. Pentachloroaniline, averaging 0.002 for the series, was found in four composites. The ning residues included HCB, selenium, PCNB, , pentachlorobenzene, dieldrin, α-BHC, arsenic, DE, and lindane. One composite contained 0.008 nercury.

R AND ADJUNCTS

netal residues were among the highest in this food Zinc, ranging from 0.10 to 16.0 ppm, was reported 20 composites and averaged 2.95 ppm. Cadmium, in 14 composites, averaged 0.011 ppm for the Lead, ranging from 0.06 to 0.14 ppm in three osites, averaged 0.015 ppm for the series. Mercury 12 ppm was reported for one composite. Other resi- were α-BHC, PCP, lindane, malathion, *o*-phenyl- l, and dichloran.

AGES

found in 19 composites at levels ranging from 0.20 0 ppm, averaged 0.46 ppm for the series. The ning residues, each found in three or fewer com- s, had the following series averages: cadmium, 0.002 ppm; lead, 0.004 ppm; mercury, 0.001 ppm; arsenic, 0.008 ppm; and PCP, 0.001 ppm.

Discussion

Of the 240 composites analyzed, 125, or 52 percent, contained organochlorine pesticide residues, compared with 49, 48, 52, and 54 percent reported for fiscal years 1975, 1974, 1973, and 1972, respectively. Organophosphorus residues in the current reporting period were found in 45, or 18.7 percent, of the composites. Corresponding findings for fiscal years 1975, 1974, 1973, and 1972 were 25, 28, 31, and 28 percent, respectively. The present report and that for FY 75 were based on 20 market baskets, whereas all earlier reports were based on 30 market baskets.

Sixty percent of the 346 organochlorine residues in the current reporting period were found in two food classes: dairy products and meat-fish-poultry. The remaining organochlorine residues were distributed among the other food classes with the garden fruits and leafy vegetables containing half of them. No organochlorine resi-

TABLE 7. *Pesticide residues in individual commodities of meat and fish composites of four market baskets, August 1 July 1976*

Residue Found	Commodity [1]						
	Roast Beef (4)	Ground Beef (4)	Pork Chops (4)	Bacon (4)	Chicken (4)	Fish Fillet (4)	Tuna (4
Dieldrin							
Times found	4	2	4	2	4		1
Range, ppm	T–0.003	0.006–0.007	0.002–0.006	T–2.25	0.002–0.007		T
p,p'-TDE							
Times found	1		1	1		2	4
Range, ppm	0.008		0.016	0.007		T–0.081	T–0.018
HCB							
Times found	3	2	1	1	2	2	1
Range, ppm	T–0.002	0.002	0.002	0.030	0.002–0.008	T–0.003	T
α-BHC							
Times found	2	2		1		2	1
Range, ppm	T–0.001	0.001		T		0.002	T
p,p'-DDE							
Times found	3	1	2	2	4	3	4
Range, ppm	T–0.048	0.031	0.002–0.152	0.002–0.019	0.002–0.028	0.010–0.875	T–0.015
Heptachlor epoxide							
Times found	2	2	2		2		
Range, ppm	0.001–0.009	0.002	T–0.005		T		
Ethion							
Times found		1					
Range, ppm		0.05					
Octachlor epoxide							
Times found	1	1	3	1			
Range, ppm	0.002	0.002	T–0.011	0.003			
trans-Nonachlor							
Times found			1	1			
Range, ppm			0.034	0.003			
p,p'-DDT							
Times found			1	2		3	
Range, ppm			0.034	T–0.141		0.023–0.130	
Endrin							
Times found					1		
Range, ppm					0.001		
PCB (Aroclor 1254)							
Times found	1				1	T	
Range, ppm	T				T	1	
Chlordane							
Times found					1	1	
Range, ppm					T	T	
Lindane							
Times found							
Range, ppm							
TCNB							
Times found							
Range, ppm							

NOTE: T = trace.
[1] Numbers in parentheses indicate the number of times the item was analyzed.

ICHEON AT (4)	FRANK-FURTERS (4)	COMMODITY[1] BEEF LIVER (4)	EGGS (4)	HAM (4)	ROUND STEAK (4)	VEAL (1)	LAMB (2)	SHRIMP (2)
2–0.006	4 0.004–0.054	1 0.014	3 T–0.018	2 T–0.002	2 0.002–0.004	1 T	1 T	
002	2 0.001–0.002	1 T	2 T		2 T		2 0.002	
1–0.003	4 T–0.004	3 T–0.004			3 T		2 T–0.003	
4–0.030	4 T–0.029	2 T–0.003	3 0.002–0.026	1 0.002	2 0.006–0.026	1 T	2 0.011–0.037	1 T
1–0.002	3 T–0.002	1 0.005			1 0.002			
003	2 T–0.002	1 T					1 0.002	
5								
011								
			1 T					
002	1 0.003							
		1 T						

TABLE 8. *Recovery data on residues found in adult total diet samples, August 1975–July 1976*

Residue	Type of Food Composite	Spike Level, ppm	Range of Unfortified Composite, ppm	Range of Total Residue Found, ppm [1,2]	No. of Recovery Attempts
Heptachlor epoxide	fatty	0.003	0–0.001	0.0023–0.0035 (0.0031)	4
	nonfatty	0.003	0–0.001	0.0027–0.0039 (0.0032)	6
Oxychlordane	fatty	0.003	0–0.0007	0.0022–0.0031 (0.0027)	4
	nonfatty	0.003	0–0.0006	0.0024–0.0035 (0.0027)	6
Ethion	fatty	0.01	0.00	0–0.0056 (—)	4
	nonfatty	0.01	0.00	0.0066–0.012 (0.0086)	6
DCPA	fatty	0.005	0.00	0.0027–0.0047 (0.0037)	6
	nonfatty	0.005	0–0.0084	0.0029–0.0059 (0.0050)	12
Perthane	fatty	0.01	0.00	T–0.0104 (0.0069)	6
	nonfatty	0.01	0.00	0.0035–0.014 (0.0091)	12
Methyl parathion	fatty	0.005	0.00	0.0022–0.0030 (0.0026)	3
	nonfatty	0.005	0.00	0.0031–0.0045 (0.0037)	5
Endosulfan sulfate	fatty	0.01	0.00	0.002–0.0076 (0.0048)	2
	nonfatty	0.01	0.00–0.004	0.0035–0.0143 (0.0095)	6
Tetradifon	fatty	0.02	0.00	T–0.027 (0.015)	4
		0.10	0.00	0.088–0.089 (—)	2
	nonfatty	0.02	0.00	0.0104–0.022 (0.0160)	8
		0.10	0.00	0.054–0.188 (0.109)	6
Malathion	fatty	0.005	0.00	0.0037–0.0038 (—)	2
	nonfatty	0.005	0.00	0.0022–0.0064 (0.0041)	6
Phosalone	fatty	0.02	0.00	0.0–0.017 (—)	3
	nonfatty	0.02	0.00–0.002	0.007–0.026 (0.0166)	6
Leptophos	fatty	0.05	0.00	0.016–0.040 (0.027)	3
	nonfatty	0.05	0.00	0.030–0.053 (0.043)	6
Fonofos	fatty	0.01	0.00	0.002	1
	nonfatty	0.01	0.00	0.0067–0.0095 (0.0083)	6
Toxaphene	fatty	0.20	0.00	0.148	1
	nonfatty	0.20	0.00	0.147–0.226 (0.187)	6
2,4-D	fatty	0.04	0.00–0.009	0.00–0.050 (0.021)	7
	nonfatty	0.04	0.00	0.008–0.046 (0.028)	14
PCP	fatty	0.02	0.00–0.003	0.0012–0.009 (0.007)	4
		0.04	0.00–0.001	0.00–0.030 (0.015)	7
	nonfatty	0.02	0.0–0.0004	0.003–0.018 (0.0084)	1
		0.04	0.00–0.0062	0.003–0.039 (0.022)	1
Picloran	fatty	0.10	0.00	0.00–0.043 (—)	
	nonfatty	0.10	0.00	0.033–0.075 (0.046)	
Silvex	fatty	0.04	0.00	0.00–0.032 (0.015)	
	nonfatty	0.04	0.00	0.020–0.053 (0.033)	
2,4-DB	fatty	0.02	0.00	T–0.005 (—)	
		0.04	0.00	0.00–0.033 (0.014)	
	nonfatty	0.02	0.00	0.002–0.015 (0.008)	
		0.04	0.00	0.00–0.038 (0.025)	
2,4,5-T	fatty	0.02	0.00–0.001	0.0058–0.021 (—)	
		0.08	0.00	0.026–0.059 (—)	
	nonfatty	0.02	0.00	0.003–0.0198 (0.014)	
		0.08	0.00	0.032–0.069 (0.048)	
MCP 2-methyl-4-chlorophenoxy-acetic acid	fatty	0.02	0.00	0.009–0.013 (0.011)	
	nonfatty	0.02	0.00	0.0055–0.026 (0.014)	
Carbaryl	nonfatty	0.20	0.00	0.00–0.20 (0.157)	
o-Phenylphenol	nonfatty	0.40	0.00	0.00–0.40 (0.24)	
Arsenic	fatty	0.30	0.00–0.35	0.26–0.81 (0.376)	
		0.40	0.00–0.28	0.37–0.86 (0.44)	
	nonfatty	0.30	0.00–0.03	0.19–0.46 (0.30)	
		0.40	0.00–0.03	0.13–0.57 (0.44)	
Cadmium	fatty	0.10	0.00–0.027	0.094–0.199 (0.113)	
	nonfatty	0.10	0.00–0.058	0.058–0.156 (0.116)	
Lead	fatty	0.20	0.00–0.14	0.020–0.340 (0.133)	
	nonfatty	0.20	0.00–0.310	0.058–0.480 (0.211)	
Mercury	fatty	0.06	0.00–0.049	0.018–0.110 (0.073)	
	nonfatty	0.06	0.00–0.011	0.062–0.088 (0.075)	
Selenium	fatty	0.20	0.00–0.23	0.00–0.39 (0.227)	
	nonfatty	0.20	0.00–0.24	0.11–0.48 (0.216)	
Zinc	fatty	5.0	1.23–6.20	5.74–11.00 (9.54)	
		25.0	4.00–76.00	29.00–99.00 (54.2)	
	nonfatty	5.0	0.10–12.00	4.68–15.0 (8.09)	
		25.0	0.38–15.50	24.38–38.0 (29.8)	

NOTE: T = trace.
[1] Numbers in parentheses represent average residue levels.
[2] These values are uncorrected for background.

s were found in beverage composites and only two e found in the legume vegetable composite.

56 organophosphorus residues constitute about 14 ent of the total pesticide residues reported, with athion representing 29 of them. Nineteen were found rain and cereal products, seven in fats and oils, and e in the sugar composites. No organophosphorus lues were found in the dairy products, potatoes, or rage composites.

carbamate pesticide carbaryl occurred in five com- tes, once at the 0.05 ppm level and four times at the e level. The method for determination of carbaryl also detect the fungicide *o*-phenylphenol, which was rted in one sugar composite at the trace level.

industrial chemicals were detected. Trace amounts PCB, Aroclor 1254, were found in one dairy com- e and in two meat-fish-poultry composites. Low s of pentachlorobenzene were found in two fat posites.

ll the residues reported, 606, or 58 percent, were ls. Zinc was reported in almost every composite, the highest levels being found in the meat com- es. Cadmium was found in 170 composites and lead 5 composites; both were found throughout the vari- classes of foods with fewest findings in the dairy and beverage composites. The 57 selenium residues, 31 ic residues, and 24 mercury residues were found ominantly in the meat-fish-poultry composites and -cereal composites.

ddition to the analysis of the various food class com- es, four market baskets, one from each region, were ted for individual item analysis of two food groups. item-by-item analysis often provides a more ex- picture as to the source of residues within a posite. The dairy and meat classes were chosen use those composites have consistently contained ighest levels of organochlorine and organophos- us residues. Tables 6 and 7 present these findings.

very studies were conducted with each market bas- Composites were fortified with known compounds senting each type of residue (metal, pesticide, etc.), corrections were made for the unfortified composite ibution. The total amount recovered through the od was determined. These results are presented in e 8.

Acknowledgments

authors acknowledge the contributions of all staff bers assigned to the Total Diet Section, Food and Administration, Kansas City District Laboratory.

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APPENDIX

Chemical Names of Compounds Discussed in This Issue

ALDRIN	Hexachlorohexahydro-*endo,exo*-dimethanonaphthalene 95% and related compounds 5%
AROCLOR 1016 or 1242	PCB, approximately 42% chlorine
AROCLOR 1242	PCB, approximately 42% chlorine
AROCLOR 1254	PCB, approximately 54% chlorine
BHC (Benzene Hexachloride)	1,2,3,4,5,6-Hexachlorocyclohexane (mixture of isomers)
CAPTAN	*N*-Trichloromethylthio-4-cyclohexene-1,2-dicarboximide
CARBARYL	1-Naphthyl methylcarbamate
CARBOPHENOTHION	*S*-[[(*p*-Chlorophenyl)thio]methyl] *O,O*-diethyl phosphorodithioate
CHLORDANE	Technical: 60% octachloro-4,7-methanotetrahydroindane and 40% related compounds
CIPC	Isopropyl *N*-(3-chlorophenyl)carbamate
2,4-D	2,4-Dichlorophenoxyacetic acid
DACTHAL	Dimethyl tetrachloroterephthalate
2,4-DB	4-(2,4-Dichlorophenoxy)butyric acid
DDE	Dichlorodiphenyldichloroethylene (degradation product of DDT)
DDMU	1-Chloro-2,2-bis(*p*-chlorophenyl) ethylene
DDT	Dichloro diphenyl trichloroethane. Principal isomer present (*p,p'*-DDT; not less than 70%: 1,1,1-trichlo bis(*p*-chlorophenyl)ethane
DIAZINON	*O,O*-Diethyl *O*-(2-isopropyl-6-methyl-4-pyrimidinyl) phosphorothioate
DICHLORAN	2,6-Dichloro-4-nitroaniline
DICOFOL	1,1-Bis(chlorophenyl)-2,2,2-trichloroethanol
DIELDRIN	Hexachloroepoxyoctahydro-*endo,exo*-dimethanonaphthalene 85% and related compounds 15%
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
ETHION	*O,O,O',O'*-Tetraethyl *S,S'*-methylene bisphosphorodithioate
FONOFOS	*O*-Ethyl *S*-phenyl ethylphosphonodithioate
HCB	Hexachlorobenzene
HEPTACHLOR	Heptachlorotetrahydro-4,7-methanoindene
HEPTACHLOR EPOXIDE	1,4,5,6,7,8,8-Heptachloro-2,3-epoxy-3a,4,7,7a-tetrahydro-4,7-methanoindan
LEPTOPHOS	*O*-(4-Bromo-2,5-dichlorophenyl) *O*-methyl phenylphosphonothioate
LINDANE	*Gamma* isomer of benzene hexachloride (BHC)
MALATHION	*O,O*-Dimethyl dithiophosphate of diethyl mercaptosuccinate
MCP	See MCPA

(*Continued next page*)

'A	2-Methyl-4-chlorophenoxyacetic acid
'HOXYCHLOR	2,2-Bis(*p*-methoxyphenyl),1,1,1-trichloroethane 88% and related compounds 12%
'HYL PARATHION	*O,O*-Dimethyl *O-p*-nitrophenyl phosphorothioate
EX	Dodecachlorooctahydro-1,3,4-metheno-1*H*-cyclobuta[cd]pentalene
NACHLOR	1,2,3,4,5,6,7,8,8-Nonachloro-3a,4,7,7a-tetrahydro-4,7-methanoindan
'ACHLOR EPOXIDE	1-*exo*-2-*endo*-4,5,6,7,8,8a-Octachloro-2,3-*exo*-epoxy-2,3,3a,4,7,7a-hexahydro-4,7-methanoindene
'CHLORDANE	1-*exo*-2-*endo*-4,5,6,7,8,8a-Octachloro-2,3-*exo*-epoxy-2,3,3a,4,7,7a-hexahydro-4,7-methanoindene
ATHION	*O,O*-Diethyl *O-p*-nitrophenyl phosphorothioate
	Pentachloroaniline
s (Polychlorinated Biphenyls)	Mixtures of chlorinated biphenyl compounds having various percentages of chlorine
B	Pentachloronitrobenzene
	Pentachlorophenol
A	Pentachlorothioanisole
s (Polychlorinated Terphenyls)	Mixtures of chlorinated terphenyl compounds having various percentages of chlorine
THANE	1,1-Bis(ethylphenyl)-2,2-dichloroethane
SALONE	*S*-[6-Chloro-3-(mercaptomethyl)-2-benzoxazolinone] *O,O*-diethyl phosphorodithioate
TOMIREX	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
LORAM	4-Amino-3,5,6-trichloropicolinic acid
NEL	*O,O*-Dimethyl *O*-(2,4,5-trichlorophenyl) phosphorothioate
-T	2,4,5-Trichlorophenoxyacetic acid
B	1,2,4,5-Tetrachloro-3-nitrobenzene
A	Tetrachlorothioanisole
	Dichloro diphenyl dichloroethane (1,1-dichloro-2,2-bis(*p*-chlorophenyl)ethane, principal component)
RADIFON	4-Chlorophenyl 2,4,5-trichlorophenyl sulfone
APHENE	Technical chlorinated camphene (67-69% chlorine)
-TP	2-(2,4,5-Trichlorophenoxy)propionic acid

ERRATUM

Pesticides Monitoring Journal, Volume 14, Number 4, page 136. The abstract of the article "Organochlorine Residues in Fish: National Pesticide Monitoring Program, 1970-74" should be corrected to read as follows:

Highest PCB residues were found in the industrialized areas of the Northeast and Midwest. . . .

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

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

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

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

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HUMANS

Chlorinated Hydrocarbon Pesticides in Blood of Newborn Babies in India

Mohammed K.J. Siddiqui,[1] Mukesh C. Saxena,[1] Ajeet K. Bhargava,[2] Coimbatore R. Krishna Murti,[2] and D. Kutty[2]

ABSTRACT

Umbilical cord blood collected during labor of 100 Indian women was analyzed for organochlorine pesticides by gas-liquid chromatography with electron-capture detection. Significant levels of p,p′*-DDT and its metabolites,* p,p′*-TDE and* p,p′*-DDE, as well as* α*-,* β*-, and* γ*-isomers of BHC were estimated. Residues in the neonatal blood were related to age, dietetic habits, and area of residence of the mothers. The study highlights the extent of placental transfer of the body burden of toxic chemicals from the mother to the fetus.*

Introduction

In recent years, man has become more conscious of the way in which the environment is polluted by chemicals that harm plants, animals, and humans. Organochlorine pesticides have been a major cause of concern to ecologists, not only because they persist so long in the environment (*11*, *14*) but also because of the readiness with which they accumulate in the human body. Their tendency to accumulate in fatty tissues (*3*), because of their lipophilic nature and resistance to biodegradation (*2*), has caused significant residue burdens in adipose tissues (*8*), blood (*1*, *4*), and even human milk (*7*, *10*, *13*, *18*).

These toxic agrichemicals have access to the growing fetus through placental tissue (*5*, *12*, *15*). Stillborn infants have been determined to be contaminated with such compounds (*6*). Earlier studies have also drawn attention to the presence of organochlorine pesticides in the cord blood of the fetus (*16*, *17*).

Persistent organochlorine pesticides like DDT, which have been banned in other countries, are still commonly used in India in agriculture and malaria eradication programs. Therefore, it was considered worthwhile to assess organochlorine residues in neonatal blood in India. The present report also relates the extent of placental transfer of these compounds from mother to child according to age, dietetic habits (vegetarian/nonvegetarian), and area of residence (rural/urban).

Materials and Methods

A total of 100 pregnant women were studied. The women were admitted to Queen Mary's Hospital, associated with the Department of Obstetrics and Gynaecology, King George's Medical College, Lucknow, capital of the most populous state in India. None of the women, on inquiry, reported any accidental or occupational exposure to any of the pesticides studied. None of the women suffered from any serious diseases except mild hypertension. Umbilical cord blood of these subjects was collected in heparinized vials during labor and stored at 10°C until the analysis was carried out, generally within 48 hours.

A 1-ml aliquot of blood was mixed with 5 ml formic acid and 2 ml *n*-hexane in a 25-ml conical flask. Contents were shaken 1 hour at 37°C in a mechanical shaker, and centrifuged 10 minutes at 2,000 rpm in a refrigerated centrifuge. Losses due to evaporation were made up by weighing the container before and after shaking. The upper layer (hexane) was recovered by disposable suction pipet. The extracted samples were further cleaned up according to the method of Dale et al. (*9*) as follows:

The hexane extract plus 1 ml distilled water in a clean test tube were kept in a liquid air–methanol bath to remove traces of formic acid. The unfrozen hexane phase was further treated with 1 ml fuming H_2SO_4 (three times) to remove the fat. Recoveries through this cleanup procedure were greater than 84% for all pesticides in the fortified samples, except lindane,

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which was recovered at about 79%. The cleaned samples in hexane were analyzed for organochlorine pesticides on a Varian Aerograph Series 2400 gas-liquid chromatograph, equipped with an electron-capture detector (^{3}H). The operating conditions of the instrument were as follows:

Carrier gas:	purified nitrogen (99.9%) passed through silica gel and molecular sieve to remove moisture and oxygen, respectively
Gas pressure:	65 psi
Flow rate:	45 ml/min
Temperatures, °C:	injector 190 colmun 180 detector 200
Attenuation:	4×10^{-9}
Current:	10^{-9} μamp
Column:	glass spiral column, 6 ft × ¼-in ID, packed with 1.5% OV-17 + 1.95% OV-210 on 80–100-mesh Gas-Chrom Q
Sample size:	4–8 μl

Pesticide standards were obtained from PolyScience Corp., Niles, Illinois. Compounds were quantitated by comparing the peak area of detected pesticides in the samples with those of known pesticide standards. The presence of detected residues was further confirmed by thin-layer chromatography.

Results and Discussion

Levels of organochlorine pesticides estimated in the neonatal blood are summarized in Tables 1–3.

The results of random sampling grouped on the basis of age (Table 1), dietetic habits (Table 2), and area of residence (Table 3) of the mother have been computed. Residues of total BHC (45.79 ppb) were highest in the neonatal blood from mothers 26–34 years old compared with 32.97 ppb observed in 18–25-year old mothers, i.e., residues were about 39% higher for the upper age group. Likewise, significant difference was observed in the levels of lindane between the two age groups ($P<0.05$). There was no variation in the concentration of total DDT (ΣDDT) residues in the two age groups. However, concentrations of *p,p'*-DDT, the parent compound, were about three times greater in the 26–34-year old group compared with those in the 18–25-year old mothers ($P<0.005$). Relatively higher concentrations of DDT metabolites (DDE, 23.1 ppb; TDE, 8.01 ppb) were detected in the neonates associated with the older women compared with the younger age group (DDE, 12.33 ppb; TDE, 5.84 ppb).

Differences in the levels of total BHC and its isomers in neonatal blood on the basis of vegetarian vs. nonvegetarian diets of the mother were not significant: Cord blood associated with vegetarian mothers contained 38.3 ppb BHC compared with 35.64 ppb BHC for nonvegetarian mothers. Cord blood associated with vegetarian mother contained 62.22 ppb total DDT compared with 50.0 ppb total DDT in cord blood associated with nonvegetarian mothers. BHC (47.38 ppb) was detected in the blood of newborns of mothers residing in urban area compared with 27.06 ppb in that of neonates of rural mothers ($P<0.05$). A statistically significant difference ($P<0.05$) was also observed in the levels of lindane (γ-BHC) between the two residential groups. There was no significant difference in total DDT residues by area of residence, but a slightly higher concentration of DDT was estimated in urban subjects, i.e., 22.81 ppb vs 15.48 ppb in rural subjects. The relatively higher level

TABLE 1. *Organochlorine pesticides detected (ppb) in cord blood collected at term from 100 pregnant women, by age group*

	Women 18–25 Years Old (58 Cases)			Women 26–34 Years Old (42 Cases)		
Pesticides Detected	Range	Arithmetic Mean	SE	Range	Arithmetic Mean	S
Total BHC	6.9–278.3	32.97	16.89	4.20–104.92	45.79	5.
Lindane*	1.60–78.69	10.27	2.18	3.10–27.98	14.99	1.
p,p'-DDE	2.16–144.37	12.33	1.98	2.05–78.14	23.10	4.
p,p'-TDE	ND–48.21	5.84	1.25	ND–48.21	8.01	2.
p,p'-DDT*	1.43–49.21	7.30	2.32	ND–57.52	22.13	2.
ΣDDT[1]	7.79–1029.85	49.55	23.23	4.59–149.62	51.18	8.

* Statistically significant ($P<0.05$ and 0.005, respectively)
[1] ΣDDT = total DDT equivalent

TABLE 2. *Organochlorine pesticides detected (ppb) in cord blood collected at term from 100 pregnant women, by dietetic habit*

	Vegetarian Diet (36 Cases)			Nonvegetarian Diet (64 Cas		
Pesticides Detected	Range	Arithmetic Mean	SE	Range	Arithmetic Mean	S
Total BHC	6.9–278.43	38.3	7.29	4.18–104.92	35.64	3
Lindane	2.1–78.68	12.47	0.34	1.8–29.81	11.41	1
p,p'-DDE	1.8–850.00	35.33	23.26	1.9 + 150.00	20.53	4
p,p'-TDE	ND–48.21	6.55	1.85	0.89–32.09	8.49	1
p,p'-DDT	ND–55.56	14.89	3.05	1.78–140.00	17.08	3
ΣDDT	4.03–1029.85	62.22	8.50	2.73–240.41	50.07	7

TABLE 3. *Organochlorine pesticides detected (ppb) in cord blood collected at term from 100 pregnant women, by area of residence*

	Urban Population (48 Cases)			Rural Population (52 Cas		
Pesticides Detected	Range	Arithmetic Mean	SE	Range	Arithmetic Mean	
Total BHC*	2.0–507.84	47.38	13.87	3.0–76.97	27.06	2
Lindane*	1.28–175.73	16.94	0.72	1.8–33.43	8.88	1
p,p'-DDE	1.02–257.50	22.81	7.05	2.2–144.37	15.48	4
p,p'-TDE	ND–48.21	7.33	3.88	ND–32.09	6.25	
p,p'-DDT	0.5–50.23	13.71	2.19	ND–140.00	17.08	4
ΣDDT	2.73–338.43	41.60	10.88	7.14–222.11	40.65	1

* Statistically significant ($P<0.05$ and 0.05, respectively).

f DDE compared with DDT suggest that mothers were xposed either to DDE or to long-term low levels of)DT, presumably the latter.

Because histories revealed no accidental or occupational xposure to any of the detected pesticides, subjects vere exposed through the food chain and the environ-ient. Placental transfer is undoubtedly responsible for ie presence of these toxicants in newborn babies. A ossible route of entry has been traced in Figure 1.

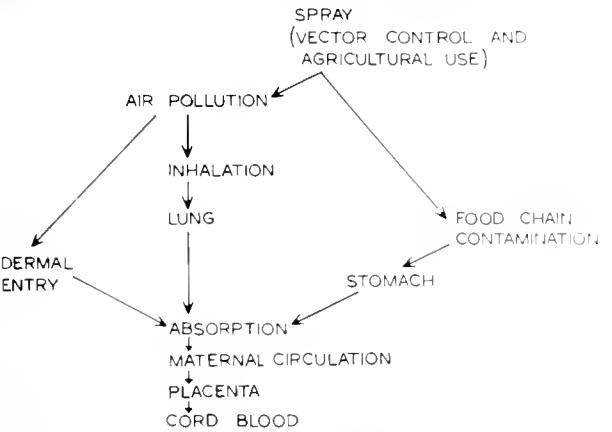

FIGURE 1. *Possible route of entry for pesticides into developing embryo.*

Relatively higher concentrations of BHC in neonatal lood associated with mothers in the older age group iay be the result of comparatively longer periods of xposure to this food and environmental contaminant. It vould be advisable for pregnant women to avoid areas vhere pesticides are sprayed and to decrease consump-on of fatty foodstuffs.

Acknowledgment

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FISH, WILDLIFE, AND ESTUARIES

Organochlorine Insecticide Residues in Soil and Earthworms in the Delhi Area, India, August–October, 1974

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ABSTRACT

DDT residues in soil and earthworms from 50 sites in Delhi were monitored. DDT was detected in all but two samples each of soil and earthworms. Among DDT residues, p,p'-DDE was most common and was found in 48 samples each of soil and earthworms; p,p'-DDT was detected in only 43 soil samples and 46 earthworm samples. p,p'-TDE and o,p'-DDT were also present in smaller concentrations in 29 and 15 soil samples and in 43 and 25 earthworm samples, respectively. Maximum total DDT concentration of 2.6 ppm was detected in the soil from Durga Nagar in the vicinity of a DDT factory. The highest concentration of 37.7 ppm total DDT in earthworms was also obtained from the same site. The maximum concentration factor found in the earthworms was 551. The total DDT concentration in the earthworms and soil showed significant correlation.

Introduction

Large-scale use of organochlorine insecticides, especially DDT, by agricultural and health agencies has resulted in global contamination of the ecosystem (*10, 24*). Because of its lipophilic tendency, coupled with its stability and persistence, DDT in the environment accumulates in nontarget organisms (*10*). DDT residues in soil are known to be concentrated by earthworms. Levels of DDT residues in soil and earthworms in a given area indicate the extent of environmental contamination over a period of time.

DDT has been used extensively in the Delhi area for agricultural and mosquito control, and so this study was undertaken to assess the extent of DDT pollution. In addition, a DDT factory in Delhi might be contributing to the environmental contamination of the surrounding areas.

Materials and Methods

Soil samples and earthworms were collected from 50 different sites in Delhi (Figure 1) from August to October 1974. The earthworms were of the one species available in the area, *Pheretima posthuma* (L. Vaill). Samples were dug from the upper 15 cm of soil, placed in polyethylene bags, and transported to the laboratory within 6 hours. In the laboratory, the living earthworms were removed from the soil, washed with water, and stored in a freezer. The soil was air-dried and mixed thoroughly, and at least three samples of 10 g each were stored in a freezer. Physical and chemical properties of the soil were not studied.

Earthworms from each site were pooled to obtain a sample weight of about 10 g. Pooled samples were accurately weighed, and insecticide residues were extracted by homogenizing the pooled samples with four times their weight of anhydrous sodium sulfate and acetone–hexane (1 + 1). The mixture was stirred for 1 hour and filtered. The residue was extracted three times more with acetone–hexane (1 + 1). The total volume of solvents used was 100 ml. The soil samples were moistened, mixed with equal weights of anhydrous sodium sulfate, and ground with a mortar and pestle. Samples were mixed with acetone–hexane (59 + 41) and shaken for 1½ hours, and filtered. The residue was extracted three times more. The total volume of solvents used was 100 ml. The extract (earthworms + soil) was washed with 100 ml of 2% sodium sulfate and the hexane layer was filtered through anhydrous sodium sulfate. The extract was then concentrated by flash evaporation and cleaned on an alumina column as described by Holden and Marsden (*14*). The cleaned sample was analyzed by gas-liquid chromatograph

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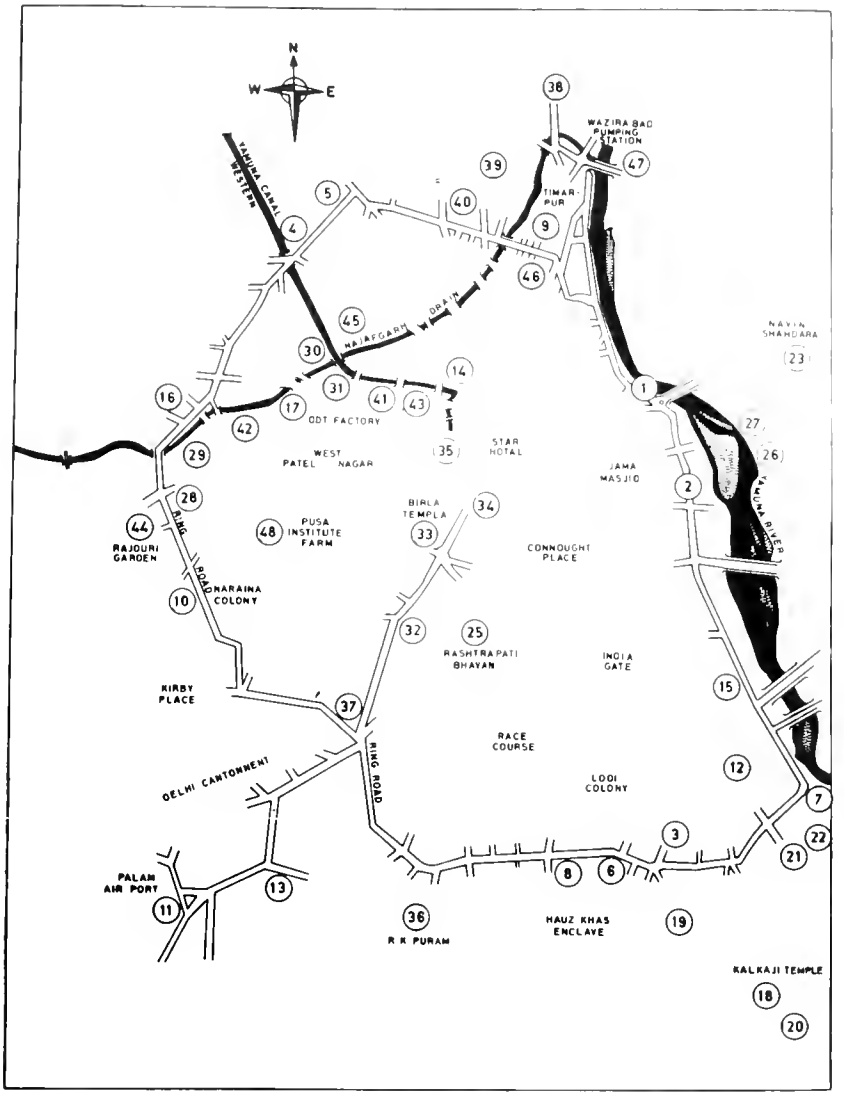

FIGURE 1. *Areas sampled for DDT residues in soil and earthworms in Delhi.*

LC). Instrument parameters and operating conditions ere as follows:

Gas-liquid chromatograph	Hewlett Packard Model 7300 series
Detector:	electron-capture
Column:	coiled glass, 2 m × 4 mm ID packed with 1.5% SP 2250/1.95% SP 2401 on 100–120-mesh Supelcon AW-DMCS
Temperatures, °C:	detector 200 injector 200 column 190
Carrier gas.	nitrogen flowing at 70 ml/min

eaks were identified by comparing relative retention nes with those of standards. Identifications were nfirmed by GLC on another column packed with 6% icone DC-11 on 80–100-mesh Chromosorb W-AW d 5% DEGS on 100–120-mesh Gas-Chrom Q. *p'*-DDT, *p,p'*-TDE, and *o,p'*-DDT were confirmed by dehydrochlorination (9). Peaks for *p,p'*-DDE and DDMU were confirmed if they coincided with the dehydrochlorinated products from *p,p'*-DDT and *p,p'*-TDE. Further confirmation was performed by thin-layer chromatography of the pooled extract. Solvent systems used were heptane–acetone (98 + 2) and hexane–chloroform (90 + 10). The spots corresponding to the position of standards were scraped, extracted, and analyzed by GLC.

Recovery of DDE, TDE, *p,p'*-DDT, and *o,p'*-DDT from spiked soil samples was 89.7%, 88.5%, 96.1%, and 91.8%; recovery was 93.6%, 93.9%, 97.8%, and 83.7% from spiked earthworms. However, data presented have not been corrected for recoveries. The detection limit of the method under the conditions used

was about 0.1 ng for DDE, TDE, *p,p'*-DDT, and *o,p'*-DDT.

Results and Discussion

The areas from which samples were collected and the range of DDT and its metabolites found are given in Figure 1. The levels of organochlorine residues in soil and earthworms, and the locations where they were found, are presented in Tables 1 and 2. Organochlorine insecticide residues detected in soil and earthworms were predominantly DDT and its metabolites. Tipathi (*19*) reported DDT in 120 of 138 samples analyzed from Tarai area in Uttar Pradesh, India. In the present study, residues in soil ranged from about 0.01 to 2.61 ppm; the highest concentration was found at Durga Nagar (Area 17), where the DDT factory is located.

Other areas, such as Inderlok (Area 31), I.A.R.I. (Area 48b), and R.K. Puram (Area 36), also had appreciably higher concentrations of total DDT residues. Concentrations of DDT residues were below detection limits at two sites, Wazirabad pumping station (Area 47) and Vivek Vihar (Area 24). Total DDT concentration as high as 29.45 ppm in agricultural soils (*7*) and 388.16 ppm in urban soils (*5*) has been reported in the United States. Lang et al. (*15*) found a maximum of 13.93 ppm total DDT from a survey of six U.S. Air Force Bases. The occurrence of DDT residues in Delhi soils might be predominantly attributed to volatilization and subsequent dispersal of DDT in the vicinity of the factory; DDT has been shown to volatilize into the atmosphere (*21*), from which it ultimately reaches the surface soils. In addition to the dispersal from the DDT factory, large-scale use of DDT in the control of malaria might have resulted in widespread contamination of Delhi soils. DDT residues in soils are highly stable and persist for a long time (*22*). However, Agnihotri et al. (*2*) reported up to 95% loss of DDT in 6 months from agricultural soils under tropical conditions. Therefore, the comparatively lesser concentration of DDT in Delhi soils might be due to their loss under the tropical environment.

In earthworms, the concentration of total DDT residues varied from 0.1 ppm to 37.74 ppm, with a maximum concentration factor of 551 (Tables 1 and 2). The highest concentration of DDT was detected in samples from Durga Nagar, where DDT concentration in the soil was also highest. However, the concentration factor, which was obtained by dividing the concentration of DDT in the earthworms by the concentration in the soil, was only 14.5 at Durga Nagar, compared with 551 at one site I.A.R.I. (Area 48a). Barker (*3*) reported total DDT as high as 680 ppm in *Lumbricus rubellus* and 492 ppm in *Helodrilus zeteki*, compared with 37.7 ppm DDT in *P. posthuma* in the present investigation. There

TABLE 1. *Concentration (range in ppm) of DDT and its metabolites in soil and earthworms collected from different areas in Delhi during 1974*

SAMPLE TYPE	*p,p'*-DDE	*o,p'*-DDT	*p,p'*-TDE	*p,p'*-DDT	TOTAL DD
Soil	0.01–0.81 (48)	0.01–0.27 (15)	0.01–0.60 (29)	0.01–1.20 (43)	0.01–2.6 (48)
Earthworms	0.02–9.78 (48)	0.02–3.89 (25)	0.01–8.69 (43)	0.03–20.60 (46)	0.10–37.7 (48)

NOTE: Fifty samples each of soil and earthworms were analyzed. Numbers parentheses indicate number of samples with positive detection

are several other reports showing the concentration DDT residues in earthworms (*12, 13, 23*). Total DD concentration in earthworms and soil from the sam area showed significant correlation ($r = 0.792$; $P < 0.01$). Similarly, Gish (*13*) observed a linea relationship between pesticide residues in earthworm and soil. Edwards and Thompson (*12*) obtaine significant correlation between residues in earthworm and soil from data collected by different worker However, Wheatley and Hardman (*23*) found that DD residues in earthworms and soil were not relate linearly.

DDT in soil and earthworms was comprised mainly *p,p'*-DDT and its metabolites *p,p'*-DDE and *p,p'*-TDI In certain samples, *o,p'*-DDT was also detected, addition to *p,p'*-DDT and its metabolites (Tables 1 a 2). These are commonly reported DDT components soils (*4, 17, 18*). Carey et al. (*6-8*) reported *o,p'*-DD and *o,p'*-TDE residues in addition to these common occurring metabolites. DDT in soils undergoes tran formation in the presence of various physical, chemica and biological factors and degrades to DDE, t terminal residue of DDT (*16*). TDE is also formed the soil, mainly a result of microbial degradation (*20*

The occurrence of DDT metabolites in earthworms m be due either to their direct uptake from soil or metabolism of DDT by the earthworms (*1, 11, 25*). T proportions of DDT metabolites (DDE and TDE) relation to unchanged DDT showed large variations different soil and earthworm samples. However, majority of these samples contained higher concentr tions of *p,p'*-DDT than its metabolites, suggesting th *p,p'*-DDT was being transferred quite frequently these soils. The higher proportions of DDE and TDE certain samples may be due to the faster degradation *p,p'*-DDT in soil in those particular areas; DI degradation depends on various environmental facto Ware et al. (*21*) showed a shift in DDE:DDT ratio fr 56:44 to 62:38 after 3 years in Arizona soils. T variable proportions of DDT metabolites in relation unchanged DDT in the earthworms might have be due to variations in the duration of exposure to t insecticide and its concentration in the soils.

TABLE 2. *Concentration (in ppm) of DDT and its metabolites in soil(S) and earthworms(E) from different areas in Delhi during 1974*

AREAS		*p.p'*-DDE	*o.p'*-DDT	*p.p'*-TDE	*p.p'*-DDT	TOTAL DDT	CONCN FACTOR
1. Old Jamuna Bridge	S	0.08	0.01	—	0.21	0.30	
Kashmere Gate	E	0.32	—	0.01	1.02	1 35	4.5
2. Raj Ghat	S	0.07	—	—	0.01	0 08	
	E	0.18	—	0.15	0.81	1 14	14.3
3. Lajpat Nagar	S	0.01	—	—	0.08	0 09	
	E	0.23	—	0.24	0.76	1 23	13.7
4. Wazirpur	S	0.05	—	—	0.02	0.07	
	E	0.69	0.09	0.98	2.41	4 17	59.6
5. Azadpur	S	0.08	—	—	0.02	0 10	
	E	0 03	—	—	0.07	0.10	1.0
6. South Extn. Pt.-II	S	0.10	—	0.04	0.05	0.19	
	E	0.03	—	0.10	0.14	0 27	1 4
7. Kalindi Colony	S	0.05	—	—	0.01	0.06	
	E	0.03	—	0.01	0.14	0 18	3.0
8. Safdarjang Enclave	S	0.06	—	—	0.04	0 10	
	E	0.92	0.05	0.04	0.65	1.66	16.6
9. Timarpur	S	0.19	—	—	0.04	0.23	
	E	0.05	—	—	0.06	0.11	0.48
10. Naraina	S	0.05	—	0.50	—	0.55	
	E	0.05	0.02	0.83	—	0.90	1.6
11. Delhi Airport	S	0.14	—	0.04	0.20	0.38	
	E	0.89	0.19	0 24	1.13	2.45	6.4
12. Kataria Nursury	S	0.11	—	—	0.04	0.15	
Nizamuddin	E	1.65	0.37	0.02	1.80	3.84	25.6
13. Palam Road	S	0.06	—	—	0.02	0.08	
	E	0.75	—	—	1.54	2.29	28.6
14. Roshanara Garden	S	0 10	0.02	0.06	0.08	0.26	
	E	0.18	—	0.02	0.27	0.47	1.8
15. Delhi Zoo	S	0.03	—	0.02	0.01	0.06	
	E	0.14	—	0.03	0.20	0.37	6.2
16. Punjabi Bagh	S	0.06	—	0.01	0.02	0.09	
	E	0.40	—	0 68	0.77	1.85	20.6
17. Durga Nagar	S	0.76	0.08	0.57	1 20	2 61	
	E	5.24	3.21	8 69	20.60	37 74	14.5
18. Kalkaji	S	0.02	—	—	—	0.02	
	E	0.19	—	—	0.16	0.35	17.5
19. Greater Kailash	S	0.02	—	—	—	0 02	
	E	0.58	0.10	0.08	0.43	1 19	59.5
20. Govind Puri	S	0.05	—	0.04	0 04	0 13	
	E	0.02	—	0.97	0.97	1.96	15.1
21. Jamia Nagar	S	0.15	—	0.03	0.04	0 22	
	E	0.59	—	0.01	0.03	0.63	2.9
22. Okhla	S	0.02	—	0 01	0.02	0.05	
	E	0.12	—	0.07	0.14	0.33	6 6
23. Navin Shahdara	S	0.10	0.02	0.05	0.27	0.44	
	E	0.26	—	0.03	0.30	0 59	1.3
24. Vivek Vihar	S	—	—	—	—	—	
	E	—	—	—	—	—	—
25. Central	S	0.04	—	0.05	0.05	0 14	
Secretariat	E	0.13	—	0.49	0 27	0.89	6.4
26. Geeta Colony	S	0.06	0.01	0.02	0.05	0 14	
	E	0.92	—	0 62	1.56	3 10	22.1
27. Jheel	S	0 03	—	0.01	0.02	0.06	
	E	1.72	—	—	—	1 72	28.7
28. Tilak Nagar	S	0.09	—	0 01	—	0.1	
	E	0.54	—	0.44	0.2	1.18	11 8
29. Moti Nagar	S	0.03	—	—	0.03	0 06	
	E	6 10	1.50	1.90	8.60	18.10	302
30. Shanti Nagar	S	0.01	—	—	—	0 01	
	E	1 20	—	0.05	0.03	1 28	128

continued

TABLE 2. *(cont'd).*

31. Inderlok	S	0.19	0 27	0.60	0.91	1.97	
	E	9.78	2.30	5.63	9.30	27.01	13.7
32. Budha Memorial Park	S	0.02	0.01	0.01	0.02	0.06	
	E	0 83	0.02	0.22	0.62	1.69	28.2
33. Pusa Chowk Karol Bagh	S	0 04	—	0.03	0 20	0 27	
	E	0 38	0.02	0.17	1 29	1.86	6.9
34 Pahar Ganj	S	0.04	—	0.01	0 27	0.32	
	E	0.05	0.04	0.05	0 78	0.92	2.9
35. Ajmal Khan Park	S	0.01	—	0 10	0.01	0.12	
	E	0.02	—	0.10	0.07	0.19	1.6
36. R.K Puram	S	0.19	0.03	0.01	0.57	0.80	
	E	0.87	0.04	0.08	2.55	3.54	4.4
37. Dhaula Kuan	S	0.04	—	—	0.11	0.15	
	E	0.22	0.04	0.03	1.03	1.32	8.8
38 Wazirabad	S	0.19	0.01	0.01	0.38	0.59	
	E	0.26	—	0.11	0.48	0.85	1.4
39 Nirankari Colony	S	0.02	0.01	0.01	0.09	0.13	
	E	0.31	0.03	0.14	0 63	1.11	8.5
40. Radio Colony	S	0.81	—	0.04	0.16	1.01	
	E	3.16	0.02	0.33	0.42	3.93	3.9
41. Subhadra Colony	S	0.34	—	0.06	0.89	0.69	
	E	1.55	0.05	0.50	1.54	3.64	5.3
42. Karam Pura	S	0.11	0.01	0.09	0.29	0.50	
	E	0.26	0.09	0 20	2.13	2.68	5.4
43. Bharat Nagar	S	0.03	0.02	0.02	0.17	0.24	
	E	0 03	0.02	0.43	0.23	0.71	3.0
44. Raja Garden	S	0.09	0 02	0.32	0.24	0.67	
	E	0.14	0.02	0.22	0.34	0.72	1.1
45. Daya Basti	S	0.12	0 03	0.06	0.32	0.53	
	E	0.18	0 05	0.17	0.72	1.12	2.11
46. Delhi University	S	0.02	—	—	0.03	0.05	
	E	0.31	0.26	0.22	0.73	1.52	30.4
47. Wazirabad Pumping Station	S	—	—	—	—	—	
	E	—	—	—	—	—	—
48. Indian Agric. Research Inst	S	0.02	—	—	0.01	0.03	
	E	0.57	3.89	2 32	9.74	16.52	551
48(a) Indian Agric. Research Inst.	S	0.05	—	—	0.08	0.13	
	E	0.12	0.20	0.08	0.51	0.91	7
48(b) Indian Agric. Research Inst.	S	0.75	0.10	—	0.27	1.12	
	E	0.36	1.77	1.12	6.00	9.25	8.3

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Organochlorine Insecticide Concentrations in Fish of the Des Moines River, Iowa, 1977–78[1]

Ross V. Bulkley,[2] Siu-Yin Theresa Leung,[3] and John J. Richard [4]

ABSTRACT

Organochlorine insecticides were measured in fish of the Des Moines River, Iowa, in 1977 and 1978 to determine whether concentrations exceeded allowable levels and to compare differences among species. Significant differences in mean concentrations of dieldrin, ΣDDT, and heptachlor epoxide in whole-body samples of seven species of fish, Dorosoma cepedianum, Carpiodes carpio, Cyprinus carpio, Ictalurus punctatus, Pomoxis annularis, Micropterus salmoides, Stizostedion vitreum, *could not be adequately explained by body size, position of species in the food chain, or percent body fat.*

Introduction

The use of organochlorine insecticides on midwestern farmland to control agricultural insects has caused widespread contamination of fish in streams and rivers. Dieldrin residues in catfish (*Ictalurus*) and buffalo fish (*Ictiobus*) caused closure of certain commercial fisheries in Iowa during the 1970's and generated considerable public concern (*2, 3, 4, 9, 10, 14*). Several years after DDT, aldrin, dieldrin, and other insecticides were removed from the market, these chemicals or their breakdown products were still present in water, sediment, and fish of the Des Moines River and at least dieldrin was evidently still being washed into the river from farmland (*11*). Leung (*11*) examined pesticide concentrations in water, sediment, and seven species of fish collected from 1977 to 1978 in conjunction with the impoundment of water behind the newly constructed Saylorville Dam in central Iowa. She detected no noteworthy seasonal or spatial differences in concentration of dieldrin, ΣDDT, or heptachlor expoxide in whole-body analyses of Des Moines River fish. The portion of the study reported here concerns variation in insecticide residues in different species of fish.

The Des Moines River rises in the glacial moraine area of southwestern Minnesota and flows southeasterly across Iowa to the Mississippi. It is the largest river in Iowa. About 79% of the watershed upstream from Des Moines is cropland (primarily corn and soybeans), 6% is permanent pasture, 5% is forest, and 7% is urban (*7*). Normal annual precipitation over the drainage area ranges from 62.5 to 77.5 cm from north to south and averages 70.7 cm (*19*). The major source of pollution in the river is nonpoint agricultural runoff (*8*).

Sampling and Analysis

SAMPLE COLLECTION AND PREPARATION

Three collection sites were established on the Des Moines River in central Iowa. The drainage area total about 14,530 km^2 above Station 1 at Boone, 15,081 km above Station 2, and 15,128 km^2 above Station 3 at Saylorville. Stream distance from Station 1 to Station 3 is about 76 km.

Fish samples were collected quarterly from October 1977 to October 1978 with gill nets, hoop nets, and electrofishing gear. Species analyzed for pesticide residues were three forage fish, including gizzard shad (*Dorosoma cepedianum*), river carpsucker (*Carpiodes carpio*), and carp (*Cyprinus carpio*); and four piscivorous fish, including channel catfish (*Ictalurus punctatus*), white crappie (*Pomoxis annularis*), largemouth bass (*Micropterus salmoides*), and walleye (*Stizostedion vitreum*). Each species was not always collected at every station during each quarter, but all species were collected at one or more stations each quarter. Specimens were grouped by collection data, location, species, and length. Authors attempted to collect small juveniles within a limited length range and to avoid large, old fish of each species. Individuals in the same group were ground together in a hand grinder and then mixed manually in an effort to obtain a homogenous mixture. Subsamples were then taken, wrapped in aluminum foil, and frozen until analysis.

ANALYSIS

The method of tissue analysis described in the Pesticide Analytical Manual of the U.S. Department of Health

[1] This study was conducted as part of Project 2225 of the Iowa Agriculture and Home Economics Experiment Station, Ames, Iowa, in cooperation with the Iowa Cooperative Fishery Research Unit, which is sponsored by the Iowa State Conservation Commission, Iowa State University, and the Fish and Wildlife Service, U.S. Department of the Interior.

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and Human Services (*18*) was used, with slight modification. After samples were thawed, a 25–30 g subsample was extracted with 200 ml of 65% acetonitrile–water for 5 minutes in a 1-liter stainless steel blender. The samples were filtered and transferred to a 1-liter separatory funnel; 100 ml petroleum ether, 600 ml water, and 10 ml saturated aqueous sodium chloride were added. The pesticides were partitioned into the organic layer by vigorously shaking for 30–60 seconds. The aqueous layer was discarded. The petroleum ether layer was washed with two 100-ml portions of water to remove the remaining acetonitrile, and then transferred to a 100-ml graduated cylinder, and the recovered volume was recorded. The wet weights of tissue samples were corrected for the losses of acetonitrile–water mixture and petroleum ether. The extracts were subjected to Florisil column cleanup. The eluate was concentrated to 10 ml for quantification. Results were expressed in nanograms of pesticide per gram of fish tissue (ppb wet weight).

Dieldrin, *p,p'*-DDE, *p,p'*-TDE, *p,p'*-DDT, and heptachlor epoxide were quantified by gas chromatography. Instrument parameters and operating conditions were as follows:

Gas chromatograph:	Tracor 550
Detector:	^{63}Ni electron-capture
Columns:	packed with 10% DC-200 packed with 4% SE-30/6% OV-210
Temperatures, °C	detector 340 columns 210
Carrier gas:	flowing at 90–100 ml/min

Values were not corrected for the ca 80% recovery obtained in extraction. Preliminary tests revealed little interference from polychlorinated biphenyls (PCBs) and chlordane. The majority of the PCBs were present as Aroclor 1242 or 1246 which did not interfere in the other pesticide analyses. No chlordane was observed in water or fish samples. Pesticide detection limits were about 10 ppb. One of the authors, John J. Richard, supervised all analyses. Authors transformed data on pesticide concentrations to log 10 values before conducting analysis of variance or *t*-tests or computing correlation coefficients.

Results

Carp were most abundant and walleyes were least abundant in the collections (Table 1). Because large older fish were not included in the composited samples, mean length of samples for the seven species was within a 120-mm range. Average length of forage fish was 56 mm less than that of piscivorous fish.

Dieldrin and ΣDDT were detected in all 173 samples analyzed. Heptachlor epoxide was present in quantifiable amounts in most samples but was not detected in at least 15% of the samples from a given species; it was not found in 33% of river carpsucker samples, 27% of carp samples, and 15%–23% of the samples of other species. Most of the samples with undetectable heptachlor epoxide were collected at Station 2 in October 1977. Average concentrations of dieldrin and ΣDDT were somewhat similar; concentrations of heptachlor epoxide, when present, were considerably lower.

TABLE 1. *Number and length of fish collected from Des Moines River, Iowa, 1977–78*

Species	No Fish	Total Length, mm	
		Mean	Range
Gizzard shad	377	137	56–212
River carpsucker	302	178	76–400
Carp	536	151	83–402
Channel catfish	86	253	98–487
White crappie	217	134	75–332
Walleye	40	232	144–430
Largemouth bass	132	225	95–387

Comparison of concentrations of the three insecticides indicated significant differences among fish species for all three chemicals (Table 2). Differences were greatest in dieldrin concentrations ($P < 0.01$). Levels of dieldrin were highest in gizzard shad and channel catfish (114 ppb), and lowest in walleyes (28 ppb). Patterns of heptachlor epoxide concentrations were similar to those for dieldrin ($P < 0.01$). Concentrations of ΣDDT were more similar among species, but still significantly different ($P < 0.05$).

TABLE 2. *Mean insecticide concentrations in whole-body samples of fish from Des Moines River, Iowa, 1977–78*

Species	No Samples	Concentration, ppb		
		Dieldrin	ΣDDT	Heptachlor Epoxide
Gizzard shad	20	114 (14–191)	57 (8–188)	14 (0–68)
River carpsucker	39	63 (7–197)	64 (10–329)	7 (0–42)
Carp	39	35 (13–62)	42 (12–125)	5 (0–23)
Channel catfish	17	114 (31–240)	67 (16–136)	16 (0–42)
White crappie	23	60 (15–301)	44 (6–72)	6 (0–19)
Walleye	11	28 (7–62)	76 (7–138)	2 (0–6)
Largemouth bass	24	58 (15–182)	65 (7–109)	7 (0–23)

NOTE: Range is given in parentheses.

Levels of insecticides in the three forage species were compared with those found in the four piscivorous species to determine if bioaccumulation through the food chain was evident. Differences between concentrations found in the forage fish and the fish-eating species were not statistically significant for any of the three

chemicals. Average whole-body concentrations (ppb) were as follows:

	Dieldrin	*ΣDDT*	*Heptachlor epoxide*
Forage fish	71	54	9
Piscivorous fish	65	65	8

Inasmuch as whole-body concentrations of the three insecticides failed to correlate significantly with position of species in the food chain, authors compared pesticide concentration to percent body fat. Only fish sampled during the last two quarters, July and October 1978, were available for fat analysis (Table 3). Average percent body fat was highest in gizzard shad (17) and lowest (2) in walleyes. Fat concentrations were similar in July and October samples of each species except gizzard shad. Concentrations of fat in shad samples were 7% in July and 29% in October.

TABLE 3. *Average percent fat content and mean whole-body insecticide levels in seven species of fish collected in July and October 1978*

Fish Species	No Fish	Fat, %	Concentration, ppm[1] Dieldrin	ΣDDT	Heptachlor Epoxide
Gizzard shad	104	17.0	81 (0.48)	55 (0.32)	14 (0.08)
River carpsucker	72	5.4	45 (0.83)	39 (0.72)	3 (0.06)
Carp	91	4.5	35 (0.78)	45 (1.00)	6 (0.13)
Channel catfish	3	8.5	101 (1.19)	101 (1.19)	10 (0.12)
White crappie	79	2.7	56 (2.07)	46 (1.70)	8 (0.30)
Walleye	26	2.0	26 (1.30)	106 (5.30)	2 (0.10)
Largemouth bass	52	4.0	61 (1.52)	75 (1.87)	8 (0.20)

[1]Based on ppm fat shown in parentheses.

The correlation between percentage fat and insecticide concentrations within each species was first examined. In July samples, correlation was significant at the 0.01 level between percent fat and dieldrin and heptachlor epoxide levels for white crappies and between percent fat and ΣDDT for gizzard shad. In October samples, correlation was significant at the 0.05 level between percent fat and dieldrin and heptachlor epoxide in largemouth bass. Percent fat was not significantly correlated with insecticide concentrations in the other species.

In combined July and October samples (Table 3), the relation between percent fat and dieldrin was significant at the 0.05 level or higher in river carpsucker, carp, white crappies, and largemouth bass (Table 4). Correlation coefficients for gizzard shad and walleyes, although not statistically significant, suggested a similar relation. Body fat was significantly correlated with ΣDDT only in gizzard shad, whereas correlation between fat and heptachlor epoxide was significant in both white crappies and largemouth bass.

TABLE 4. *Correlation coefficient (r) between percent body fat and insecticide concentrations for combined composite samples of fish collected during July and October 1978*

Species	No Samples	Dieldrin	ΣDDT	Heptachlor Epoxide
Gizzard shad	5	0.70	0.93*	0.45
River carpsucker	9	0.73*	0.25	0.69
Carp	8	0.83**	0.32	0.26
Channel catfish	1	—	—	—
White crappie	10	0.90**	0.41	0.82**
Walleye	6	0.70	0.47	0.46
Largemouth bass	13	0.84**	0.36	0.85**

*Significant at 0.05 probability level.
**Significant at 0.01 probability level.

But even though fish species varied widely in mean percent body fat, differences in concentrations of each of the three insecticides were evidently not caused by differences in body fat. When the seven species were compared, correlation coefficients were 0.65 for fat vs. whole-body dieldrin concentrations, −0.12 for fat vs. whole-body ΣDDT concentrations, and 0.80 for fat vs. whole-body heptachlor epoxide concentrations. These coefficients were not statistically significant.

Expression of insecticide concentrations on the basis of fat content also failed to reduce species differences (Table 3). White crappies contained over 2 ppm dieldrin on a fat basis and gizzard shad only 0.48 ppm. Walleyes contained the highest ΣDDT concentrations on the basis of fat (5.30 ppm) and gizzard shad the lowest (0.32 ppm), whereas concentrations of heptachlor epoxide in terms of fat were very low in all species.

These relatively high levels of pesticide per unit of body fat in white crappies, walleyes, and other species (Table 3) suggested one additional comparison—concentration of pesticide in forage fish vs. piscivorous fish on a fat basis, for evidence of biological magnification. Mean concentrations of insecticide on a fat basis in gizzard shad, river carpsucker, and carp (forage fish) were lower than those in catfish, crappies, walleyes, and bass (piscivorous fish) as follows: dieldrin, 0.70 ppm vs. 1.52 ppm; ΣDDT, 0.68 ppm vs. 2.51 ppm; and heptachlor epoxide, 0.09 ppm vs. 0.18 ppm. These differences suggested that biological magnification in the food chain was occurring. However, even though concentrations were seemingly higher on the basis of fat in all piscivorous fish than in forage fish (except for heptachlor epoxide in carp), only those for dieldrin were significantly higher ($P = 0.05$, $t = 3.50$).

Discussion

Body concentrations of an insecticide frequently differ from one species of fish to another from the same body of water. Many factors, including length and weight

age, food, fat content, enzyme systems, and trophic levels, have been considered by researchers to explain species variation in insecticide concentrations (*5, 8*). Lyman et al. (*12*) and Matsumura (*13*) observed that fish species also vary greatly in their ability to metabolize and eliminate insecticides. Additional variation may arise from uneven exposure due to differences in location of capture or time of year. In our study, five samples were collected over a 1-year period at three locations on the river. Seasonal and spatial differences in pesticide concentrations were not statistically significant within species, with minor exceptions (*11*). However, fish may be captured at the same location and still have been exposed to different levels of pesticide. Bottom-dwelling species are in contact with greater concentrations of pesticide adsorbed on bottom and suspended sediment than are species occupying strata near the water surface where suspended sediment levels are lower. Whether fish can absorb pesticides directly from sediment in significant amounts is still uncertain.

Percent body fat tended to explain levels of insecticides within certain species, as has been noted by many researchers (*1, 6, 16, 17*), but did not explain differences in concentrations among the seven species in the present study. Gizzard shad and channel catfish had higher percent fat in their bodies than did other species tested and also accumulated greater concentrations of dieldrin and heptachlor epoxide on a wet-weight basis. Even expression of concentrations in the seven species of fish on the basis of fat or oil content did not reduce differences in insecticide level among species. Reinert (*16*) found less difference in DDT and dieldrin concentrations in fish species when concentrations were expressed in terms of oil content of the fish.

Position of a species in the food chain was related to insecticide concentration—especially dieldrin—in the present study when concentrations were expressed on the basis of fat content. Most striking was a 5.30-ppm ΣDDT level in the highly piscivorous walleye vs. 0.32, 0.72, and 1.00 ppm in the three forage species. This relation between position in the food chain and insecticide level was not evident when the comparisons were based on whole-body concentrations instead of on fat content alone. Authors' data illustrate once again the many factors influencing insecticide dynamics in freshwater fish and the difficulty in attributing differences to a single factor.

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Organochlorine and Metal Residues in Eggs of Waterfowl Nesting on Islands in Lake Michigan off Door County, Wisconsin, 1977–78

Susan D. Haseltine, Gary H. Heinz, William L. Reichel, and John F. Moore[1]

ABSTRACT

*One egg from each of 114 red-breasted merganser (*Mergus serrator*) nests in 1977 and 92 nests in 1978 was collected and later analyzed for organochlorines, polybrominated biphenyls (PBBs), polychlorinated styrenes (PCSs), and metals. One egg was also collected from each of the dabbling duck nests located. Twenty-nine of these eggs were analyzed for organochlorines and metals in 1977; 10 eggs were analyzed in 1978. All merganser eggs contained DDE, polychlorinated biphenyls (PCBs), and dieldrin; all but one egg collected in 1978 contained DDT. DDE and PCB levels had declined since 1975 to a geometric mean of 7.4 ppm DDE and 20 ppm PCBs in 1977 and 7.6 ppm DDE and 19 ppm PCBs in 1978. Dieldrin residues in eggs had not declined from 1975 levels; the geometric mean was 0.78 ppm in 1977 and 0.76 ppm in 1978. Other organochlorines were present at low levels. Mercury residues averaged >0.50 ppm in merganser eggs and had not declined since 1975. Other metals were present at low levels. Dabbling ducks generally had much lower organochlorine and Hg residues than mergansers; DDE and PCBs were the only organochlorines present in the majority of eggs. Geometric means of PCBs and DDT in dabbling duck eggs did not exceed 2.0 ppm and 1.0 ppm, respectively. PBBs and PCSs were detected only in a few merganser eggs, at low levels. Eggshell thickness for red-breasted merganser eggs averaged 0.359 mm in 1977 and 0.355 mm in 1978, which is only 2%-3% below pre-1946 thicknesses. Mallard (*Anas platyrhynchos*) eggshell thicknesses averaged 0.331 mm in 1977 and 0.337 mm in 1978.*

Introduction

Organochlorine residues, especially polychlorinated biphenyls (PCBs) (*18*), have been a contaminant problem in Lake Michigan biota for years, and fish have accumulated high concentrations of these lipid-soluble compounds (*26*). The build-up is especially persistent in the Green Bay watershed (*2*). Fish-eating birds nesting in this watershed accumulate high organochlorine residues (*10*) and exhibit significant eggshell thinning (*6*).

In 1975, red-breasted merganser (*Mergus serrator*) and common merganser (*Mergus merganser*) eggs collected on islands off Door County, Wisconsin, contained up to 29 ppm DDE and 113 ppm PCBs; shells were 17.7% thinner than eggshells collected before the use of DDT (*27*). In 1977 and 1978, authors studied the reproductive success of mergansers on several islands in the same area (Figure 1). The present paper reports the levels of organochlorines and metals in eggs randomly collected from the nests of mergansers and other waterfowl on the islands.

Sample Collection and Preparation

All but two of the eggs in the present study were obtained from Spider, Hog, and Pilot islands (Figure 1).

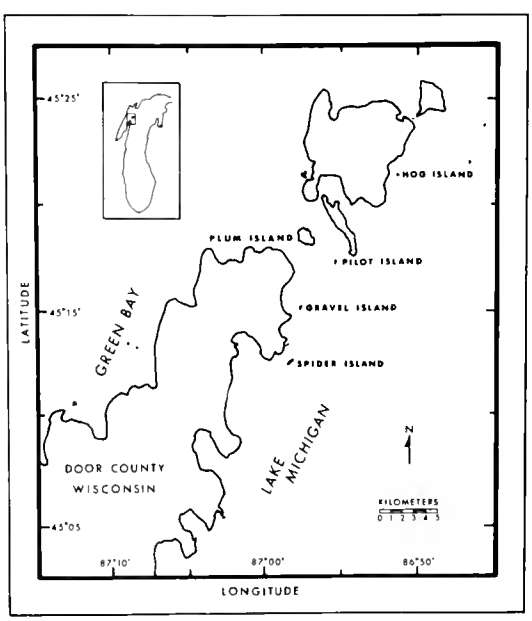

FIGURE 1. *Location of islands where waterfowl eggs were collected for residue analyses, Lake michigan, 1977 and 1978.*

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

One red-breasted merganser nest each was found on Gravel and Plum islands. The main three islands were divided into 5–6-m transects and each transect was searched by at least two people. Eggs were randomly selected, one egg per clutch, from all merganser and many dabbling duck nests that contained three or more eggs. Nests containing fewer than three eggs were revisited several times and, if more eggs were added, then they too were sampled.

Waterfowl nesting on the three islands during the 2-year study included red-breasted mergansers, common mergansers, mallards (*Anas platyrhynchos*), gadwalls (*Anas strepera*), and black ducks (*Anas rubripes*). Red-breasted mergansers were by far the most prevalent species; eggs were taken from 114 nests in 1977 and 92 nests in 1978. Common merganser nests (two) were found only in 1978. In 1977, 22 mallard, 4 gadwall, and 3 black duck nests were sampled. In 1978, eggs from five mallard and five gadwall nests were collected and analyzed for organochlorines and a few metals.

Eggs were labeled and carried in egg cartons to the laboratory. Eggs were cleaned and the length, breadth, and weight of each was measured. Volume was measured by water displacement if whole and if cracked was considered comparable to another egg of the same species with the same length and breadth measurements. Because dehydration and/or loss of lipid may occur in embryonated eggs, a specific gravity of 1.0 was assumed for all eggs; residue values (ppm) were based on egg volume (*25*).

All eggs were opened at the equator and the contents were stored frozen in a glass jar until chemical analysis. Stage of embryonic development based on the mallard was noted. Eggshells were rinsed with membranes intact and air-dried for at least 2 weeks before being measured and weighed. Thickness was measured three times at the equator of each egg with a Starrett 1010M micrometer having 0.01-mm graduations. A mean of these three values was considered the shell thickness for each egg.

Statistical Analysis

Comparisons of organochlorine and metal levels in eggs randomly collected during 1977 and 1978 were made by using a Mann-Whitney U-test. Geometric means and ranges and nonparametric correlations are presented because some organochlorines did not show a normal distribution. Pre-1946 eggshell thicknesses in red-breasted and common mergansers, as reported by White and Cromartie (*27*), were compared with 1977 and 1978 values by means of Student's *t*-test. Intercorrelations of residues were tested with Spearman correlation coefficients.

Analytical Procedures

ORGANOCHLORINES, POLYCHLORINATED STYRENES, AND POLYBROMINATED BIPHENYLS

Eggs were analyzed for *p,p'*-DDE, *p,p'*-TDE, *p,p'*-DDT, dieldrin, heptachlor epoxide, oxychlordane, *cis*-chlordane, *trans*-nonachlor, *cis*-nonachlor, endrin, hexachlorobenzene (HCB), mirex, toxaphene, PCB, PBB, and PCS residues. Samples were ground with anhydrous sodium sulfate and extracted in a Soxhlet apparatus. Extracts were cleaned on a Florisil column, and pesticides and PCBs were separated into three fractions on a SilicAR® column, as described by Cromartie et al. (*4*). The SilicAR procedure was modified for the 1978 samples: The cleaned extracts were separated into four fractions, which produces a discrete fraction for endrin and dieldrin (*16*).

Instrument parameters and operating conditions for quantitation of PCB, PCS, PBB, and pesticide residues were as follows:

Gas-liquid chromatograph:	Hewlett-Packard Model 5713 or 5840A equipped with automatic sampler and digital processor
Detector:	^{63}Ni
Columns:	PCBs, PCSs, pesticides: glass, 183 × 0.4 cm ID, packed with 1.5% OV-17/1 95% QF-1 on 100–120-mesh Supelcoport at 196–198°C and with 5% methane in argon flowing at 60 ml/min
	PBBs: glass, 183 × 0.4 cm ID, packed with 3% OV-1 on 80–100-mesh Supelcoport at 245°C and with 5% methane in argon flowing at 100 ml/min

Pesticides were measured by digital integration of peak areas; PCBs were estimated by comparing total area with that of Aroclor 1260; PCS values were estimated on the octachlorostyrene peak (*24*), and PBB values were based on hexabromobiphenyl. Toxaphene estimates were based on the area of two peaks eluting after DDT (*23*).

Average percentage recoveries from spiked chicken eggs were DDE, 91; TDE, 97; DDT, 93; dieldrin, 99; heptachlor epoxide, 78; oxychlordane, 97; *cis*-chlordane, 102; *trans*-nonachlor, 99; endrin, 90; HCB, 75; mirex, 92; and Aroclor 1260, 101. Residue levels were not corrected for recovery. The lower limits of reportable residues were 0.10 ppm for pesticides, 0.50 ppm for PCBs, 0.02 ppm for PBBs, and 0.05 ppm for PCSs. Endrin was quantified as low as 0.05 ppm in the 1977 samples and as low as 0.02 ppm in the 1978 samples. Residues in 63 specimens were confirmed on an LKB 9000 or a Finnigan 4000 Series gas chromatograph–mass spectrometer (*16*).

METALS

Analyses for chromium (Cr), lead (Pb), copper (Cu), zinc (Zn), cadmium (Cd), arsenic (As), and selenium (Se) in 1978 were performed at Patuxent Wildlife Research Center, Laurel, Maryland. Eggs were homogenized in a Virtis blender. A 5-g portion was placed in a Vycor crucible for Pb, Cu, Zn, Cd, and Cr analyses, and a 2-g portion was placed in a 125-ml Erlenmeyer flask for As and Se analyses.

Pb, Cu, Zn, Cd, Cr—After drying for 2 hours at 110°C, the Vycor crucible was covered and placed in a muffle furnace at 200°C for 2 hours. The temperature was then increased to 550°C at a rate of 100°C/hr and the sample was left to ash overnight. The ash was cooled, dissolved in approximately 4 ml nitric and hydrochloric acids over a hot plate, transferred to a 12-ml polypropylene tube, and diluted to 10 ml with distilled, deionized water. Residues were determined by comparison with aqueous standards on a Perkin-Elmer Model 703 atomic absorption spectrophotometer. Except for the Pb line of 217.0 nm, the standard conditions as published by the manufacturer were used.

As, Se—The 2-g sample was dissolved in 40 ml concentrated nitric acid over a hot plate and heated slowly to boil away all but 1 ml of acid, which was then transferred to a 50-ml polypropylene tube and diluted to 50 ml with distilled, deionized water. Arsenic and selenium were determined by the method of additions on a Perkin-Elmer Model 403 atomic absorption spectrophotometer equipped with a Perkin-Elmer MHS-1 hydride generator. Authors performed the As analyses at 193.7 nm with a 5% $NaBH_4$ reducing solution at 1,000°C, and the Se analyses at 196.0 nm with a 10% $NaBH_4$ reducing solution at 900°C.

Recoveries from spiked chicken livers ranged from 83% to 110%; residues were not corrected on the basis of these data. The lower limits of reportable residues, on a wet-weight basis, were 0.10 ppm for Pb, Cu, Zn, Cd, and Se, and 0.05 ppm for Cr and As.

All mercury (Hg) analyses and As and Se analyses in 1977 were made by Environmental Trace Substances Research Center, Columbia, Missouri. Mercury samples were first wet-digested in nitric acid. Stannous chloride was added to reduce ionic Hg to elemental Hg, which was measured photometrically in the vapor phase by atomic absorption. The lower limit of quantification was 0.001 ppm Hg, wet weight.

Arsenic samples of 0.25 g were added to 15 ml concentrated nitric acid and 1 ml perchloric acid and heated to fumes. The samples were cooled and diluted to 25 ml with distilled, deionized water. A 10-ml aliquot of each sample was run in duplicate on a Perkin-Elmer MHS-1 hydride system with a $NaBH_4$ pellet at 1,000°C. The lower limit of quantification was 0.005 ppm As, dry weight.

Selenium was determined with the Se 77^m method outlined by McKown and Morris (*21*). The lower limit of quantification was 0.01 ppm Se, dry weight.

Results and Discussion

MERGANSERS

Organochlorines—In 1977, all 114 red-breasted merganser eggs contained PCBs, DDE, dieldrin, and DDT. Geometric means for these four organochlorines were 20, 7.4, 0.78, and 0.36 ppm, wet weight, respectively. In 1978, all 92 of the red-breasted merganser eggs contained PCBs, DDE, and dieldrin; 91 of the 92 eggs contained DDT. Geometric means for the four residues were 19, 7.6, 0.76, and 0.31 ppm, respectively (Table 1). The means of these four organochlorines did not change significantly ($P>0.05$) between 1977 and 1978, but the range of PCBs (up to 229 ppm in 1977, but only 36 ppm in 1978) and of DDE (up to 28 ppm in 1977, but only 16 ppm in 1978) decreased. The range of dieldrin and DDT did not change dramatically between 1977 and 1978.

Although PCB values from the present study are not easily compared quantitatively with previous findings, there is a general downward trend. In 1969, Faber and Hickey (*6*) reported an arithmetic mean of 84 ppm PCBs, wet weight, in red-breasted merganser eggs from the Green Bay area. In 1975, the mean had decreased to 45 ppm PCBs (*27*). Our arithmetic means were 25 ppm and 20 ppm, respectively. The same trend was apparent in DDE residues for these 4 years: 44 ppm in 1969 (*6*), 16 ppm in 1975 (*27*), 8.3 ppm in 1977, and 8.1 ppm in 1978. Dieldrin residues showed no such decrease; arithmetic means for the 4 years were 0.77 ppm in 1969, 1.0 ppm in 1975, 0.86 ppm in 1977, and 0.81 ppm in 1978. DDT was not reported singly in 1969, but in 1975 the mean (0.62 ppm) was slightly higher than in 1977 and 1978. This is also true for TDE values. The mean value of 0.40 ppm reported in 1975, with 17 of 18 eggs containing TDE, was higher than the 0.16 ppm and 0.07 ppm means found in 1977 and 1978, respectively. The incidence of TDE had also dropped dramatically in 1978 (Table 1). A slight decrease was also apparent in the 1978 common merganser eggs with regard to DDE, PCBs, DDT, and TDE when compared to 1975 values (*27*). The 1978 dieldrin values ($\bar{x}=1.7$ ppm) were higher than those found in 1975 ($\bar{x}=0.64$ ppm).

Other organochlorine residues were found at low levels in merganser eggs collected during 1977 and 1978. Mirex and endrin residues decreased from 1975 values

TABLE 1. *Organochlorine, PBB, and PCS residues in the eggs of waterfowl nesting on three Lake Michigan islands off the tip of Door County, Wisconsin, 1977-78*

PCB[1]	DDE	DDT	TDE	Dieldrin	Heptachlor Epoxide	Toxaphene	HCB	Mirex	Endrin	Oxychlordane	cis Nonachlor	trans Nonachlor	cis-Chlordane	PCS	PBB
RED-BREASTED MERGANSER, 1977 (114)[2]															
20 0[3] 4 9–229[4] 114[5]	7 4 2 4–28 114	0.36 0 09–1 7 114	0 14 ND–0 71 97	0 78 0 25–2.3 114	0.20 ND–0 88 109	0 14 ND–0 89 57	0 06 ND–0 3 24	0 05 ND–0 25 12	0 05 ND–0 05 3	0 30 ND–0 84 111	0 11 ND–0 41 79	0 22 ND–0 73 103	0 08 ND–0 28 46	NA	0 06 ND–0 13 109
RED-BREASTED MERGANSER, 1978 (92)															
19 0 6.6–36 92	7 6 2.3–16 92	0.31 ND–0 61 91	0 06[6] ND–0.33 19	0 76 0 20–1 9 92	0 22 ND–0 55 91	0 27[7] ND–0 64 88	0 05 ND–0 2 11	0 05 ND–0 4 7	0 03 ND–0 08 28	0 41[8] ND–0 9 91	0 14 ND–0 31 86	0 33[8] ND–0 67 90	0 15[8] ND–0 28 87	0 04 ND–0.80 29	NA
COMMON MERGANSER, 1978 (2)															
40 0 33–48 2	19 0 19–20 2	0 18 0 1–0 34 2	0 07 ND–0 11 1	1 7 1 5–1.9 2	0 44 2	0 24 0 20–0 28 2	0.14 ND–0 37 1	ND	ND	0 76 0 73–0 80 2	0 44 2	1 2 0 96–1.5 2	0 22 2	0 08 ND–0 25 1	NA
MALLARD, 1977 (22)															
2.0 ND–10 18	0 89 ND–3 6 21	0 06 ND–0 27 4	ND	0 06 ND–0 18 2	ND	0 05 ND–0 12 2	ND	ND	ND	0 05 ND–0 09 1	ND -	0 05 ND–0 13 3	ND	NA	ND
MALLARD, 1978 (5)															
1 1 0 25–4 9 5	1 0 0 28–4 2 5	ND	ND	0 13 ND–0 53 3	ND	ND	ND	ND	ND	ND	ND	0 06 ND–0 13 1	ND	ND	NA
GADWALL, 1977 (4)															
1 1 0.78–2 2 4	0 35 0 13–0.55 5	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	NA	ND
GADWALL, 1978 (5)															
1 3 0 73–2.5 5	0 80 0 45–1.4 5	ND	ND	0 24 ND–0 56 4	ND	0.06 ND–0.10 1	ND	ND	ND	ND	ND	0 06 ND–0 09 1	ND	ND	NA
BLACK DUCK, 1977 (3)															
2 2 0.71–6.7 3	0 77 0 21–2 5 3	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	NA	ND

NOTE. NA = no analyses performed for that substance, ND = No residue of quantifiable level. Levels over which quantification was possible were 0 1 ppm for all chemicals except endrin, 0 05 ppm (1977), 0 02 ppm (1978), PCB = 0 50 ppm; PCS = 0 05 ppm, PBB = 0 02 ppm. Samples with no detectable residues were calculated in the means as one-half the quantification level.

[1] PCB as Aroclor 1260

[2] Number in parentheses = total number of eggs analyzed

[3] Geometric mean, ppm wet weight

[4] Range.

[5] Number of total samples analyzed which contained residues of reportable level

[6] Significantly different from residues in the eggs of the same species, 1977, Mann-Whitney U-test, $P < 0.01$

[7] Significantly different from residues in the eggs of the same species, 1977, Mann-Whitney U-test, $P < 0.025$

[8] Significantly different from residues in the eggs of the same species, 1977, Mann-Whitney U-test, $P < 0.005$

(27, Table 1). In fact, mirex was detected in only 12 and 7 eggs collected from red-breasted merganser nests in 1977 and 1978, respectively, and endrin in only 3 and 28 eggs, respectively. Levels of toxaphene, oxychlordane, *trans*-nonachlor, and *cis*-chlordane increased slightly, but significantly, from 1977 to 1978. PBBs were detected in 109 of the 114 red-breasted merganser eggs analyzed in 1977, and PCSs were detected in 29 of the 92 red-breasted merganser eggs analyzed in 1978 and in one of the two common merganser eggs. The residues were extremely low (Table 1).

Metals—Mercury was detected in all merganser eggs in 1977 and 1978 (Table 2). The arithmetic mean in both years for red-breasted merganser eggs was 0.55 ppm Hg, which is similar to the 0.56-ppm Hg levels found during 1975. The mean value of Hg in common merganser eggs did not differ significantly in 1975 (0.56 ppm Hg) and 1978 (0.58 ppm). Arsenic and

TABLE 2. *Metal residues in the eggs of waterfowl nesting on three Lake Michigan islands off Door County, Wisconsin, 1977-78*

Species and Year	Residues, ppm Wet Weight							
	Hg	As	Se	Cr	Pb	Cu	Zn	Cd
Red-breasted merganser 1977	0.52[1] 0.24–1.3[2] (113/113)[3]	0.060 0.040–0.083 (5/5)	0.74 0.60–0.82 (5/5)	NA	NA	NA	NA	NA
Red-breasted merganser 1978	0.51 0.26–1.3 (92/92)	0.060 ND–0.11 (1/7)	0.61 0.47–1.0 (7/7)	0.12 ND–0.24 (6/7)	0.93 0.53–1.4 (7/7)	0.75 0.54–1.0 (7/7)	15 12–20 (7/7)	ND
Common merganser 1978	0.58 0.46–0.73 (2/2)	NA	NA	NA	NA	NA	NA	NA
Mallard 1977	0.08 0.07–0.39 (22/22)	0.013 ND–0.022 (3/5)	0.54 0.28–0.81 (5/5)	NA	NA	NA	NA	NA
Mallard 1978	0.08 0.05–0.17 (5/5)	NA	NA	NA	NA	NA	NA	NA
Gadwall 1977	0.07 0.04–0.13 (4/4)	NA	NA	NA	NA	NA	NA	NA
Gadwall 1978	0.04 0.03–0.12 (5/5)	NA	NA	NA	NA	NA	NA	NA
Black duck 1977	0.12 0.06–0.19 (3/3)	NA	NA	NA	NA	NA	NA	NA

NOTE: NA = not analyzed; ND = None detected above the level of quantification. Any egg containing less than this level of residue was averaged into the mean using one-half the lower limit of detection.

[1] Geometric mean.

[2] Range.

[3] (Number of samples that contained quantifiable levels of residue/number of eggs analyzed).

selenium residues in merganser eggs were generally low (Table 2) and did not change from 1977 to 1978. Chromium, lead, copper, and zinc were detected in 1978 in the seven eggs analyzed; geometric means were 0.12, 0.93, 0.75, and 15 ppm, respectively. Cadmium was not detected at quantifiable levels.

Banded Hens—Six red-breasted merganser hens, captured and banded on their nests in 1977, were recaptured on their nests in 1978. The residues of six of the major contaminants in the eggs collected from these nests are listed in Table 3. As was the case with other nests checked, the only significant change between 1977 and 1978 was the TDE residues; both the amount and incidence of TDE had decreased. Levels of Hg were slightly, but not significantly, higher in the eggs from the nests of banded hens; otherwise, residues were comparable.

DABBLING DUCKS

Organochlorines—Generally, organochlorine residues were much lower in dabbling duck than in merganser eggs (Table 1). DDE and PCBs were the only organochlorines found in the majority of dabbling duck eggs. Geometric means of DDE for the 2 years ranged from 0.35 ppm in 1977 gadwall eggs to 1.0 ppm in 1978 mallard eggs. Geometric means for PCBs in dabbling duck eggs ranged from 1.1 ppm in 1977 gadwall and 1978 mallard eggs to 2.2 ppm PCBs in 1977 black duck eggs. Other organochlorines—DDT, dieldrin, toxaphene, oxychlordane, *trans*-nonachlor—were detected at very low levels in a few eggs. PCSs and PBBs were not present in any of the eggs analyzed.

Metals—Mercury residues were also lower in dabbling duck eggs than in merganser eggs (Table 2). Geometric means ranged from 0.04 ppm Hg in 1978 gadwall eggs to 0.12 ppm Hg in 1977 black duck eggs. Arsenic and selenium were measured in 1977 mallard eggs, and the geometric means were 0.013 ppm As and 0.54 ppm Se, wet weight. Three of five eggs contained As; all five eggs contained Se.

EGGSHELL THICKNESS

Mean eggshell thickness for 92 randomly collected red-breasted merganser eggs of less than 9 days incubation was 0.359 mm in 1977. In 1978, the mean thickness for 87 eggshells was 0.355 mm. This is a 2.2% and 3.3% decrease from pre-1946 values, respectively (Table 4), but a 14%–15% increase in the shell thickness over those measured in 1969 (*6*) and 1975 (*27*). The same pattern is reflected in common

TABLE 3. *Organochlorine and mercury residues in randomly sampled eggs from clutches of the same six red-breasted mergansers in Door County, Wisconsin, 1977-78*[1]

Year	Residues ppm Wet Weight					
	DDE	PCB	TDE	DDT	Dieldrin	Hg
1977	7.5 ± 1.92[2] 6[3]	19 ± 4.3 6	0.10 ± 0.012 5	0.28 ± 0.048 6	0.67 ± 0.113 6	0.62 ± 0.080 6
1978	7.9 ± 1.14 6	20 ± 1.0 6	0.06 ± 0.008 1	0.32 ± 0.066 6	0.85 ± 0.145 6	0.70 ± 0.130 6

[1] The same six nests were sampled both years.
[2] Mean ± standard error.
[3] Number of samples that contained quantifiable levels of a residue. Those under that level were assigned a value of one-half the detection limit

merganser eggshells. The 0.414-mm mean found in 1978 eggs was only 3.2% lower than the pre-DDT reports, whereas the 1975 values were 23.5% thinner. Mallard eggshell thickness from the study averaged 0.331 mm in 1977 and 0.337 mm in 1978. Although authors could locate no measurements of mallard eggshell thickness from the pre-DDT era for comparison with these values, they are comparable to those of black duck eggs from the Atlantic Flyway collected before the use of DDT and in 1978 (*12*).

The decrease in DDE over the sampling years, rather than any change in residue levels of other organochlorines or metals, is most likely responsible for the improvement in eggshell thickness in both species of mergansers. DDE has been implicated in both field (*3, 6, 10*) and laboratory studies (*11, 20*) as the primary cause of avian eggshell thinning. And again in this study, DDE was correlated with eggshell thickness in the red-breasted mergansers (Figure 2, $r^2 = 0.029$). The slope of the relation was significantly different from zero ($P < 0.02$). The correlation was weak, but significant, as was the correlation of several other organochlorines (oxychlordane, *trans*-nonachlor, hexachlorobenzene) to eggshell thickness. Because of the additional significant correlations, authors cannot show statistically that decreasing residues of DDE were alone responsible for improved eggshell thickness in 1977 and 1978. We do, however, feel that the evidence points to DDE, and that other organochlorines are correlated with eggshell thickness because all the major chlorinated hydrocarbons react similarly in biological systems and their residues are therefore correlated with each other (Table 5). The only major residue which is not correlated to the others is Hg. DDE residues were correlated to this metal in the 1978 sample. Other organochlorines show no such correlation.

POTENTIAL BIOLOGICAL EFFECTS

The relationship of contaminants and reproductive success of red-breasted mergansers will be thoroughly discussed in a manuscript now in preparation, but some general observations on the effects of contaminants on waterfowl are discussed below. PCBs were the most abundant contaminant found in red-breasted merganser eggs. The levels detected were below levels found to have no effect on hatchability and survival of young in pen studies with mallards. This is true of studies where both natural (*5*) and artificial (*13*) incubation were used. Comparable levels in the egg were associated with embryo mortality in ring doves (*Streptopelia risoria*) (*22*) and decreased growth in young chickens (*Gallus domesticus*) (*15*).

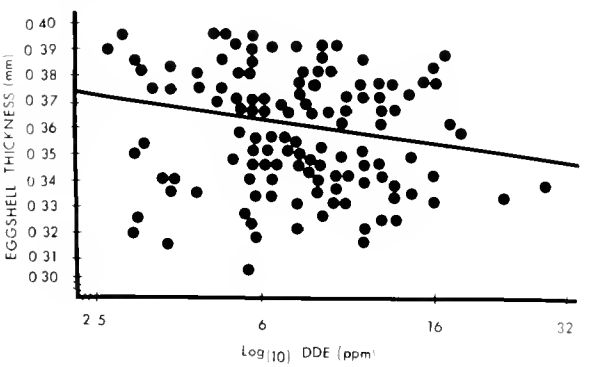

FIGURE 2. *Correlation of DDE residues (log, ppm wet weight) with eggshell thickness of red-breasted merganser eggs collected in 1977 and 1978 on islands in northern Lake Michigan.*

TABLE 4. *Shell thickness in eggs of waterfowl nesting on islands in northern Lake Michigan*[1]

Year	Shell Thickness, mm		
	Red-breasted Merganser	Common Merganser	Mallard
Pre-1946	0.367 ± 0.001[2a] (8/105)[4]	0.426 ± 0.011[2a] (3/33)	—[3]
1975	0.302 ± 0.004[2b] (18/178)	0.314 ± 0.006[2b] (2/16)	—
1977	0.359 ± 0.002[c] (92/92)	—	0.331 ± 0.008 (6 6)
1978	0.355 ± 0.002[c] (87/87)	0.414 ± 0.003[c] (2/2)	0.337 ± 0.025 (4 4)

[1] Mean ± standard error of the mean of all eggs measured, means with different letters are statistically different, Student's *t*-test, $P < 0.01$
[2] Data are from White and Cromartie (1977).
[3] No data are available.
[4] (Number of clutches represented/number of eggs measured).

TABLE 5. *Correlation of five organochlorines and mercury in the eggs of red-breasted mergansers, Door County, Wisconsin, 1977-78*[1]

Residue	DDE	DDT	Dieldrin	Heptachlor Epoxide	Hg
			1977		
PCBs	0.699**	0.315**	0.244**	0.392**	0.154
DDE		0.503**	0.476**	0.594**	0.149
DDT			0.706**	0.661**	0.035
Dieldrin				0.836**	0.036
Heptachlor epoxide					0.040
			1978		
PCBs	0.878**	0.344**	0.459**	0.620**	0.183
DDE		0.379**	0.498**	0.692**	0.207*
DDT			0.718**	0.490**	0.028
Dieldrin				0.734**	0.048
Heptachlor epoxide					0.092

[1] Spearman correlation coefficient.
* $P<0.05$
** $P<0.01$

DDE residues in the mergansers were below those associated with significant eggshell thinning and lowered reproductive success in captive black ducks (*20*) and mallards (*11*), but above levels found in populations of brown pelicans (*Pelecanus occidentalis*) which displayed eggshell thinning and reproductive problems, along with a variety of organochlorine-associated problems (*3*). Dieldrin residues in the merganser eggs were lower than residues in the eggs of barn owls (*Tyto alba*) on a 0.5-ppm dieldrin diet over 2 years (Mendenhall, V., E. Klaas, and A. McLane, manuscript in preparation) and in the eggs of ring-necked pheasant (*Phasianus colchicus*) on a 20-ppm dieldrin diet (*1*). Field populations of purple gallinules (*Porphyrula martinica*) reproduced successfully with egg dieldrin residues of 9–17 ppm (*9*), but brown pelican reproduction was affected when eggs carried a dieldrin burden in the same range as the merganser eggs (*3*).

Mercury contamination in red-breasted merganser eggs was above the 0.5-ppm level suggested to be associated with decreased hatchability in pheasant eggs (*7*), but below that found in mallard eggs from hens on a 0.5-ppm Hg diet (*14*) and below Hg levels in two red-breasted merganser eggs collected near a site of Hg contamination in New Brunswick (*8*). Other metal residues found in merganser eggs were in the same range as metal residues found in eggs of other wild species of bird (*3, 12, 17, 19*).

In spite of contaminant levels in the eggs, which have been associated with reproductive problems in other fish-eating or waterfowl species in the laboratory or field, red-breasted mergansers were fairly successful in hatching broods on the islands in Lake Michigan. Hatching success averaged 81.7% in 1977 and 82.6% in 1978. Dabbling ducks showed far lower contaminant levels in their eggs and averaged a little better in hatching success—90.2% in 1977, 92.1% in 1978.

Summary

DDE and PCB residues in red-breasted merganser eggs collected in Door County, Wisconsin, during 1977 and 1978 had decreased from levels found in 1975. Dieldrin and Hg residues in the eggs had not decreased since 1975. Low levels of other organochlorines were found in the eggs. Eggshell thickness was only 2%–3% below that of pre-1946 eggshells, but the difference was statistically significant. This was a substantial increase from thickness measurements in 1975, which authors believe was primarily due to the decrease in DDE residues in the population. Although the contaminant levels in eggs are considered deleterious in other species and environments, and a general, low-level contamination by many organochlorines was found, hatching success appeared unaffected or only marginally affected in the red-breasted merganser. Dabbling ducks—mallards, gadwalls, black ducks—nesting on the same islands laid eggs containing low levels of PCBs and DDE; a few eggs contained extremely low levels of chlordane isomers, toxaphene, and dieldrin. Hatching success was slightly better in dabbling duck nests than in merganser nests.

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Persistence of Dieldrin in Water and Channel Catfish from the Des Moines River, Iowa, 1971–73 and 1978[1]

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ABSTRACT

This study was conducted to determine if dieldrin concentrations in water and fish of the Des Moines River, Iowa, decreased after registration of the compound was withdrawn by the Environmental Protection Agency in 1975. Mean June concentrations of dieldrin in river water decreased from 50 ppt in 1971 to 11 ppt in 1978. Average daily transport of dieldrin was 156 g in 1971 and 70 g in 1978. July levels in channel catfish muscle were 75 ppb in 1973 and 46 ppb in 1978. Dieldrin was still present in significant concentrations in the aquatic system 3 years after registration withdrawal.

Introduction

Des Moines River, the largest river in Iowa, rises in the glacial moraine area of southwestern Minnesota and flows southeasterly across Iowa to the Mississippi River (Figure 1). About 79% of the watershed upstream from Des Moines in central Iowa is cropland, primarily corn and soybeans; 6% is permanent pasture, 5% is forest, and 7% is urban (*2*). Normal annual precipitation over the drainage area ranges from 62.5 to 77.5 cm from north to south and averages 70.7 cm (*9*). Monthly precipitation is usually greatest in June. Heavy rainfall and cloudbursts occasionally cause high river flows in summer and early fall. The major source of pollution in the river is nonpoint agricultural runoff (*2*).

From 1961 to 1965, aldrin was applied to Iowa soil at the rate of 5–6.5 million pounds per year for control of western corn rootworm. Use decreased to 2 million pounds annually by 1973 as rootworms became increasingly resistant to aldrin (*5*). Although use of aldrin was finally banned by the U.S. Environmental Protection Agency in 1975, this compound and its degradation products are still being detected in the aquatic environment.

From 1971 to 1973, Kellogg and Bulkley (*4, 5*) studied seasonal dieldrin concentrations in river water, channel catfish (*Ictalurus punctatus*), and catfish-food organisms. During 1977 and 1978, Leung conducted another study of the Des Moines River (*6*), including the collection site used by Kellogg and Bulkley. In the present study, authors compare dieldrin levels in water and fish of the Des Moines River, Iowa, before and after banning of the parent compound, aldrin.

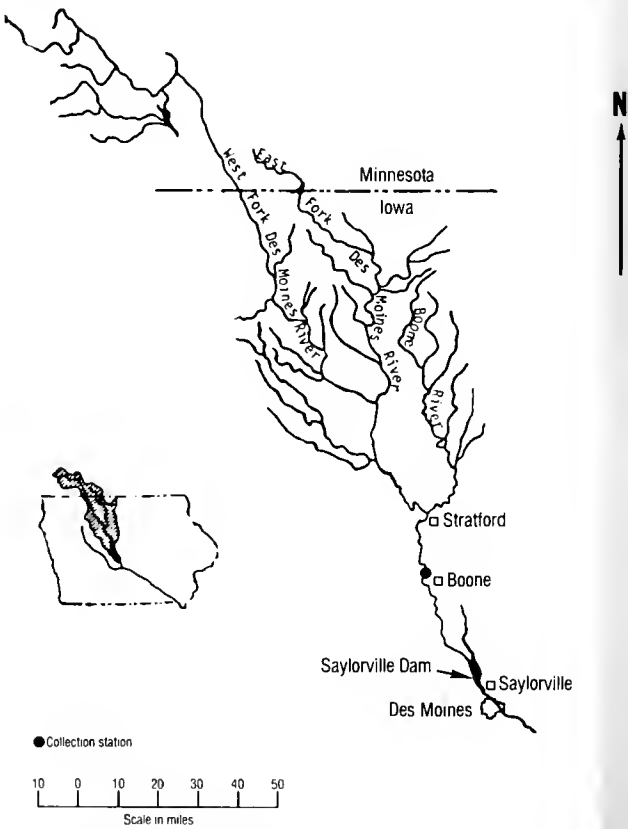

FIGURE 1. *Des Moines River watershed including common sampling site of Kellogg and Bulkley (5) and present study.*

[1] This study was conducted by the Iowa Cooperative Fishery Research Unit as part of Project 2225 of the Iowa Agriculture and Home Economic Experiment Station, Ames, Iowa, in cooperation with the Iowa State Conservation Commission, Iowa State University, and the Fish and Wildlife Service, U.S. Department of the Interior.

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The common collection site of Kellogg and Bulkley (*4, 5*) and the present authors is located near Boone, about 426 km (265 miles) upstream from the mouth of the river. Drainage area of the stream above this point is about 14,530 km^2 (5,610 square miles). Some calculations on river flow and sediment load were based on data collected by the U.S. Geological Survey (*11–14*) at Saylorville, Iowa, 76 km downstream from Boone.

Materials and Methods

WATER

From April through November, single 1-liter water samples were collected monthly during 1971, two 1-liter samples were collected weekly or at 2-week intervals during 1972, three 2-liter samples were collected twice weekly or weekly during 1973 (*5*), and single 4-liter samples were collected weekly or at 2-week intervals during 1978. In 1971, 1972, and 1973, samples were collected by submerging a clean glass container approximately 30 cm below the water surface and sealing it with a Teflon- or aluminum-foil-lined screw cap. The 1978 samples were similarly collected in a stainless steel sampling bucket and stored in amber reagent bottles sealed with Teflon-lined screw caps.

Unfiltered samples were extracted twice with 60 ml of 15% ethyl ether–hexane in 1971 and with 60 ml hexane in 1972 (*15*). Extracts were combined and concentrated to 1 ml in a Kuderna-Danish evaporator for quantitation. The 1973 and 1978 samples were filtered through pre-extracted Whatman No. 40 filter paper to separate the dissolved from the suspended fractions. The filter paper containing the suspended pesticides was Soxhlet-extracted with 300 ml acetonitrile for 18 hours. The pesticides were then partitioned into petroleum ether by adding 1,200–1,400 ml redistilled water and extracting with 180 ml petroleum ether. Florisil cleanup was applied on 1972 samples but not on 1978 samples. The samples were concentrated to 1 ml for quantitation, as described above.

The dissolved fraction (filtrate) of the samples was analyzed for pesticide residues differently in 1973 than in 1978. In 1973, the filtrate was extracted twice with 120 ml of 15% ethyl ether–hexane, followed by a third extraction with 150 ml hexane. The extracts were combined and concentrated to 1 ml for quantitation. Florisil cleanup was applied when necessary. In 1978, macroreticular resin, XAD-2, was used to extract dissolved pesticides (*3*). The filtrate was decanted into a 5-liter glass reservoir and passed through a resin column by gravity at a flow rate of 20–30 ml/min. The pesticides were eluted from the column with 30 ml diethyl ether into a 60-ml separatory funnel. The first 20-ml portion was collected and passed through the column again. Then a fresh 10-ml portion of ether was passed through and combined with the original 20 ml. The water layer was drained from the separatory funnel and the final traces of water were removed from the eluate by adding 10–15 ml petroleum ether and 2–3 g anhydrous sodium sulfate. The mixture was shaken about 30 seconds and the extract was transferred to a concentration flask. The sample was then concentrated to 1 ml for quantitation without further treatment.

FISH

Channel catfish were collected with gill nets and hoop nets and by electrofishing. The samples were grouped by collection data and total length. Samples of dorsal muscle tissue from individuals in the same group were ground, pooled, homogenized, wrapped in aluminum foil, and frozen until analysis. Tissues were analyzed by the method described in the *Pesticide Analytical Manual* of the U.S. Department of Health and Human Services (*10*), with slight modification. After the samples were thawed, 20–65 g subsamples were extracted with 200–350 ml of 65% acetonitrile–water for 5–10 minutes in a 1-liter blender. The samples were filtered and transferred to a 1-liter separatory funnel, to which 100 ml petroleum ether, 600 ml water, and 10 ml saturated aqueous sodium chloride were added. The pesticides were partitioned into the organic layer by vigorously shaking 30–60 seconds. The aqueous layer was discarded and the petroleum ether layer was washed twice with 100 ml water. Interferences were removed by Florisil cleanup; additional charcoal cleanup was used in 1973. The elution was concentrated to 1–10 ml for quantitation. The wet weights of tissue samples were corrected for losses of the acetonitrile–water mixture and petroleum ether. Concentrations were expressed in nanograms of pesticide per gram of fish tissue (ppb) on a wet-weight basis.

QUANTIFICATION

Instrument parameters and operating conditions for quantification and confirmation were as follows:

1971, 1972, and 1973	
Gas chromatograph:	Beckman GC-5
Detector:	discharge electron-capture
Columns:	packed with 5% OV-210, at 180°C packed with a mixture of 1.5% OV-17 and 1.95% QF, at 200°C
Carrier gas:	helium flowing at 100 ml/min
1978	
Gas chromatograph:	Tracor, Model 550
Detector:	^{63}Ni electron-capture, maintained at 340°C
Columns:	packed with 10% DC-200, at 210°C packed with a mixture of 4% OV-210 and 6% SE-130 at 210°C
Carrier gas:	nitrogen, flowing at 90–100 ml/min

Values obtained were not corrected for percent recovery. Detection limits were approximately 10 ppt for water and 10 ppb for fish tissue. All analyses were conducted under the supervision of one of the authors,

John J. Richard, at the Ames Laboratory, U.S. Department of Energy, Iowa State University, Ames, Iowa.

Results

Dieldrin is transported in rivers in two forms: dissolved in the water and adsorbed on suspended sediment and organic material. During the study period, combined (total) concentrations of dissolved and suspended dieldrin in the Des Moines River tended to be highest in June and July, although monthly differences were much less in 1973 and 1978 than earlier (Table 1). Kellogg and Bulkley (*5*) attributed this seasonal trend to application of aldrin to farmland during the April–May planting season and to spring rainfall. For the period May-October 1971-1973, mean combined dieldrin concentrations decreased 70% (from 30 to 9 ppt), whereas the difference between 1973 and 1978 concentrations (9 vs. 7 ppt) was not statistically significant.

TABLE 1. *Monthly mean dieldrin concentrations in Des Moines River water near Boone, Iowa*

	Mean concentration, ng/liter[1]				% Total in Dissolved State	
Month	1971	1972	1973	1978	1973	1978
May	10(1)	10(4)	8(7)	5(5)	74	61
June	50(1)	24(5)	10(8)	11(4)	63	46
July	40(1)	23(2)	12(7)	8(3)	64	64
August	30(1)	10(2)	6(6)	5(4)	67	43
September	30(1)	10(1)	4(4)	8(4)	62	28
October	20(1)	10(1)	3(3)	6(3)	60	18
Mean	30	11	9	7	65	43

NOTE: Number of measurements in parentheses.
[1] 1971–73 data from Kellogg (*4*).

One apparent difference was that the percentage of dieldrin in the dissolved state decreased on the average from 65% in 1973 to 43% in 1978 (Table 1). The percentage was similar only in July of the 2 years (64%). Inasmuch as dieldrin is more readily available to aquatic organisms in the dissolved state, concentrations in dissolved and suspended states were examined for the 2 years for which data were available (Table 2). Dissolved dieldrin levels were slightly lower each month (except November) in 1978 than in 1973, but differences were not statistically significant.

Changes in pesticide residues in the aquatic habitat may also be compared on the basis of estimated amounts of the chemical being transported downriver. Estimates are based on concentrations in the dissolved and suspended states, stream flow, and sediment load. Mean stream flow on sampling days was lowest in 1971, the year when concentrations of total dieldrin were highest (Table 3). Flows in 1973 were the highest on the

TABLE 2. *Monthly mean dissolved and suspended dieldrin concentrations in Des Moines River water near Boone, Iowa, 1973 and 1978*

	1973[1]			1978		
		Concn, ng/liter			Concn, ng/liter	
Month	No of Measurements	Dissolved	Suspended	No of Measurements	Dissolved	Suspended
April	2	12	3	4	2	5
May	7	6	3	5	3	2
June	8	6	4	4	5	6
July	7	8	4	3	5	3
August	6	4	2	4	2	3
September	4	3	2	4	2	6
October	3	3	1	3	1	5
November	1	1	1	2	1	1
Overall mean		5	3		3	4

[1] Kellogg (*4*).

TABLE 3. *Mean daily stream flow and sediment load, Des Moines River, Iowa—May to October, 1971–73, 1978*[1]

	Mean Daily Stream Flow, m^3/sec				Mean Sediment Load, mg/liter			
Month	1971	1972	1973	1978	1971	1972	1973	1978
May	66.1	137.9	244.6	105.6	205	459	448	93
June	110.9	116.4	175.1	132.3	390	287	384	196
July	97.9	83.6	92.5	161.1	300	275	377	256
August	14.7	114.9	26.4	82.1	61	420	205	173
September	5.7	42.3	44.2	94.0	35	212	245	334
October	4.3	59.7	186.4	70.8	7	233	357	55
Mean	49.9	92.5	128.2	107.6	166	314	336	184

[1] 1971–73 data from Kellogg (*4*) and Kellogg and Bulkley (*5*).

TABLE 4. *Estimated transport of dieldrin in Des Moines River, Iowa, 1971–73, 1978*

	Dieldrin, g/day			
Month	1971	1972	1973	1978
May	57	119	169	46
June	479	242	151	126
July	338	166	96	111
August	38	99	14	35
September	15	36	15	65
October	7	52	58	37
Mean	156	119	84	70

average for the 4 years of sampling. Stream flow for the 6-month sampling period averaged 20.6 m^3/sec higher, and mean sediment concentration averaged 152 mg/liter greater, in 1973 than in 1978. Data summarized in Tables 1 and 2 were used to estimate dieldrin transport. Variation in daily amounts was greatest in 1971, when 479 g/day was transported in June and only 7 g/day in October (Table 4). Variation was least in 1978, 35–126 g/day. Mean daily transport decreased continuously from 1971 to 1978, from 156 to 70 g/day. Total amount

of dieldrin transported down river during the period May-October decreased rapidly from 1971 to 1973 and then leveled off (Figure 2). Rate of annual decrease was 5 kg/year between 1971 and 1972, 6.5 kg/year between 1972 and 1973, and only 0.5 kg/year from 1973 to 1978.

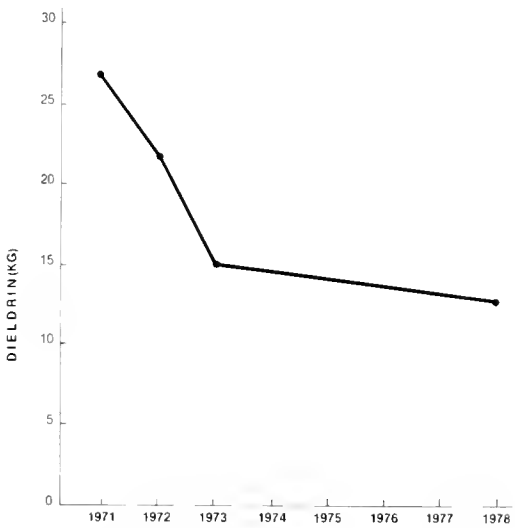

FIGURE 2. *Estimated amounts of dieldrin transported in the Des Moines River past Boone, Iowa, May to October 1971–78.*

Concentrations in muscle tissue of channel catfish were examined next to determine if dieldrin residues in fish had decreased. Comparisons of dieldrin in Des Moines River catfish were made on fish of similar length captured during the same season of the year (*1*). Under these restrictions, only data on catfish 201–300 mm in total length, collected from June to September, were compared (Table 5). Concentrations were higher in 1973 than in 1971 in all months except June. Mean levels for the 4-month period were 43 ppb in 1971 and 86 ppb in 1973. Comparison of data for July suggested a 39% reduction in concentration from 1973 to 1978.

TABLE 5. *Dieldrin concentrations in the muscle tissue of channel catfish 201–300 mm long from the Des Moines River near Boone, Iowa, 1971, 1973, and 1978*

	1971[1]		1973[1]		1978	
Month	No of Fish	Dieldrin, ppb	No of Fish	Dieldrin, ppb	No of Fish	Dieldrin, ppb
June	9	33	12	22	—	—
July	6	61	12	75	8	46
August	4	35	12	133	—	—
September	3	44	12	113	—	—

[1] Data from Kellogg (*4*) and Kellogg and Bulkley (*5*).

Discussion

It is not uncommon for pesticide residues in water to increase with rainfall and stream flow. Dieldrin concentrations might vary directly or inversely with flow in the Des Moines River (*5*). The amount of pesticide transported by any one storm depends on variables such as duration of storm runoff, antecedent soil/moisture conditions, rainfall intensity, and the source of runoff in the watershed. During the study years, most Iowa farmland was plowed in late fall so that the land was clear of vegetation in early spring when final preparations, including aldrin application, were made for planting. Heavy rains during the spring sometimes transport huge quantities of soil from the bare fields into the streams. Dieldrin concentrations may follow sediment and flow levels on these occasions. Over half the sediment in Iowa streams comes from sheet erosion of the land. Later in the growing season, when vegetation covers much of the soil and tends to trap sediments, a higher proportion of the suspended sediment resulting from rainfall may be due to sloughing of the river banks. Thus, dieldrin concentrations under these conditions may be unrelated to flow or suspended sediment levels. Timing of rainfall and runoff in relation to time of aldrin application also complicates the relationship between flow and dieldrin concentrations in river water. In our study we made monthly comparisons to depress day-to-day differences in dieldrin concentrations in water that resulted from these variables.

Dieldrin concentrations in the Des Moines River decreased greatly from 1971 to 1973 but not significantly from 1973 to 1978. During July, concentrations in catfish muscle were lower in 1978 than in 1973, but the difference was less than that between monthly samples in 1973, and between several 1971 and 1973 samples. Inasmuch as dieldrin was banned in 1975, these data demonstrate the persistence of this compound in the environment. Our data suggest that dieldrin is still being washed into the river from croplands. Even after surface transport ceases, the long half-life of this chemical under certain environmental conditions indicates that it will be present in the river for some years. Nash and Woolson (*7*) reported that dieldrin in soils had a half-life of 8–10 years. In certain watersheds, dieldrin half-life was 4–9 years (*8*). Differences in analytical techniques used in the authors' two studies could have resulted in an underestimate of the rate of decrease from 1971 to 1978 because the later techniques used were presumably more accurate; however, considerable dieldrin was obviously still present in the river and in channel catfish in 1978.

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DDT and BHC Residues in Some Body Tissues of Goats, Buffalo, and Chickens, Lucknow, India

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ABSTRACT

Muscle, liver, brain, and abdominal body fat samples of goats, buffalo, and chickens, all common meat sources in India, were analyzed by gas-liquid chromatography (GLC) for residues of DDT and benzene hexachloride (BHC). A few samples of goat and buffalo bone marrow were also included. Relatively high residue levels were found in body fat and bone marrow compared with other tissues. DDT and BHC residue levels were highest in chicken body fat, averaging 4.157 ppm ΣDDT and 3.879 ppm BHC. DDT content was much higher in goat and buffalo bone marrow than in the corresponding body fat. DDT levels in brain samples were highest (0.138 ppm) in buffalo. p,p'-TDE levels were higher than p,p'-DDE levels in buffalo; overall DDT levels were lowest in goats. BHC residues were generally low in buffalo; α-BHC accounted for most BHC residues in brain tissues. Greater accumulations of DDT and BHC were found in leg muscles than in breast muscles of chickens.

Introduction

Pesticide residues in animals and poultry killed to meet human food needs are an important source of human pesticide burdens. Pesticide residues in human foods, especially meat products, have been sufficiently documented in many countries (*2, 4, 6, 8, 10*). About half the observed pesticide residues in human diets are of animal origin (*5, 13*). High levels of pesticide residues have been detected in the meat or in food cooked in animal fat (*15*) and about 35%-40% of the ΣDDT intake by humans has been through meat, fish, and poultry (*7*). Body fat of people abstaining from eating meat contained about half as much ΣDDT as fat from people in the general population (*9*).

In a study conducted in India, four of 11 meat samples contained pesticide residues (*1*). However, information available on residues in India is scanty, although DDT and BHC are still used in large quantities. Thus, data on DDT and BHC residues in the tissues of goats, buffalo, and chickens, the common meat sources in India, are presented in this communication.

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Materials and Methods

High-purity analytical reagent grade chemicals and solvents were used. Glassware was rinsed with acetone before use.

COLLECTION OF SAMPLES

Generally, breast muscle, liver, whole brain, and abdominal fat samples of goats, buffalo, and chickens were collected from slaughterhouses situated in and around the city of Lucknow. That city is the capital of the largest state, Uttar Pradesh, where 14% of the total livestock population of India is raised. A few samples of goat and buffalo bone marrow were also collected. Collected samples were placed in aluminum foil and frozen until analysis. Whole brain was mixed thoroughly before being weighed for extraction. Analyses were performed within one week after collection of samples.

EXTRACTION AND CLEANUP

Homogenization of biological tissues in the presence of concentrated formic acid disrupts cell structure for efficient extraction of organochlorine pesticide residues in a suitable organic solvent (*3*). This technique is particularly convenient when a large number of biological samples must be analyzed.

Finely minced 2-g samples of muscle, brain, and liver tissues were homogenized thoroughly with 7 ml formic acid and transferred to 50-ml conical flasks. The homogenizing tube and pestle were washed twice with 5 ml portions of *n*-hexane which were then added to the conical flask. For body fat and bone marrow samples, 1 g of each was homogenized with 5 ml formic acid and 5 ml *n*-hexane and transferred to a conical flask. Again, the homogenizing tube and pestle were washed twice with 5 ml portions of the solvent which were added to the conical flask. The contents were shaken in a 40°C shaker water bath for 1 hr. The solvent phase was withdrawn after centrifugation. The residue material was extracted again with 5 ml solvent, and the solvent extracts were combined. Fat in the extracts of body fat, bone marrow, and brain samples was removed by acetonitrile partitioning (*11*), and pesticide residues

were re-extracted in *n*-hexane solvent. The solvent phase was isolated and washed twice with glass-distilled water. Finally, the solvent phase was dried by passing it through an anhydrous sodium sulfate column into a round-bottom flask. The column was washed with 10 ml solvent, the eluate was collected in the round-bottom flask, and the solvent phase was evaporated to dryness. The residue was then dissolved in 5 ml *n*-hexane and the solvent layer (2 ml) was mixed with 2 ml concentrated sulfuric acid. The solvent phase was recovered after centrifugation at 3000 rpm for 3 minutes and was transferred to clean glass-stoppered vials. Aliquots were passed through a silica gel column to check for PCB contamination (*12*). Samples were analyzed by gas-liquid chromatography (GLC) with the following instrument parameters and operating conditions:

Chromatograph	Varian Aerograph, Series 2400
Detector	H electron-capture
Column	glass spiral, 6 ft long by ⅛-in ID, packed with 80–100-mesh Gas-Chrom Q coated with a mixture of 1.5% OV-17 and 1.95% OV-210 by weight
Temperatures, °C	injector 200 detector 200 column 180
Carrier gas	IOLAR-I grade nitrogen purified by being passed through silica gel and a molecular sieve to remove moisture and oxygen, respectively, pressure, 65 psi, flowing at 40 ml/min

Residue peaks were confirmed by thin-layer chromatography (TLC), using reference standards obtained from PolyScience Corp., Niles, Illinois. Recoveries of isomers and metabolites of DDT and BHC ranged from 70% to 89% from the fortified samples of liver, brain, muscles, and body fat. Sensitivity of the method was 0.001 ppm for isomers of BHC, aldrin, and *p,p'*-DDE, and 0.002 ppm for *p,p'*-TDE and *p,p'*-DDT.

Results and Discussion

Widespread application of pesticides and spillage during their transportation or storage are the main sources of environmental contamination. Domestic animals and poultry have little chance for contact with industrial chemicals. However, their feed has been found to be a major source of DDT and BHC (*14*), and domestic food animals and poultry are a major source of pesticide contamination of the human body.

DDT and BHC residues found in goats, buffalo, and chickens are presented in Tables 1, 2, and 3, respectively. Table 4 shows the relative accumulation of pesticide residues in chicken leg and breast muscles. ΣBHC, lindane (γ-BHC), *p,p'*-DDE, *p,p'*-TDE, *o,p'*-DDT, and *p,p'*-DDT were determined in the present study. Results are expressed on a whole-tissue, wet-weight basis and are not corrected for recovery.

GOATS

All goat tissues contained DDT residues except *o,p'*-DDT which was not detected in bone marrow, body fat, or liver tissues. Average levels of ΣDDT in specific tissues were 0.577 ppm in bone marrow, 0.193 ppm in body fat, 0.053 ppm in liver, 0.019 ppm in brain, and 0.020 ppm in muscle. Generally, among DDT residues, *p,p'*-DDE was found in the greatest quantity. Average BHC and lindane levels were 0.536 ppm and 0.134 ppm in body fat and 0.203 ppm and 0.063 ppm in bone marrow samples, respectively. BHC residue levels were lowest in muscle tissue, but higher in brain than in liver tissues.

BUFFALO

DDT residues were detected generally in all buffalo tissues. *o,p'*-DDT was detected only in muscle tissues. Of the DDT residues, *p,p'*-TDE residues were highest and were detected in all body tissues.

The average levels of ΣDDT in specific tissues were: 3.009 ppm in bone marrow, 1.043 ppm in body fat,

TABLE 1. *Residue levels of BHC and DDT in some body tissues of goats, Lucknow, India*

	Residues, ppm Wet Weight						
Tissue	Lindane	BHC	*p,p'*-DDE	*p,p'*-TDE	*o,p'* DDT	*p,p'*-DDT	ΣDDT
Muscle (24) Range	0.003–0.007	0.010–0.034	0.001–0.003	0.002–0.005	ND–0.011	0.002–0.039	0.008–0.045
Mean ± SE	0.005 ± 0.001	0.018 ± 0.002	0.002 ± 0.001	0.002 ± 0.001	0.006 ± 0.001	0.008 ± 0.001	0.020 ± 0.003
Tissues with residues	(24)	(24)	(24)	(24)	(22)	(24)	(24)
Brain (14) Range	0.008–0.018	0.033–0.115	0.002–0.008	0.003–0.013	ND–0.003	ND–0.015	0.013–0.027
Mean ± SE	0.010 ± 0.001	0.068 ± 0.007	0.004 ± 0.001	0.005 ± 0.001	0.001 ± 0.001	0.007 ± 0.001	0.019 ± 0.001
Tissues with residues	(14)	(14)	(14)	(14)	(3)	(13)	(14)
Liver (18) Range	0.006–0.014	0.020–0.067	0.002–0.115	0.004–0.039	0.003	ND–0.015	0.009–0.190
Mean ± SE	0.009 ± 0.001	0.032 ± 0.002	0.028 ± 0.001	0.013 ± 0.002	—	0.007 ± 0.001	0.053 ± 0.011
Tissues with residues	(18)	(18)	(18)	(18)	(1)	(17)	(18)
Body fat (16) Range	0.054–0.347	0.146–1.522	0.017–0.467	0.006–0.420	ND	0.006–0.097	0.039–1.014
Mean ± SE	0.134 ± 0.024	0.536 ± 0.100	0.093 ± 0.029	0.056 ± 0.026	ND	0.027 ± 0.006	0.193 ± 0.061
Tissues with residues	(16)	(16)	(16)	(16)		(16)	(16)
Bone marrow (8) Range	0.036–0.123	0.114–0.470	0.093–1.806	0.025–0.294	ND	0.023–0.476	0.169–2.816
Mean ± SE	0.063 ± 0.013	0.203 ± 0.044	0.358 ± 0.207	0.065 ± 0.032		0.106 ± 0.055	0.577 ± 0.320
Tissues with residues	(8)	(8)	(8)	(8)		(8)	(8)

NOTE: Number in first column indicates number of samples analyzed. SE = standard error, ND = not detected

TABLE 2. *Residue levels of BHC and DDT in some body tissues of buffalo, Lucknow, India*

Tissue	Residues, ppm Wet Weight						
	Lindane	BHC	*p,p'*-DDE	*p,p'*-TDE	*o,p'*-DDT	*p,p'*-DDT	ΣDDT
Muscle (22) Range	0.001–0.015	0.006–0.029	0.001–0.011	0.002–0.045	0.002–0.008	0.002–0.0[illegible]	0.011–0.081
Mean ± SE	0.004 ± 0.001	0.012 ± 0.002	0.005 ± 0.001	0.011 ± 0.001	0.003 ± 0.001	0.006 ± 0.001	0.028 ± 0.006
Tissues with residues	(22)	(22)	(22)	(22)	(22)	(22)	(22)
Brain (16) Range	0.007–0.016	0.024–0.117	0.009–0.071	0.009–0.054	ND	0.007–0.078	0.027–0.211
Mean ± SE	0.012 ± 0.001	0.076 ± 0.006	0.047 ± 0.004	0.038 ± 0.003		0.044 ± 0.004	0.138 ± 0.012
Tissues with residues	(16)	(16)	(16)	(16)		(16)	(16)
Liver (17) Range	0.005–0.022	0.020–0.090	0.011–0.478	0.024–0.285	ND	0.002–0.107	0.043–0.635
Mean ± SE	0.012 ± 0.001	0.038 ± 0.004	0.074 ± 0.027	0.093 ± 0.019		0.018 ± 0.007	0.205 ± 0.045
Tissues with residues	(17)	(17)	(17)	(17)		(17)	(17)
Body fat (17) Range	0.011–0.209	0.039–0.485	0.036–0.587	0.049–1.414	ND	0.021–0.920	0.116–3.143
Mean ± SE	0.058 ± 0.011	0.165 ± 0.027	0.284 ± 0.041	0.490 ± 0.086		0.183 ± 0.055	1.043 ± 0.181
Tissues with residues	(17)	(17)	(17)	(17)		(17)	(17)
Bone marrow (5) Range	0.041–0.198	0.123–0.366	0.135–1.544	0.165–2.605	ND	0.019–1.718	0.337–5.038
Mean ± SE	0.121 ± 0.033	0.252 ± 0.52	0.773 ± 0.246	1.289 ± 0.446		0.720 ± 0.351	3.069 ± 0.985
Tissues with residues	(5)	(5)	(5)	(5)		(5)	(5)

NOTE See note, Table 1

TABLE 3. *Residue levels of BHC and DDT in some body tissues of chickens, Lucknow, India*

Tissue	Residues, ppm Wet Weight						
	Lindane	BHC	*p,p'*-DDE	*p,p'*-TDE	*o,p'*-DDT	*p,p'*-DDT	ΣDDT
Muscle (10) Range	0.002–0.037	0.014–0.243	0.007–0.251	0.002–0.021		0.002–0.107	0.010–0.366
Mean ± SE	0.017 ± 0.003	0.109 ± 0.024	0.090 ± 0.024	0.007 ± 0.002	ND	0.030 ± 0.010	0.138 ± 0.030
Tissues with residues	(10)	(10)	(10)	(10)		(10)	(10)
Brain (19) Range	0.012–0.051	0.108–0.230	0.009–0.052	0.002–0.505	ND–0.024	ND–0.022	0.022–0.121
Mean ± SE	0.027 ± 0.002	0.162 ± 0.007	0.022 ± 0.003	0.038 ± 0.002	0.005 ± 0.001	0.011 ± 0.002	0.082 ± 0.006
Tissues with residues	(19)	(19)	(19)	(19)	(10)	(16)	(19)
Liver (20) Range	0.004–0.091	0.040–0.445	0.039–0.537	0.047–0.447	ND–0.130	ND–0.130	0.134–1.447
Mean ± SE	0.049 ± 0.004	0.195 ± 0.018	0.253 ± 0.025	0.170 ± 0.023	0.040 ± 0.013	0.025 ± 0.006	0.535 ± 0.068
Tissues with residues	(20)	(20)	(20)	(20)	(18)	(18)	(20)
Body fat (22) Range	0.284–4.150	0.819–14.104	0.095–10.939	0.043–6.372	ND	ND–3.200	0.480–20.832
Mean ± SE	1.217 ± 0.188	3.879 ± 0.580	2.377 ± 0.586	0.778 ± 0.306		0.644 ± 0.301	4.157 ± 1.027
Tissues with residues	(22)	(22)	(22)	(22)		(20)	(22)

NOTE See note, Table 1

TABLE 4. *Relative accumulation of BHC and DDT residues in chicken leg and breast muscle, Lucknow, India*

Sample	Residues, ppm Wet Weight					
	Lindane	BHC	*p,p'*-DDE	*p,p'*-TDE	*p,p'*-DDT	ΣDDT
Chicken A Leg	0.036	0.243	0.251	0.016	0.068	0.366
Breast	0.018	0.132	0.117	0.005	0.019	0.154
Chicken B Leg	0.037	0.216	0.170	0.021	0.107	0.326
Breast	0.019	0.177	0.062	0.004	0.011	0.084
Chicken C Leg	0.007	0.034	0.063	0.008	0.031	0.110
Breast	0.002	0.014	0.018	0.003	0.008	0.031

0.205 ppm in liver, 0.138 ppm in brain, and 0.028 ppm in muscle. BHC levels were 0.252, 0.165, 0.038, 0.076, and 0.012 ppm in the respective tissues. Relatively high levels of lindane which accounted for about half of the total BHC residues were detected in bone marrow samples. Mean values of lindane were comparable in liver and brain samples.

CHICKENS

DDT residues as high as 20.832 ppm DDT, 10.939 ppm *p,p'*-DDE, 6.372 ppm *p,p'*-TDE, and 3.2 ppm *p,p'*-DDT were detected in chicken body fat. ΣDDT averages in specific tissues were 4.157 ppm in body fat, 0.535 ppm in liver, 0.138 ppm in muscle, and 0.082 ppm in brain. All chicken body tissues contained *p,p'*-DDE and *p,p'*-TDE residues. *p,p'*-DDE accounted for most of the DDT residues except in brain samples, where *p,p'*-TDE was highest. *o,p'*-DDT was not detected in muscle and body fat samples.

BHC residues were also detected in all chicken tissues. Average levels were comparable to ΣDDT levels in the

body fat, brain, and muscles. In chicken body fat samples, total BHC varied from 0.819 to 14.104 ppm and lindane varied from 0.284 to 4.15 ppm. The accumulation of organochlorine pesticide residues (Table 4) was always higher in leg muscle than in breast muscle.

Conclusion

Accumulation of persistent organochlorine pesticide residues in the body and their *in vitro* biotransformation varies from species to species. Various environmental factors and dietary habits of individual species are also involved in bioaccumulation and biodegradation of the residues. Buffalo brain contained highest DDT residues in brain, although overall DDT contamination was highest in chickens. DDT concentration was always higher in goat and buffalo bone marrow than in body fat. In general, *p,p'*-DDE was the major metabolite found in biological tissues, but *p,p'*-TDE was the major metabolite in buffalo body tissues and accounted for nearly 40%–50% of ΣDDT. The levels of *p,p'*-TDE were also higher than *p,p'*-DDE levels in chicken brain tissue. The accumulation of residues was always higher in leg muscle than in the breast muscle of chickens. DDT levels were found in the following order of increasing concentration: goat<buffalo<chicken. Total BHC levels were also higher in chicken than in the other food animals, and α-BHC accounted for the major amount of total BHC in their brain tissues.

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APPENDIX

Chemical Names of Compounds Discussed in This Issue

ALDRIN	Hexachlorohexahydro-*endo, exo*-dimethanonaphthalene 95% and related compounds 5%
AROCLOR 1242	PCB, approximately 42% chlorine
AROCLOR 1246	PCB, approximately 46% chlorine
AROCLOR 1260	PCB, approximately 60% chlorine
BHC (Benzene Hexachloride)	1,2,3,4,5,6-Hexachlorocyclohexane (mixture of isomers)
CHLORDANE	Technical 60% octachloro-4,7-methanotetrahydroindane and 40% related compounds
DDE	Dichlorodiphenyldichloroethylene (degradation product of DDT)
DDMU	1-Chloro-2,2-bis(*p*-chlorophenyl) ethylene
DDT	Dichloro diphenyl trichloroethane. Principal isomer present (*p,p'*-DDT not less than 70%) 1,1,1-trichloro-2,2-bis(*p*-chlorophenyl)ethane
DICOFOL	1,1-Bis(chlorophenyl)-2,2,2-trichloroethanol
DIELDRIN	Hexachloroepoxyoctahydro-*endo,exo*-dimethanonaphthalene 85% and related compounds 15%
ENDRIN	Hexachloroepoxyoctahydro-*endo,endo*-dimethanonaphthalene
HCB	Hexachlorobenzene
HEPTACHLOR EPOXIDE	1,4,5,6,7,8,8-Heptachloro-2,3-epoxy-3a,4,7,7a-tetrahydro-4,7-methanoindan
LINDANE	*Gamma* isomer of benzene hexachloride (BHC)
MIREX	Dodecachlorooctahydro-1,3,4-metheno-1*H*-cyclobuta[cd]pentalene
NONACHLOR	1,2,3,4,5,6,7,8,8-Nonachloro-3a,4,7,7a-tetrahydro-4,7-methanoindan
OXYCHLORDANE	1-*exo*-2-*endo*-4,5,6,7,8,8a-Octachloro2,3-*exo*-epoxy-2,3,3a,4,7,7a-hexahydro-4,7-methanoindene
PBBs (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
PCSs (Polychlorinated Styrenes)	Mixtures of chlorinated styrenes having various percentages of chlorine
TDE	Dichloro diphenyl dichloroethane (1,1-dichloro-2,2-bis(*p*-chlorophenyl)ethane, principal component)
TOXAPHENE	Technical chlorinated camphene (67–69% chlorine)

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CONTENTS

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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.

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FISH, WILDLIFE, AND ESTUARIES

Factors Influencing Dieldrin and DDT Residues in Carp from the Des Moines River, Iowa, 1977–80 [1]

Wayne H. Hubert and Edward D. Ricci [2]

ABSTRACT

Concentrations of dieldrin and DDT in muscle tissue and fat of carp, Cyprinus carpio, *from the Des Moines River, Iowa, differed significantly with month of collection, fish age, and sampling location. Pesticide levels expressed on the basis of wet weight of flesh often differed from those expressed on a fat basis. Fish from reservoirs tended to have higher levels of dieldrin, but not of DDT, than did fish from riverine locations.*

Introduction

Interpretation of data from organochlorine pesticide residue monitoring programs for freshwater fish is difficult because numerous factors influence sample variability. Identification of the factors that contribute to sample variability would improve the reliability of monitoring programs. Authors assessed the influence of selected variables in concentrations of aldrin and DDT in carp *(Cyprinus carpio)* from a midwest river, the Des Moines.

Aldrin and DDT were extensively used to control insects on midwestern cropland for many years. About 3 million kg of aldrin was applied to Iowa cropland in the mid-1960's to control corn rootworm and cutworm (*16*). The U.S. Environmental Protection Agency canceled registration of aldrin in 1975, and its use was discontinued in 1978. The pesticide DDT was used primarily to control European cornborer, Dutch elm disease, and mosquitoes during the 1950's and 1960's; it use was banned in 1970.

Both aldrin and DDT convert to persistent forms in nature, dieldrin and DDE or TDE, respectively. These compounds have long half-lives under field conditions—8–10 years for dieldrin and 10–20 years for DDE (*13, 15*)—and tend to be strongly adsorbed to soil particles (*7, 14*). Because of these factors and the widespread use of these compounds on cropland, midwestern waters continue to be contaminated through soil erosion. Chlorinated hydrocarbons, being hydrophobic, lipophilic chemicals, are absorbed from water into the fat of fish.

The Des Moines River is the largest stream within Iowa. More than 80% of its drainage is cultivated, and the major source of contamination of the river is nonpoint agricultural runoff (*9*). Two reservoirs have been constructed on the river for flood control, water quality control, and recreational purposes. Red Rock Dam, completed in 1969, impounds 4,200 ha of water at normal pool level. Saylorville Dam, completed in 1977, impounds 2,200 ha at normal pool level. A pesticide monitoring program was established on the Des Moines River in 1977, and several fish species were assessed for organochlorine pesticide residues from 1977 to 1979 (*2, 3, 12*). The cost of monitoring several species led to consideration of limiting analysis to a single sentinel species. Carp were selected because they are abundant and easy to collect in both the river and reservoirs. The objectives of the present paper are to compare wet weight of flesh- and fat-based units of measure for dieldrin and ΣDDT residues in carp; to assess the influence of sampling month, fish age, and sampling location in the river on residue concentrations; and to evaluate trends in dieldrin and ΣDDT residue concentrations in Des Moines River carp from 1977 to 1980.

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[2] Iowa Cooperative Fishery Research Unit, Iowa State University, Ames, IA 50011. The Unit is jointly supported by Iowa State University, the Iowa State Conservation Commission, and the Fish and Wildlife Service, U.S. Department of the Interior.

Methods

Sampling stations were established at two impounded and two riverine locations on the Des Moines River (Figure 1): Red Rock Reservoir; the river 80 km upstream from Red Rock Reservoir at Des Moines; Saylorville Reservoir; and the river 80 km upstream from Saylorville Dam at Boone. Carp were collected from each location by electrofishing and hoop netting. Five samples were made up from each sampling location in June and in September. Each sample consisted of equal weights of lateral muscle from 10 fish of the same age. Fish ages were determined by standard scale-reading techniques (*11*); only 2- to 4-year-old fish were used. Fat content of individual samples was determined by the modified Babcock method (*1*).

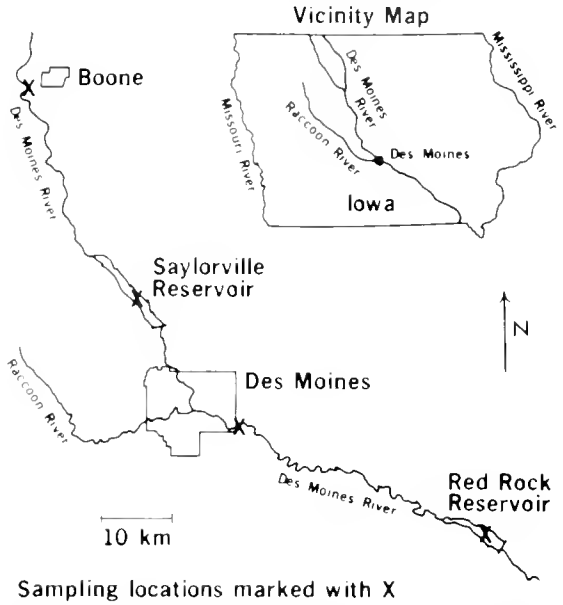

FIGURE 1. *Sampling stations for carp on the Des Moines River, Iowa.*

Lateral muscle tissue samples were analyzed for dieldrin, *p,p'*-DDT, *p,p'*-TDE, and *p,p'*-DDE by the methods described in the *Pesticide Analytical Manual* (*8*). Tissue samples were ground in a 35% water–acetonitrile solution with a high-speed blender for 10 minutes. The sample was filtered, the filtrate was transferred to a 1-liter separatory funnel, 100 ml petroleum ether was added, and the mixture was shaken briefly. Then, 600 ml distilled water and 10 ml saturated saline solution were added and mixed by tumbling for 1 minute. After the layers had separated, the aqueous fraction was discarded. The solvent layer was washed with distilled water and filtered through a 50-cm anhydrous sodium sulfate column. The sample volume was recorded, and the extract was subjected to the standard Florisil clean-up procedure (*8*).

A Tracor 550 gas chromatograph equipped with a ^{63}Ni electron-capture detector was used for gas chromatographic analysis. A 4% SE-30/6% SP-2401 column was used for separating and quantifying the pesticides. Detected values were corrected for 80% extraction efficiency.

Statistical procedures included the Student's *t*-test and the Pearson Product Movement Correlation Coefficient. All decisions to reject null hypotheses were at $P < 0.10$, because sources of variability were being sought.

Results

FAT IN CARP MUSCLE

Fat content of carp muscle ranged from 0.8% to 3.3% (Table 1). Between June and September, fat content of fish decreased significantly at the two riverine sites, Des Moines ($0.10 > P > 0.05$) and Boone ($0.01 > P > 0.001$), increased significantly in Saylorville Reservoir fish ($0.3 > P > 0.01$), and did not change significantly in Red Rock Reservoir fish. Fat content differed significantly between fish samples from Saylorville Reservoir and those from the river at Boone in both June and September. Fat levels were higher in river fish in June ($0.02 > P > 0.01$) and in reservoir fish in September ($0.01 > P > 0.001$). These demonstrated variations in fat content indicated the need to consider this variable in the pesticide residue analyses.

TABLE 1. *Fat content of carp muscle used for pesticide analysis from the Des Moines River, Iowa, 1980*

Month of Collection	Carp Age, Years	Percent Fat			
		Red Rock Reservoir	River at Des Moines	Saylorville Reservoir	River at Boone
June	3	1.5	1.8	1.4	1.8
		1.8	1.9	1.6	1.9
		2.3	2.2	1.6	2.3
	4	1.7	2.2	1.4	1.8
		1.9	3.3	—	2.4
(Mean)		(1.8)	(2.3)	(1.6)	(2.0)
Sept.	2	1.4	1.6	1.8	0.8
		1.1	2.0	2.4	1.1
	3	1.9	1.3	1.7	1.2
		2.6	1.4	2.5	1.6
	4	1.7	1.8	2.2	1.6
(Mean)		(1.7)	(1.6)	(2.1)	(1.3)

DIELDRIN

In 1980, concentrations of dieldrin ranged from 10 to 128 μg/kg of flesh and from 630 to 5,790 μg/kg of fat (Table 2). Mean levels of dieldrin in flesh and in fat declined between June and September at the four sampling locations. The differences in mean levels were statistically significant at Red Rock Reservoir ($0.10 > P > 0.05$), the river at Des Moines ($0.10 > P > 0.05$),

TABLE 2. *Dieldrin residues in muscle of carp from the Des Moines River, Iowa, 1980*

Month of Collection	Carp Age, Years	Residues, μg/kg							
		Red Rock Reservoir		River at Des Moines		Saylorville Reservoir		River at Boone	
		Flesh [1]	Fat	Flesh [1]	Fat	Flesh [1]	Fat	Flesh [1]	Fat
June	3	83	4,580	30	1,360	33	2,850	41	2,170
		73	3,150	55	3,060	51	2,030	41	1,790
		63	4,170	33	1,710	54	3,840	50	2,780
		—	—	—	—	56	3,520	—	—
	4	75	4,410	55	3,860	34	2,410	48	2,760
		110	5,790	128	2,500	—	—	66	2,640
(Mean)		(81)	(4,420)	(60)	(2,500)	(46)	(2,930)	(49)	(2,430)
Sept.	2	34	3,070	11	630	29	1,600	16	2,030
		53	3,750	15	750	43	1,770	21	1,930
	3	58	3,090	10	770	36	1,450	15	1,250
		59	2,210	41	2,950	45	2,650	24	1,480
	4	84	4,930	23	1,250	30	1,360	36	2,270
(Mean)		(58)	(3,410)	(20)	(1,270)	(37)	(1,770)	(22)	(1,790)

[1] Wet-weight basis.

and the river at Boone ($0.01 > P > 0.001$) when expressed on a wet-weight flesh basis. On a fat basis, the differences were statistically significant in the river at Des Moines ($0.10 > P > 0.05$), the Saylorville Reservoir ($0.05 > P > 0.02$), and the river at Boone ($0.05 > P > 0.02$).

Statistically significant variation in mean dieldrin level related to fish age was noted in June ($0.10 > P > 0.05$) but not in September, when wet-weight flesh was used as the analytical basis. No statistically significant variation due to age was observed in either June or September on a fat basis.

Differences in mean levels of dieldrin in carp samples occurred between some sampling locations. In June, no significant differences occurred between the reservoirs and their associated riverine stations when concentrations were expressed on a flesh basis, but a significantly higher level was observed in Red Rock Reservoir fish compared with fish from the river at Des Moines ($0.02 > P > 0.01$) on a fat basis. In September, dieldrin concentrations in fish were significantly higher at both Red Rock and Saylorville reservoirs than at the upstream locations ($0.01 > P > 0.001$ and $0.05 > P > 0.02$, respectively) on a flesh basis, but a significant difference was observed only between Red Rock Reservoir and the river at Des Moines on a fat basis.

Levels of dieldrin were significantly higher in samples from Red Rock Reservoir than in those from Saylorville Reservoir in June ($0.01 > P > 0.001$ for flesh, $0.05 > P >> 0.02$ for fat) and in September ($0.05 > P > 0.02$ for flesh, $0.02 > P > 0.01$ for fat). No significant differences were observed between riverine locations.

Trends in mean concentrations of dieldrin in carp muscle at the four sampling locations from 1977 to 1980 are illustrated in Figure 2. The 1977–79 samples were collected and analyzed in the same manner as described for 1980 samples. Size ranges of the fish indicate that the 1977-79 samples were predominantly composed of 2- and 3-year-old fish. Fish from the impounded sites tended to have higher levels of dieldrin than did those from the riverine sites (Figure 2). Substantial variation in dieldrin levels between sampling periods occurred at all locations, but the magnitude of the fluctuations was greatest in the reservoirs.

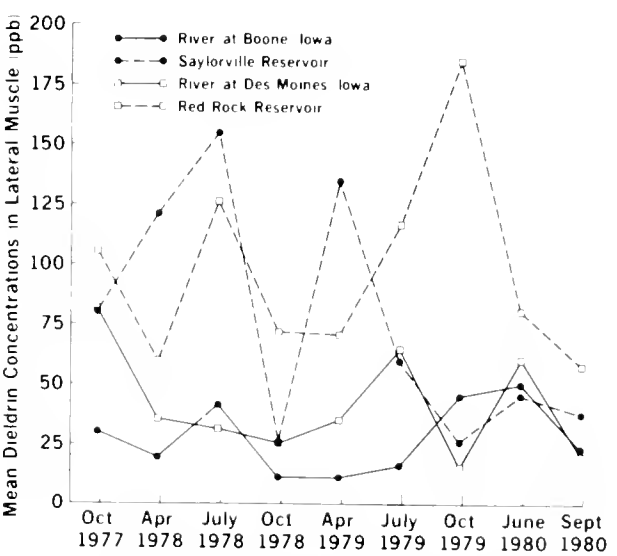

FIGURE 2. *Variation in dieldrin residues in flesh of carp from four sampling locations on the Des Moines River, Iowa, 1977–80. Data for 1977–79 taken from Baumann et al. (2, 3).*

TOTAL DDT

The concentration of ΣDDT (DDT, TDE, and DDE) in carp muscle ranged from 18 to 191 μg/kg of flesh and from 1,090 to 9,910 μg/kg of fat in 1980 samples (Table 3). In June, ΣDDT was composed of 54.8% DDE, 24.6% TDE, and 20.6% DDT in the average sample. Proportions were similar in September—53.3% DDE, 27.9% TDE, and 18.8% DDT.

ΣDDT levels in fish samples declined from June to September. The difference was statistically significant on a flesh basis at all sampling locations: Red Rock Reservoir ($0.02 > P > 0.01$), the river at Des Moines ($0.05 > P > 0.02$), Saylorville Reservoir ($0.10 > P > 0.05$) and the river at Boone ($0.01 > P > 0.001$). The concentration of ΣDDT in the fat was significantly lower in September only in fish from the reservoirs: Red Rock ($0.02 > P > 0.01$) and Saylorville ($0.05 > P > 0.02$).

The mean level of ΣDDT was significantly higher in 4-year-old fish than in 3-year-old fish on both flesh ($0.02 > P > 0.01$) and fat ($0.10 > P > 0.05$) bases in June. No differences among samples of 2-, 3-, and 4-year-old fish were observed in September.

Mean ΣDDT in carp varied significantly between some sampling locations. Concentrations were significantly higher in samples from Saylorville Reservoir than in samples from the upstream site near Boone in both June ($0.10 > P > 0.05$) and September ($P > 0.001$) on a flesh basis, but only in June on a fat basis ($0.02 > P > 0.01$). In September, mean level of ΣDDT was significantly higher in fish from the river at Des Moines than in fish from Saylorville Reservoir on both flesh ($0.10 > P > 0.05$) and fat ($0.01 > P > 0.001$) bases. This was the only comparison made in which the mean level of pesticide residues was higher in samples from a riverine location than in samples from the associated downstream impoundment.

Comparison of samples from the two reservoirs showed no significant differences in mean ΣDDT. However, statistically significant differences in mean ΣDDT occurred between fish from the two riverine sites in both June and September. Mean levels of ΣDDT were significantly higher in both flesh ($0.02 > P > 0.01$ in June, $0.01 > P > 0.001$ in September) and fat ($0.01 > P > 0.001$ in June, $0.01 > P > 0.001$ in September) of fish sampled near Des Moines than in those collected at Boone.

Mean ΣDDT concentration in carp samples declined substantially between October 1977 and July 1978 at the two riverine locations (Figure 3). ΣDDT levels in

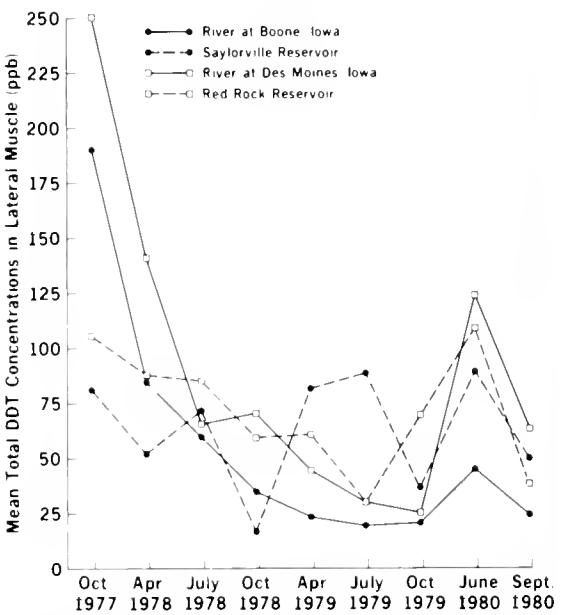

FIGURE 3. *Variation in total DDT residues in flesh of carp from four sampling locations on the Des Moines River, Iowa, 1977–80. Data for 1977–79 taken from Baumann et al. (2, 3).*

TABLE 3. *Total DDT (DDT, TDE, and DDE) residues in muscles of carp from the Des Moines River, Iowa, 1980*

Month of Collection	Carp Age, Years	Residues, μg/kg							
		Red Rock Reservoir		River at Des Moines		Saylorville Reservoir		River at Boone	
		Flesh	Fat	Flesh	Fat	Flesh	Fat	Flesh	Fat
June	3	55	4,240	83	3,980	96	4,720	35	2,890
		126	5,490	88	4,860	74	2,820	50	2,170
		76	2,670	88	4,340	46	5,270	55	1,560
		—	—	—	—	85	6,020	—	—
	4	149	7,650	191	4,810	185	9,910	28	1,830
		130	7,830	159	8,690	—	—	55	1,290
(Mean)		(107)	(5,780)	(122)	(5,340)	(97)	(5,760)	(45)	(1,950)
Sept.	2	31	2,230	51	3,200	40	2,920	28	2,500
		20	1,820	79	3,940	53	1,670	21	2,660
	3	41	2,170	43	3,270	53	2,150	23	1,880
		44	1,680	50	3,570	54	3,090	18	1,090
	4	56	3,310	91	5,070	43	1,930	29	1,800
(Mean)		(38)	(2,240)	(63)	(3,810)	(49)	(2,350)	(24)	(1,990)

carp have fluctuated substantially at all locations since 1978, with no indication of significant differences in trends between impounded and riverine locations.

Discussion

The lipophilic nature of organochlorine pesticide residues results in significant associations between fat content and pesticide levels in fish (*4, 5, 12*). It has been suggested that the variance in organochlorine pesticide residue samples may be reduced by normalizing on a fat basis. Statistically significant variation in fat content of Des Moines River carp was observed between sampling months, ages of fish, and sampling location, indicating a need to consider the fat content in data analyses. However, normalization on a fat basis in Des Moines River carp samples did not reduce the variability of the data. Comparisons of dieldrin and ΣDDT concentrations between sampling months, fish ages, and sampling locations produced results that were different on fat and flesh bases in several instances.

The mean levels of both dieldrin and ΣDDT in Des Moines River carp varied between sampling periods. A decline was observed between June and September 1980. Concentrations of dieldrin and ΣDDT in carp from the Des Moines River fluctuated dramatically between sampling periods from 1977 to 1979, but a spring-to-autumn decline did not consistently occur. During 1971–73, before the use of dieldrin was discontinued, seasonal trends in dieldrin concentrations in Des Moines River channel catfish (*Ictalurus punctatus*) were related to corn planting and aldrin application (*10*). Present patterns are more complicated and probably relate to several factors, including water temperature (and, consequently, metabolic rates of fish) before sampling (*6*), fat content of the fish (*4, 5*), extent of pesticide contamination in bottom sediments and on agricultural land within the watershed (*17*), tillage practices by farmers, and precipitation before sampling. The results indicate that evaluation of variations in organochlorine pesticide residues relative to sampling locations or time should be made on fish of the same age. The need to consider fish age was shown in June when levels of dieldrin and ΣDDT were significantly higher in 4-year-old than in 3-year-old fish. Similar variation relative to age has been described in channel catfish from the Des Moines River (*4, 5*).

The present study showed that impoundments within a river system may affect the data developed in a monitoring project. Dieldrin in carp muscle tended to be higher in fish from reservoirs than from upstream riverine sites, but the same trend did not hold consistently for ΣDDT. Whole-body analyses of carp in 1977 and 1978 showed no difference in either dieldrin or ΣDDT levels between Saylorville Reservoir and either upstream or downstream locations (*12*). Differences in dieldrin and ΣDDT occurrence relative to the impoundments indicated that the dynamics of the two types of pesticide residues are different within reservoirs. Differences also were noted between riverine and impounded locations.

Concentrations of dieldrin and ΣDDT in 1980 carp samples from the Des Moines River were below Food and Drug Administration, U.S. Department of Health and Human Services, standards of 300 ppb dieldrin and 5 ppm DDT for food fish. Dieldrin in some samples of channel catfish flesh from Des Moines River impoundments in 1977 (*6*) and 1979 (*3*) exceeded those standards, thereby indicating the need for monitoring as well as the need to define the relation between organochlorine pesticide residues in sentinel species, such as carp, and other fish species.

Analysis of 1977–79 data (*2, 3*) from the Des Moines River showed a significant correlation ($r = 0.51$, $0.02 > P > 0.01$) between mean levels of dieldrin in carp and channel catfish samples taken at the same time and location, but not between concentrations in carp and those in walleye (*Stizostedion vitreum vitreum*), or largemouth bass (*Micropterus salmoides*). From 1977 to 1979, the mean dieldrin level in channel catfish exceeded that of carp by 2.2 times in samples from Red Rock Reservoir and by 3.1 times in samples from Saylorville Reservoir; however, the factor varied substantially between sampling dates. Leung (*12*) found a positive correlation ($r = 0.56$) between percentage fat of various species found in the Des Moines River and dieldrin levels in the flesh. She noted that channel catfish tended to have double the fat content and triple the dieldrin concentrations of carp, but observed no similar relations in ΣDDT concentrations. The extent of the relation between species and fat content provides some basis for extrapolating dieldrin levels observed in carp to those in channel catfish, but not for ΣDDT or for other species. The relation between dieldrin levels in carp and catfish would probably be strengthened if variables such as fish age, fat content, and capture location were controlled.

Acknowledgments

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Influence of a New Impoundment on Pesticide Concentrations in Warmwater Fish, Saylorville Reservoir, Des Moines River, Iowa, 1977–78 [1]

Siu-Yin Theresa Leung,[2] Ross V. Bulkley,[3] and John J. Richard [4]

ABSTRACT

Samples of seven species of warmwater fish were collected above, within, and below newly impounded Saylorville Reservoir, Des Moines River, Iowa, from October 1977 to October 1978. Whole-body analyses by gas chromatography were significantly higher in river carpsucker (Carpiodes *cyanazine and for the organochlorine insecticides dieldrin,* p,p'-*DDE,* p,p'-*TDE,* p,p'-*DDT, and heptachlor epoxide. Only the organochlorine insecticides were detected in fish tissue. Concentrations of dieldrin and heptachlor epoxide were significantly higher in river carpsucker* (Carpiodes carpio) *from the reservoir than in those from the river. Other species of fish showed no differences in pesticide concentration related to locality of collection.*

Introduction

The construction of a reservoir on a river increases the complexity of pesticide dynamics in the aquatic system. Impoundments for flood control, water supplies, energy development, recreation, and other purposes are becoming increasingly numerous in the United States. During 1977–78, a study was conducted on Saylorville Reservoir, a new impoundment on the Des Moines River up stream from Des Moines, Iowa, to determine the rate of pesticide deposition in the reservoir and the effect of impoundment on pesticide accumulation in different species of fish. The discussion here addresses pesticide accumulation in the fish. Elsewhere, Leung (*6*) reported on seasonal pesticide fluctuations and pesticide deposition in the reservoir.

The Des Moines River rises in the glacial moraine area of southwestern Minnesota and flows southeasterly across Iowa to join the Mississippi (Figure 1). It is the largest river in Iowa. About 79% of the watershed upstream from Des Moines is cropland, primarily corn

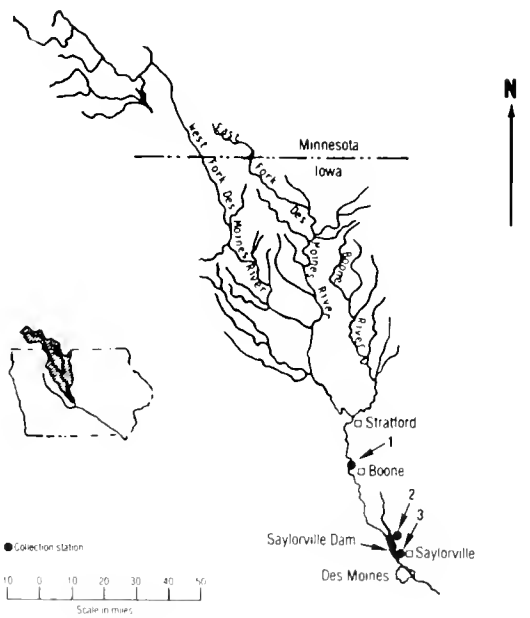

FIGURE 1. *Upper Des Moines River watershed, showing sampling sites.*

and soybeans; 6% is permanent pasture, 5% is forest, and 7% is urban (*4*). Normal annual precipitation over the drainage area ranges from 62.5 to 77.5 cm from north to south and averages 70.7 cm (*8*). Precipitation is usually heaviest in June, but heavy rainfall and cloudbursts occasionally cause high river flows in summer and early fall. The major source of contamination of the river is agricultural runoff.

Three collection stations were set up for this study: Station 1 at Boone, Iowa, is about 73 km upstream from Saylorville Dam; Station 2 is located in Saylorville Reservoir; and Station 3 is located at the town of Saylorville, about 3 km downstream from Saylorville Dam. Drainage areas at the three points, upstream to downstream, are 14,530, 15,081, and 15,128 km^2, respectively.

Gates on the Saylorville Reservoir were closed in April 1977. During the study period, the reservoir remained

[1] This study was conducted as part of Project 2225 of the Iowa Agriculture and Home Economics Experiment Station, Ames, Iowa, in cooperation with the Iowa Cooperative Fishery Research Unit, which is jointly sponsored by the Iowa State Conservation Commission, Iowa State University, and the Fish and Wildlife Service, U.S. Department of the Interior.

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within 1.2 m of conservation pool level, and average water retention time was about 40 days (*1*). Volume at conservation pool level was about 90 million m^3.

Materials and Methods

Fish samples were collected quarterly at Stations 1, 2, and 3 from October 1977 to October 1978, with gill nets, hoop nets, and electroshockers. Species analyzed for pesticide residues were gizzard shad *(Dorosoma cepedianum)*, river carpsucker *(Carpiodes carpio)*, common carp *(Cyprinus carpio)*, channel catfish *(Ictalurus punctatus)*, white crappie *(Pomoxis annularis)*, largemouth bass *(Micropterus salmoides)*, and walleye *(Stizostedion vitreum)*. Specimens were grouped by collection date, location, species, and body length. An attempt was made to collect small specimens and to avoid large, old fish of each species. Small fish were selected on the assumption that most of their life occurred after impoundment, and that they would be less likely than old fish to have migrated between sampling stations. With few exceptions, all fish selected for sampling were subadult, and many were young-of-the-year. Mean total lengths ranged from 137 mm for gizzard shad to 232 mm for walleyes (Table 1).

Fish in the same group were ground together in a hand grinder and then mixed manually in an effort to obtain a homogeneous mixture. Subsamples were then wrapped in aluminum foil and frozen until analysis. Because preliminary analyses indicated that atrazine, alachlor, cyanazine, dieldrin, *p,p'*-DDE, *p,p'*-TDE, *p,p'*-DDT, and heptachlor epoxide were present in water or fish, these substances were selected for study. Concentrations of pesticides in water are listed in Table 2.

TABLE 2. *Mean weekly dissolved pesticide concentrations (ng/liter) at each Des Moines River station where fish were collected, September 1977 to November 1978* [1]

Chemical	Station 1	Station 2	Station 3	Mean
Atrazine	225 (<10–1356)	221 (0–1167)	222 (<10–1000)	223
Alachlor	115 (0–1450)	80 (0–1125)	72 (0–725)	89
Cyanazine	71 (0–500)	90 (0–660)	111 (0–640)	91
Dieldrin	3 (0–14)	3 (<1–6)	3 (<1–6)	3
p,p'-DDE [2]	<1	<1	<1	<1

NOTE: Numbers in parentheses are ranges.
[1] Values are from Ref. 6.
[2] Mean concentration of *p,p'*-DDE on suspended sediment was 7 ng/kg (0–66) at Station 1, 4 ng/kg (0–25) at Station 2, and 6 ng/liter (0–132) at Station 3.

Authors used standard methods of tissue analysis (*7*) with slight modification. After thawing, 25–30-g samples were extracted with 200 ml of 65% acetonitrile–water for 5 minutes in a 1-liter stainless steel blender. The sample was then filtered into a 250-ml graduated

TABLE 1. *Number of fish and range in length of fish collected from the Des Moines River for pesticide residue analysis, 1977–78*

Station [1]	Date	Length, mm [2]						
		Gizzard Shad	River Carpsucker	Common Carp	Channel Catfish	White Crappie	Walleye	Largemouth Bass
1	Oct. 1977	45 (136–199)	33 (76–278)	64 (83–402)	0	0	4 (144–180)	1 (195)
	Apr. 1978	0	46 (85–328)	91 (85–130)	0	0	0	0
	Jul. 1978	0	58 (103–368)	42 (131–269)	34 (98–247)	13 (108–141)	19 (175–430)	8 (230–315)
	Oct. 1978	40 (146–205)	23 (152–400)	52 (140–272)	5 (154–413)	16 (132–170)	4 (180–279)	18 (120–348)
2	Oct. 1977	56 (104–163)	6 (131–307)	35 (103–191)	10 (310–487)	31 (75–295)	5 (160–300)	46 (95–260)
	Apr. 1978	6 (128–195)	6 (198–367)	69 (105–216)	17 (232–430)	4 (87–98)	3 (245–282)	6 (96–262)
	Jul. 1978	34 (67–212)	25 (177–381)	18 (155–241)	9 (285–457)	10 (137–305)	2 (350–351)	26 (123–387)
	Oct. 1978	63 (100–199)	27 (176–400)	39 (165–312)	8 (240–398)	7 (160–178)	0	23 (166–310)
3	Apr. 1978	0	22 (140–335)	40 (100–189)	0	46 (81–324)	0	0
	Jul. 1978	40 (56–101)	7 (140–290)	47 (135–238)	3 (220–290)	56 (112–332)	3 (202–286)	4 (246–310)
	Oct. 1978	93 (112–189)	49 (141–342)	39 (131–226)	0	34 (82–189)	0	0
	Total fish	377	302	536	86	217	40	132

[1] See Figure 1 for locations of stations.
[2] Range is in parentheses.

cylinder and transferred to a 1-liter separatory funnel; 100 ml petroleum ether, 600 ml water, and 10 ml saturated aqueous sodium chloride were added to the filtrate. The pesticides were partitioned into the organic layer by vigorous shaking for 30–60 seconds. The aqueous layer was discarded. The petroleum ether layer was washed with two 100-ml portions of water to remove the remaining acetonitrile and was transferred to a 100-ml graduated cylinder, and the recovered volume was recorded. The wet weight of a tissue sample was corrected for the losses of acetonitrile–water mixture and petroleum ether. The extracts were then subjected to Florisil column cleanup. The eluate was concentrated to 10 ml for quantification. Results were expressed in nanograms of pesticide per gram of fish tissue (parts per billion, wet-weight basis).

Instrument parameters and operating conditions for the quantification of (a) alachlor, cyanazine, dieldrin, *p,p'*-DDE, *p,p'*-TDE, *p,p'*-DDT, and heptachlor epoxide, and (b) atrazine follow:

Gas chromatograph:	Tracor 550
Detectors:	(a) ^{63}Ni electron capture
	(b) N-P
Columns:	glass, 4 mm id packed with 10% DC-200 on 80–100-mesh Gas-Chrom Q glass, 4 mm id packed with a mixture of 4% SC-30 and 6% OV-210 on 80–100-mesh Gas-Chrom Q
Temperatures:	detectors (a) 340° C (b) 240° C column 210° C
Carrier gas:	nitrogen flowing at 90–100 ml/min

Values were not corrected for the ca 80% recovery rate obtained in the extraction. Previous studies (5) and preliminary tests revealed little interference from polychlorinated biphenyls (PCBs) and chlordane. The majority of the PCBs were present as Aroclor 1242 or 1246, which did not interfere with the other pesticide analyses. No chlordane was observed in water or fish samples. Pesticide detection limits were about 10 μg/kg. Where necessary, authors transformed data on pesticide concentrations to log 10 values before conducting analysis-of-variance or *t*-tests or computing correlation coefficients.

Results

The herbicides atrazine, alachlor, and cyanazine were not detected in the fish samples. The insecticides dieldrin and *p,p'*-DDE were found in all samples, and heptachlor expoxide, *p,p'*-DDT, and *p,p'*-TDE were found in most. Dieldrin usually occurred in greater concentrations than did other insecticides. DDT occurred in lower concentrations than did its metabolite. Probably because the length of fish within samples was limited, no consistent relation was evident between pesticide concentration and body length in any species except largemouth bass ($r = 0.66$, $P = 0.01$). Therefore, data were pooled for each species except bass to compare location and time of year (Table 3).

Because gizzard shad, channel catfish, white crappies, and walleyes were not captured at each station on each

TABLE 3. *Monthly mean whole-body insecticide levels in seven species of Des Moines River fish, 1977–78*

Species	Station	Date	Number of Analyses [1]	Residues, μg/kg Wet Weight					
				Dieldrin		ΣDDT		Heptachlor Epoxide	
				Mean	Range	Mean	Range	Mean	Range
Gizzard shad	1	Oct. 1977	3	171	142–191	24	8–49	10	8–13
		Apr. 1978	0	—	—	—	—	—	—
		Jul. 1978	0	—	—	—	—	—	—
		Oct. 1978	2	112	87–137	71	71–72	16	12–21
		Mean		147		43		13	
	2	Oct. 1977	3	66	64–77	20	13–27	0	—
		Apr. 1978	1	119	—	188	—	10	—
		Jul. 1978	3	73	53–111	61	42–71	14	7–26
		Oct. 1978	3	143	132–157	54	52–59	17	15–19
		Mean		96		59		10	
	3	Oct. 1977	0	—	—	—	—	—	—
		Apr. 1978	0	—	—	—	—	—	—
		Jul. 1978	1	14	—	31	—	2	—
		Oct. 1978	4	137	107–182	69	56–104	29	12–68
		Mean		113		61		21	
River carpsucker	1	Oct. 1977	4	44	24–58	72	49–99	0	—
		Apr. 1978	6	34	7–33	52	19–86	3	0–4
		Jul. 1978	4	58	11–114	40	10–64	7	0–13
		Oct. 1978	4	69	20–197	35	18–64	3	0–11
		Mean		49		50		3	
	2	Oct. 1977	2	39	31–48	56	19–94	0	—
		Apr. 1978	1	182	—	66	—	28	—
		Jul. 1978	4	146	122–175	61	44–89	31	23–42
		Oct. 1978	4	100	46–148	59	49–67	12	3–20
		Mean		113		60		18	

TABLE 3. (cont'd.). *Monthly mean whole-body insecticide levels in seven species of Des Moines River fish, 1977–78*

Species	Station	Date	Number of Analyses [1]	Residues, μg/kg Wet Weight					
				Dieldrin		ΣDDT		Heptachlor Epoxide	
				Mean	Range	Mean	Range	Mean	Range
	3	Oct. 1977	0	—	—	—	—	—	—
		Apr. 1978	3	47	13–71	220	89–329	7	2–6
		Jul. 1978	2	25	7–44	36	27–46	6	2–11
		Oct. 1978	5	26	8–50	39	29–63	1	0–3
		Mean		32		93		4	
Carp	1	Oct. 1977	4	47	43–51	64	39–101	1	0–2
		Apr. 1978	3	48	31–62	38	18–62	4	3–4
		Jul. 1978	4	47	42–51	32	15–70	13	8–23
		Oct. 1978	6	26	14–40	29	12–56	2	0–4
		Mean		40		43		5	
	2	Oct. 1977	3	19	13–27	18	14–25	0	—
		Apr. 1978	4	34	23–52	46	22–78	9	5–13
		Jul. 1978	2	46	34–59	35	21–49	9	7–11
		Oct. 1978	4	29	19–51	61	35–125	1	0–3
		Mean		31		43		4	
	3	Oct. 1977	0	—	—	—	—	—	—
		Apr. 1978	3	24	13–31	31	20–43	7	3–14
		Jul. 1978	3	47	39–59	50	45–57	11	7–14
		Oct. 1978	3	32	23–39	60	42–85	3	2–4
		Mean		35		47		7	
Channel catfish	1	Oct. 1977	0	—	—	—	—	—	—
		Apr. 1978	0	—	—	—	—	—	—
		Jul. 1978	3	59	31–98	29	22–37	12	6–22
		Oct. 1978	2	79	73–85	132	129–136	8	7–9
		Mean		67		70		10	
	2	Oct. 1977	3	71	69–74	25	16–40	0	—
		Apr. 1978	3	158	115–240	79	53–109	19	9–25
		Jul. 1978	3	192	180–215	90	73–118	40	37–42
		Oct. 1978	2	120	73–168	51	42–61	14	9–19
		Mean		136		62		18	
	3		1	101	—	101	—	10	—
White crappie	1	Oct. 1977	0	—	—	—	—	—	—
		Apr. 1978	0	—	—	—	—	—	—
		Jul. 1978	2	53	50–56	49	47–51	7	6–8
		Oct. 1978	1	29	—	59	—	1	—
		Mean		45		52		5	
	2	Oct. 1977	4	39	15–63	17	6–35	0	—
		Apr. 1978	1	21	—	37	—	5	—
		Jul. 1978	4	58	38–79	47	38–53	7	3–11
		Oct. 1978	1	88	—	71	—	6	—
		Mean		50		36		4	
	3	Oct. 1977	0	—	—	—	—	—	—
		Apr. 1978	4	94	31–301	49	28–60	8	4–19
		Jul. 1978	4	55	24–100	44	40–54	10	4–18
		Oct. 1978	2	63	63–64	63	54–72	5	4–6
		Mean		76		50		8	
Walleye	1	Oct. 1977	1	11	—	100	—	0	—
		Apr. 1978	0	—	—	—	—	—	—
		Jul. 1978	3	31	12–44	101	70–138	3	1–5
		Oct. 1978	2	15	14–17	119	119–120	0	—
		Mean		22		107		1	
	2	Oct. 1977	2	20	7–34	8	7–10	0	—
		Apr. 1978	1	42	—	30	—	5	—
		Jul. 1978	1	62	—	55	—	6	—
		Oct. 1978	0	—	—	—	—	—	—
		Mean		36		25		3	
	3	Oct. 1977	0	—	—	—	—	—	—
		Apr. 1978	0	—	—	—	—	—	—
		Jul. 1978	1	33	—	92	—	2	—
		Oct. 1978	0	—	—	—	—	—	—
		Mean		33		92		2	
Largemouth bass	1	Oct. 1977	1	50	—	84	—	2	—
		Apr. 1978	0	—	—	—	—	—	—
		Jul. 1978	3	43	31–66	64	36–90	8	6–12
		Oct. 1978	5	81	22–182	82	60–109	7	0–23
		Mean		65		76		7	

TABLE 3. (cont'd.). *Monthly mean whole-body insecticide levels in seven species of Des Moines River fish, 1977–78*

Species	Station	Date	Number of Analyses [1]	Residues, μg/kg Wet Weight					
				Dieldrin		ΣDDT		Heptachlor Epoxide	
				Mean	Range	Mean	Range	Mean	Range
	2	Oct. 1977	3	37	15–50	14	7–20	0	—
		Apr. 1978	2	73	22–124	55	32–80	12	6–18
		Jul. 1978	5	50	22–90	69	50–93	8	4–10
		Oct. 1978	4	65	21–125	70	31–90	7	1–11
		Mean		55		55		6	
	3	Oct. 1977	0	—	—	—	—	—	—
		Apr. 1978	0	—	—	—	—	—	—
		Jul. 1978	1	49	—	72	—	9	—
		Oct. 1978	0	—	—	—	—	—	—
		Mean		49		72		9	

[1] Number of fish pooled for each analysis can be estimated by dividing total fish caught for that species on the collecting date and station given in Table 1 by number of analyses run.

collection date, spatial and temporal trends of pesticide levels in these species were difficult to determine and were examined selectively. Data from Station 2 that were suitable for checking seasonal trends in pesticide concentration revealed no consistent seasonal trend in dieldrin concentrations among these four species. Concentrations of dieldrin were highest in gizzard shad and white crappies in October 1978 and in channel catfish and walleyes in July. Available data revealed no statistically significant difference in dieldrin levels in the four species above, in, or below the reservoir.

More detailed data were available for river carpsuckers and carp. Dieldrin levels in individual samples of river carpsuckers ranged from 7 to 197 ppb; the mean was 63 ppb (Table 3). Again, no consistent seasonal trend was observed among fish from the three stations, and differences with respect to time of year were not statistically significant. Although dissolved dieldrin concentrations in water samples were similar at all three stations, carpsuckers collected in the reservoir during 1978 contained significantly higher dieldrin concentrations than did those collected above or below the reservoir during the corresponding sampling period ($F = 11.3$, $P = 0.001$).

Dieldrin concentrations in carp ranged from 13 to 62 ppb; mean was 36 ppb (Table 3). Seasonal differences in dieldrin concentration in carp were significant ($F = 5.79$, $P = 0.01$). Dieldrin concentrations were nearly constant in carp collected at Station 1 in October 1977 and April and July 1978 and had decreased in October 1978; the concentrations in carp collected at Stations 2 and 3 were highest in July. No consistent spatial trend was found among sampling dates. Mean dieldrin concentrations in carp collected at Stations 1, 2, and 3 were not significantly different throughout the sampling period.

Because dieldrin concentration in largemouth bass was related significantly to fish length, authors did not consider length when examining spatial and seasonal trends. Residues obtained by determining the difference between measured dieldrin concentration and calculated concentration, based on the regression formula of body length versus dieldrin (dieldrin [ppb] = 44.01 + 0.43 total body length [mm]), were used to compare stations. Largemouth bass of similar length, captured above and within the reservoirs, had similar concentrations of dieldrin. The single sample from below the reservoir was insufficient for comparison. Data on fish from Station 2 suggested that dieldrin concentrations in bass of similar length were highest in April, but the differences among sampling dates were not statistically significant.

No consistent seasonal trend for combined DDT–DDE–TDE (ΣDDT) levels was evident for any species of fish examined (Table 3). Greatest mean values occurred in October 1978 for five species and in April 1978 for the other two. At Station 2 (in the reservoir), where data were most nearly complete, concentrations were greatest in April in gizzard shad and river carpsuckers; in October 1978 in carp, crappies, and bass; and in July in channel catfish and walleye. Differences among stations were also not statistically significant. Mean concentrations in all species were greater in fish captured below the reservoir than in fish captured in the reservoir. In five species, mean concentrations in reservoir fish were either lower or equal to those found in fish collected above the reservoir.

Heptachlor epoxide occurred at lower levels than did dieldrin and ΣDDT in all species (Table 3). Concentrations were usually greatest in fish collected during July 1978. No distinct and consistent spatial trend was observed among species, except in river carpsuckers.

Heptachlor epoxide levels in 1978 were significantly higher in river carpsuckers collected in the reservoir than in those collected either above or below it ($F = 20.39$, $P = 0.0001$).

Discussion

The lack of measurable amounts of atrazine, alachlor, or cyanazine in fish tissue, even though significant concentrations of these compounds were usually present in the surrounding water, agreed with reports of rapid elimination of herbicides by exposed fish, with little or no accumulation of the compounds in body tissue (*2, 3, 9, 10*).

Not only did reservoir-captured fish other than river carpsucker fail to contain greater concentrations of insecticide than did fish captured above or below the reservoir, but fish collected where total insecticide concentrations in water were greatest also did not contain greater levels than fish collected elsewhere. Total concentrations of dieldrin in the river water above the reservoir were significantly higher than those within and below the reservoir (*6*), but concentrations in the fish collected from those locations did not reflect this spatial difference. A possible reason is that they absorbed only dieldrin in the dissolved state. Average concentrations of dieldrin detected in the aqueous phase of the river water were similar at all three locations over the study period (Table 2). Higher concentrations of dieldrin detected above the reservoir were due to the portion that was adsorbed onto the suspended sediment of the water. This adsorbed portion would probably be less available to fish. Another possibility is that the insecticide concentrations in the river water were so low at all three stations that fish were capable of metabolizing and eliminating the compounds as fast as they were absorbed and thus showed no difference in trace amounts left in the body.

Another possible explanation for lack of difference in pesticide concentrations in fish above, in, and below the reservoir may have been the newness of the reservoir and the short retention time for water. The reservoir was impounded in April 1977; consequently, the study period covered most of the first year of impoundment. Leung (*6*) estimated that 16 kg of dieldrin and 20 kg of *p,p'*-DDE were deposited in the reservoir between September 1977 and October 1978. Perhaps these amounts were too small to be recycled in sufficient quantity from sediment and accumulated by the fish through the food chain, if in fact bioaccumulation occurs in the reservoir. The potential for recycling pesticides from bottom sediment exists because dieldrin was present in all samples of Saylorville Reservoir bottom sediment analyzed during the study and ranged from 0.6 to 12.0 μg/kg (*6*). *ΣDDT* was present in some form in most samples and ranged from 0.0 to 17.1 μg/kg. Heptachlor epoxide was detected in four of 42 bottom samples collected and never exceeded 2.0 μg/kg. Also, water passed through the reservoir in fewer than 40 days during most of the study period because the reservoir was not full. The short retention time might also have affected movement of the deposited pesticide through the food chain by inhibiting buildup of phytoplankton and zooplankton populations. The effect of retention time in the reservoir on pesticide dynamics is not well known and would require further study. Also, inasmuch as this investigation covered only the first year of impoundment and deposition of pesticide-laden sediment, the occurrence and distribution of pesticides should be re-examined after several years of reservoir aging.

Acknowledgments

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Polychlorinated Biphenyls in Clams and Oysters from New Bedford Harbor, Massachusetts, March 1978 [1]

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ABSTRACT

Polychlorinated biphenyl (PCB) concentrations in clams (Mercenaria mercenaria) *and oysters* (Crassostrea virginica) *from 17 stations of the western and New Bedford Harbor areas of Buzzards Bay, Massachusetts, clearly show that the New Bedford Harbor area is severely polluted. Up to 5 ppm PCBs (dry weight) were found in shellfish tissue. The most likely sources of the PCBs are chronic releases from two electrical component manufacturers in New Bedford. Close proximity of the shellfish to the source of input is indicated by a high relative abundance of the di-, tri-, and tetrachlorobiphenyls. The data suggest that the New Bedford Harbor area should be considered, along with the Hudson River and Chesapeake Bay, one of the major sources of PCB inputs to the northeastern United States coastal area.*

Introduction

Following Jensen's report identifying polychlorinated biphenyls (PCBs) in organisms inhabiting Swedish waters (*10*), there emerged with each succeeding year further evidence of worldwide contamination (*15*). Although the U.S. Toxic Substances Control Act (1976) restricts further contamination, the toxicity of these compounds in conjunction with their resistance to environmental degradation (*7*) requires examination of their proximate and long-term effects on marine life. Their distribution and movement through the environment must be continuously monitored. Of particular concern are coastal areas where commercial and recreational shellfishing and fishing in benthic environments known to possess hazardous levels of PCBs may result in human consumption of contaminated organisms.

The presence of two large electrical component manufacturers, which use and discharge PCBs, combined with the existence of a local fishery suggested the importance of studying the distribution and accumulation of PCBs in the New Bedford, Massachusetts, area. This study used edible clams *(Mercenaria mercenaria* L.) and oysters *(Crassostrea virginica)* as indicators for several reasons: They are sessile and thus indicative of regional PCB distribution; they inhabit the benthic sediments in which large quantities of PCBs have been identified; they are microphagous and selectively process particles of the size range that adsorb PCBs (*3*; private communication: B. Dangle. 1978. U.S. Environmental Protection Agency, Toxic Substances Pesticides Branch, Air and Hazardous Material Division, Boston, Mass.); and they are significant in local sport and commercial fisheries.

Materials and Methods

COLLECTION OF SPECIES

Clams ranging in size from 37 to 106 mm were obtained with an epibenthic sled at depths varying from 3 to 12 meters. The majority of sampling sites were located in Buzzards Bay within a 5.8-nautical-mile radius of the entrance to New Bedford Harbor (Figure 1). For comparison, additional specimens were collected from the Westport River, 1.0 nautical miles from its mouth and 14.0 nautical miles from New Bedford Harbor. These organisms served as low-level control samples. The precise locations of sampling sites within the study area were determined largely by the distribution of the organisms. The Slocum River estuary was also sampled. Because *M. mercenaria* was not available, authors collected *Crassostrea virginica* (Gmelin) as the representative bivalve for this area.

All sampling was conducted during the week of March 11, 1978. Thus, the reported effects of water temperature on PCB concentrations (*4*) were obviated. Bottom characteristics of collection sites ranged from soft mud to unsorted sand densely infiltrated with shell debris.

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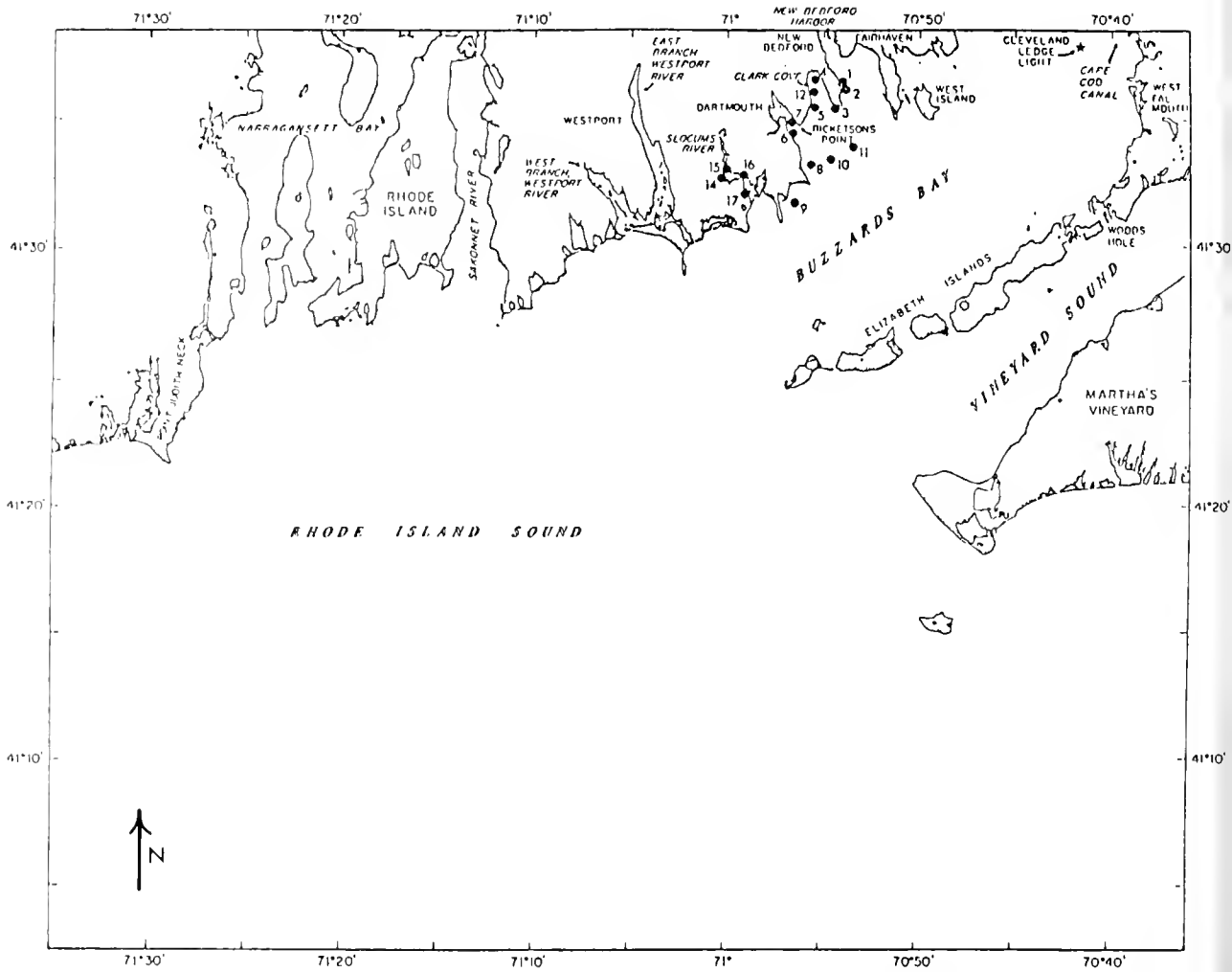

FIGURE 1. *Sites along Buzzards Bay for the sampling of shellfish contaminated with PCBs.*

ANALYTICAL METHODS

PCBs were quantitatively determined in pooled tissue homogenates. All chromatographic reagents, glassware, and equipment contacting the samples were copiously rinsed with reagent grade, redistilled solvents (Fisher Scientific Co.), in the following sequence: methanol, acetone, toluene, and hexane.

The shucked clams including mantle cavity water were homogenized (Polytron R. Kinematica GmbH), lyophilized, and extracted three times with hexane—one 50-ml portion and two 25-ml portions. The extracts were filtered through a column of powdered sodium sulfate (Na_2SO_4) to remove residual water and particulates and then concentrated to 1 ml for column chromatographic cleanup. The cleanup columns were packed with 10 g of 200-mesh alumina and 8 g of 60–200-mesh silica gel, both deactivated 5% with water. The columns were first eluted with 15 ml hexane. PCBs were then collected in a 50-ml hexane–toluene (80 + 20) elution and quantitatively concentrated for gas-liquid chromatographic (GLC) analysis. GLC instrument parameters and operating conditions were as follows:

Chromatograph:	Hewlett-Packard, 7620A
Detector:	^{63}Ni electron-capture
Column:	glass, 6-ft long by 2-mm ID, packed with a mixture of 1.5% OV-17 and 1.95% QF-1 on 100–200-mesh Chromosorb W(AW)
Temperatures:	injection port 225°C oven, isothermal 190°C detector 300°C
Pulse interval:	50 mseconds
Carrier gas:	a mixture of 95% argon and 5% methane flowing at 20 ml/min
Detector purge:	40 ml/min
Chart speed:	0.5 inches/min

PCBs were quantitated by comparing the summation of eight individual peak areas with a separately injected Aroclor 1254 or 1242 standard. The limit of detection,

based on the studies of shellfish by Goldberg et al. (*6*), was 0.001 ppm dry weight. Recovery of PCBs from samples spiked with Aroclor 1254 before extraction was 80%–90% or better. PCBs were confirmed by glass capillary gas chromatographic/mass spectrometric (GCMS) analyses at the Woods Hole Oceanographic Institution Laboratory using a Finnigan Model 1015 SL system modified for glass capillary GC.

Results

PCBs reported as Aroclor 1254 were detected in all samples, ranging from 4.19 ppm dry weight in samples collected adjacent to the harbor down to 0.232 ppm in samples collected approximately 3 nautical miles from the harbor (Table 1). Samples from Westport

TABLE 1. *Aroclor 1254 concentrations in* Mercenaria mercenaria *and* Crassostrea virginica, *1978*

Sampling Site	Av. Concn $\times 10^{-6}$ g/g Dry Wt [1]	Av. Concn $\times 10^{-6}$ g/g Wet Wt	Av. Concn Corrected for 80% Extn Efficiency, $\times 10^{-6}$ g/g Dry Wt
	Mercenaria mercenaria		
1	4.19	0.524	5.24
2	1.36	0.170	1.70
3	1.75	0.218	2.19
4	0.443	0.055	0.553
5	1.54	0.192	1.92
6	1.42	0.177	1.77
7	0.290	0.036	0.362
8	0.625	0.078	0.781
9	0.537	0.067	0.671
10	0.232	0.029	0.290
11	1.04	0.130	1.30
12	0.879	0.110	1.10
13	0.008	0.001	0.010
	Crassostrea virginica		
14	0.560	0.070	0.700
15	2.57	0.321	3.21
16	2.28	0.284	2.84
17	1.47	0.184	1.84

[1] Samples were analyzed at Southeastern Massachusetts University Laboratories.

Harbor, Massachusetts (Site 13), containing 0.008 ppm PCB were considered indicative of background concentrations.

Examination of the data suggests a gradient of decreasing concentration from point-source contamination similar in pattern to that reported from the upper Hudson River (*1*). The lower concentrations found in protected coves and estuaries indicate minimal PCB input from urban runoff.

The Commonwealth of Massachusetts has prohibited commercial fishing north of a line drawn from Ricketson's Point, Dartmouth (41°34′38″N; 70°56′19″W), to Black Rock, Fairhaven (41°34′41″N; 70°51′45″W). Sampling sites south of this closed fishing area, however, showed PCB concentrations comparable to those within the restricted area. High PCB concentrations at Sites 6 and 8 may be due to transport paralleling the mass flow of water in Buzzards Bay (*14*). The elevated PCB concentration of Site 11 may be due to tidal flushing along the major shipping channel away from the harbor.

A few samples were analyzed in more detail in the Woods Hole Oceanographic Institution Laboratory. These analyses showed that the PCBs were composed of a mixture of components similar to Aroclor 1242 or 1016 and 1254. In addition, authors analyzed a sample of scallops (*Aequipecten irradians* Lamarck) from Cleveland Ledge Light (Figure 1) supplied by the Falmouth, Massachusetts, shellfish warden. The data from these analyses are presented in Table 2.

TABLE 2. *Mixture of Aroclors 1242 and 1254 in selected samples from New Bedford Harbor and Buzzards Bay, Massachusetts, 1978*

Site	Organism	Residues $\times 10^{-6}$ g/g Dry Wt [1]	
		1242	1254
3	*Mercenaria mercenaria*	1.59	1.46
10	*Mercenaria mercenaria*	0.22	0.20
Cleveland Ledge	*Aequipecten irradians*	0.093	0.185

[1] Samples were analyzed at Woods Hole Oceanographic Institute.

Discussion

In compliance with the U.S. Toxic Substance Control Act, the manufacturing facilities abutting New Bedford Harbor have severely curtailed the discharge of PCBs into harbor waters. All PCB use was, in fact, suspended as of September 1978 (Private Communications: Anonymous. 1978. Aerovox Inc. spokesperson; Robinson, W. 1978. Cornell Dubilier, Inc., spokesperson, both of New Bedford, Mass.).

However, the discharge of large amounts of PCBs over the last 38 years, coupled with the affinity of PCBs for sediments (*8*), has resulted in severely contaminated sediments in this area. The literature reveals little data for PCBs in sediments from this area. Harvey and Steinhauer (*9*) reported 8.4 x 10^{-6} g PCB/g dry weight in outer New Bedford Harbor sediment samples in 1973. Gilbert et al. (*5*), reported values of 0.175–0.543 x 10^{-6} g/g dry weight for concentrations of PCBs in surface sediments from eight stations in Buzzards Bay outside New Bedford Harbor.

deLappe and Risebrough (*3*) analyzed mussels (*Mytilus edulis* L.) from inner New Bedford Harbor and re-

ported a phenomenally high concentration of 110 x 10^{-6} g PCB/g dry weight. They also analyzed water from the area and found concentrations up to 580 x 10^{-9} g PCB/liter of dissolved and particulates combined.

Samples of shellfish, bottom fish, and sediments from the New Bedford Harbor area were analyzed in 1976 and 1977 for PCBs. Concentration ranged as follows: 0.5–620 x 10^{-6} g PCBs/dry weight sediments; up to 11.7 x 10^{-6} g PCBs/g wet weight of lobster (*Homarus americanus* Milne-Edwards) edible tissue; and up to 20.0 x 10^{-6} g PCBs/g wet weight black back flounder (*Pseudopleuronectes americanus*, Walbaum) edible tissue (unpublished data: Commonwealth of Massachusetts, Department of Environmental Quality Engineering, 1976–77). These data led to the closure of the New Bedford Harbor area as previously noted.

Summerhayes et al. (*14*) and Stoffers et al. (*12*) investigated trace metal contamination of New Bedford Harbor sediments. They found up to 1% Cu in surface sediments in the inner harbor and concluded that the harbor area was slowly leaking trace metal-contaminated sediments to nearby Buzzards Bay. Processes active in movement of trace metal-contaminated sediments are likely to be active in the movement of PCBs in the same sediments.

Thus, even though PCB discharges by industry have been curtailed, harbor sediments contain high concentrations of PCBs and can act as a source of PCB contamination of the harbor for some time to come. Young et al. (*16*) clearly demonstrated that PCB-contaminated sediments can be a source of PCB contamination for shellfish. Rhoads (*11*) showed that tidal influences in Buzzards Bay result in resuspension of surface sediments in some areas with the resulting probability of transport to other areas of the bay. Disturbance of the sediments in New Bedford Harbor by natural events such as tidal movement or storms or by man-induced activities such as dredging will probably result in contamination of other Buzzards Bay areas.

This may be the reason PCBs were detected in the bay sediments by Gilbert et al. (*5*) and in scallops at Cleveland Ledge Light in the present study. However, PCBs are so ubiquitous in coastal regions near industrialized areas that authors cannot be certain at present of the origin of the low concentrations of PCBs at Cleveland Ledge Light and Buzzards Bay surface sediments.

Data on PCBs in New Bedford Harbor are sufficient to identify this area as one of high PCB concentration in both sediments and biota. However, the exact magnitude of the problem has not yet been investigated. Critical questions of the size of the reservoir of PCBs in the sediments of the harbor and the extent to which they are a source for contamination of other areas of Buzzards Bay remain and are being pursued.

The few higher-resolution measurements available to us at this time indicate that there is a substantial concentration of the di, tri- and tetrachlorobiphenyls in the area compared with the amounts of penta- and hexachlorobiphenyls usually found in environmental samples. This indicates a proximity of the samples analyzed to source of input via effluents. The di- and trichlorobiphenyls are more reactive than the penta- and hexachlorobiphenyls and, as distance and time between input and measurement increase, there is a greater probability that the less-chlorinated biphenyls will undergo reaction (*15*). The electrical component manufacturers in New Bedford used primarily Aroclor 1242 and 1016 mixtures. Thus, the input of the less-chlorinated analogs is expected. The New Bedford Harbor and Buzzards Bay ecosystems provide a system to study the biogeochemistry of the various PCB isomers and authors are currently pursuing this investigation.

Our data on the PCBs in oysters from the Slocum River estuary (Table 1) may suggest a second problem with PCBs in the greater New Bedford area. PCB concentrations in *C. virginica* from the Slocum River estuary are in excess of those in *M. mercenaria* collected off the river mouth. It is possible that lateral transport of contaminated sediments from the New Bedford Harbor area to a point upstream in the adjacent Slocum River would exceed transport to a point off the mouth of the river. This is unlikely but cannot be ascertained because of lack of knowledge about sediment transport in the area. A second possibility is the release of PCBs from a landfill site to the aquifer feeding the Slocum River. It has been established that there are over 200,000 kg of PCBs buried in the New Bedford municipal landfill located on the aquifer feeding the Slocum River valley. A few preliminary measurements have shown that some PCBs are present in waters draining from the landfill (*13*). Extensive contamination of groundwaters was not found, based on a few measurements. However, time series measurements and mass flow calculations have not been made (*13*). This problem merits more extensive study because the aquifer represents the primary source of drinking water for the town of Dartmouth, Massachusetts.

Recent measurements of PCBs in the common blue mussel *(Mytilus edulis)* and in oysters *(Crassostrea virginica)* collected around the coast of the United States have shown that the northeastern U.S. coastal area is more contaminated with PCBs on a regional

basis than most other areas of the coast (*6*). The data and discussions presented here suggest that the New Bedford Harbor area should be considered along with the Hudson River and Chesapeake Bay as one of the sources of these regionally elevated concentrations.

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Nationwide Residues of Organochlorine Compounds in Wings of Adult Mallards and Black Ducks, 1979–80

Brian W. Cain[1]

ABSTRACT

Organochlorine residues in wings of adult mallards (Anas platyrhynchos) *and black ducks* (Anas rubripes) *were monitored nationwide from birds harvested during the 1979–80 hunting season. DDE residues were found in all samples. DDT residues had declined from levels reported in 1976 on a flyway basis but the decline was significant* ($P < 0.05$) *only in the Pacific Flyway. Levels of DDT, DDE, TDE, and dieldrin were low on a flyway basis, and all but DDE declined significantly* ($P < 0.05$) *in the percent occurrence. Polychlorinated biphenyls (PCB) levels were lower in mallard wings from all flyways compared with 1976 data, but percent occurrence had significantly* ($P < 0.05$) *increased. Pools from Alabama and New Mexico continued to show higher DDE residues than pools from other areas.*

Introduction

During the 1965–66 hunting season, the Fish and Wildlife Service, U.S. Department of the Interior, as part of the National Pesticide Monitoring Program (*2*), began to monitor organochlorine pesticides in duck wings collected by hunters. Justification for this method of collection was given by Johnson et al. (*5*). The black duck ranges over a large part of the Atlantic Flyway and the mallard is found throughout the rest of the contiguous 48 states. Thousands of wings collected each year by cooperating hunters are sent to collection sites in each of the four flyways. Waterfowl migrate twice a year within four major flyways that consist of states or parts of states in which the birds feed or rest for short periods of time. Millions of waterfowl spend the winter months in the southern portions of these flyways, and may be exposed to environmental contaminants different from those found in northern nesting areas.

Heath and Prouty (*4*) successfully tested the monitoring methodology in 1965 using mallard and black duck wings collected from New York and Pennsylvania. A later report showed there was a highly significant correlation between DDT residues in the wing and those in breast skin, breast muscle, brain, kidney, liver, and other tissues from captive mallards and scaup ducks (*1*).

This paper presents results from the mallard and black duck wings collected during the 1979–80 hunting season and includes the mean residue levels for each state. The percentage of the pools from each flyway that contain a particular contaminant residue is presented and compared with the 1976-77 hunting season. The mean value of organochlorine residues in wings by major flyways is presented and compared with the 1976 collection.

Methods

WING COLLECTIONS

During the 1979-80 hunting season, cooperating waterfowl hunters mailed approximately 11,660 wings from adult mallards or black ducks to a regional collection point within each of the four flyways. Each wing was sent in a separate envelope that listed the date, county, and state where the bird was harvested. The wings were held in frozen storage until March or early April 1980 when biologists determined the sex and maturity of each bird. Only adult wings were used for the pesticide monitoring program to maintain the sampling consistency established by Heath and Hill (*3*). Wings from each state were sorted randomly into pools of 25 wings, and random samples of these pools were made by using a random numbers table. The number of pools taken was such that about 50% of the wings submitted from a state were selected for organochlorine analyses. Each pool of 25 wings was wrapped in aluminum foil, tagged with a coded number, frozen, and shipped to Raltech Scientific Services, Inc. (formerly WARF Institute, Inc.) in Madison, Wisconsin. There were 24 pools of black duck wings and 29 pools of mallard wings from the Atlantic Flyway, 64 pools of mallard wings from the Mississippi Flyway, 54 pools of mallard wings from the Central Flyway, and 44 pools of mallard wings from the Pacific Flyway.

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

ANALYTICAL PROCEDURES

Wings in each pool were trimmed by removing most of the feathers and the distal joint with a pair of scissors. Remaining portions were homogenized in a Hobart grinder, and approximately 10 g was removed, weighed, and placed in a preweighed 150-ml beaker. The beaker and sample were oven-dried 2 weeks at 40°C and reweighed, and the sample dry weight was recorded. Approximately 40 g homogenized sample was weighed into a 250-ml beaker and mixed with 100 g anhydrous sodium sulfate, placed overnight in a hood, and then transferred to a 43-mm by 123-mm prewashed Whatman extraction thimble plugged with glass wool. The thimble was placed in a desiccator overnight and then extracted for 8 hours in a Soxhlet apparatus with a mixture of 150 ml each of ethyl ether and petroleum ether. This solution was then concentrated on a steam bath, and the residue was transferred to a 50-ml volumetric flask and diluted to volume with a mixture of dichloromethane–cyclohexane (15 + 85).

A 5-ml aliquot of the extract was placed in an Auto-Prep 1001 gel permeation chromatograph that had been standardized for chlorinated insecticides and PCB compounds. The column was glass, 600 mm by 25 mm, and packed with 60 g of 200–400-mesh Bio-Beads (SX-3). The solvent was dichloromethane–cyclohexane (15 + 85) at the flow rate of 5.5 ml/min. The resulting solution was concentrated on a flash evaporator to approximately 1 ml in the presence of 5 ml iso-octane and diluted to 25 ml with petroleum ether. A 10-ml aliquot of this gel permeation extract was placed in a 25-g silica-gel 60 column and three elutions were prepared. The first was eluted with 90 ml petroleum ether and contained hexachlorobenzene (HCB) and mirex; the second was eluted with 200 ml petroleum ether and contained PCB compounds and DDE; and the third was eluted with 150 ml of a mixture of acetonitrile–hexane–dichloromethane (1 + 19 + 80) and contained the remaining chlorinated insecticides. Fraction three was concentrated on a flash evaporator to 1 ml and diluted to 10 ml with petroleum ether. Four microliters from each fraction was injected into a gas chromatograph equipped with an electron-capture detector.

Instrument parameters and operating conditions applied to all samples except where differences are noted:

Column:	2 m by 4 mm	
Packings:	(1) organochlorine pesticides and PCBs: a mixture of 1.95% OV-17 and 1.5% QF-1 on 100–200-mesh Supelcoport (2) chlordane isomers: 3% OV-1 on 80–100-mesh Gas-Chrom Q	
Temperatures, °C	column	200
	injector	250
	detector	300
Carrier gases:	a mixture of 95% argon and 5% methane	
Flow rates	(1) 33 ml/min (2) 32 ml/min	

Lipids were determined by using a 5-ml aliquot of the Soxhlet extract in a preweighed 2-dram vial. The vial was placed in a 40°C oven for 3 days to remove the solvent and then reweighed, and the amount of the lipids was calculated.

All residues are expressed as ppm wet weight and may be converted to an approximate dry or lipid weight by dividing by 0.60 or 0.14, the mean proportions of dry or lipid material in the samples, respectively. Mean residue values were calculated by using 0.00 as the value for samples in which no residue was reported at the 0.01-ppm sensitivity level. The recovery percentages from spiked samples were DDE, 85; TDE, 125; dieldrin, 98; heptachlor epoxide, 90; and Aroclor 1254, 118. Analytical results have not been corrected for recovery. Residues in 5% of the pools were confirmed by mass spectrometry.

The percentage occurrence of the organochlorines in wings from each flyway were compared with the 1976 collection data by using a test for two population proportions. Mean residue levels of DDE, DDT, TDE, dieldrin, and PCBs were compared on a flyway basis with the published 1976 data of White (*8*) by using only those samples with a detectable residue level. A *t*-test comparison was made on each data pair that had detectable residues in at least 50% of the pools collected. A $P < 0.05$ was necessary for significance for all statistical comparisons.

Results and Discussion

Residues of DDE, DDT, TDE, dieldrin, and PCBs in the duck wings from the 1979–80 hunting season are presented in Table 1. These data, collected from 5,268 wings (215 pools), are presented as mean values for each state in a flyway and are arranged in a North to South direction. Data in Table 1 should not be interpreted on a statewide basis alone because waterfowl migrate and may cover a wide area and range of habitats in many states. Samples from some localities (i.e., Alabama and New Mexico) continue to show higher residues of DDT and DDE than do samples from the other localities. This situation in Alabama was reported earlier (*3, 7, 8*), and a possible source of the contamination was described by O'Shea et al. (*6*).

The highest DDE level, 3.28 ppm, was detected in a pool composed of wings from Arizona and New Mexico, and the lowest level of DDE residue, 0.02 ppm, occurred in pools from Florida and Kentucky. DDE residues occurred in all wing pools; however, DDT, TDE, and dieldrin were found in fewer pools in the 1979–80 wing collection than in the 1976–77 collection

TABLE 1. *Organochlorine residues in pools of wings from adult mallards and black ducks, 1979–80*

State	Number of Pools	Residues, ppm Wet Weight									
		DDE		DDT		TDE		Dieldrin		PCBs	
		$\bar{x} \pm$ 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	2	0.13 ± 0.00 (2)	0.12–0.15	ND		ND		ND		0.21 ± 0.00 (2)	0.19–0.23
Vermont	1[1]	0.12 ± 0.00	—	ND		ND		ND		0.42 ± 0.00	—
New Hampshire	1[1]	0.42 ± 0.00	—	0.01 ± 0.00	—	ND		ND		0.74 ± 0.00	—
Massachusetts	2	0.54 ± 0.07 (2)	0.47–0.60	0.03 ± 0.01 (2)	0.02–0.03	0.11 ± 0.09 (2)	0.02–0.20	0.09 ± 0.06 (2)	0.03–0.14	0.87 ± 0.03 (2)	0.84–0.89
Connecticut	1	0.08 ± 0.00	—	0.02 ± 0.00	—	ND		0.01 ± 0.00	—	1.49 ± 0.00	—
Rhode Island	2[1]	0.47 ± 0.11 (2)	0.36–0.58	0.03 ± 0.01 (2)	0.02–0.03	0.02 ± 0.01 (2)	0.01–0.02	0.03 ± 0.01 (2)	0.02–0.03	0.84 ± 0.25 (2)	0.59–1.09
New York	2	0.44 ± 0.22 (2)	0.22–0.66	0.02 ± 0.00 (1)	ND–0.02	0.02 ± 0.00 (1)	ND–0.02	0.02 ± 0.00 (2)	0.02–0.02	1.31 ± 0.25 (2)	0.82–1.80
Pennsylvania	1	0.11 ± 0.00	—	ND		ND		ND		0.49 ± 0.00	—
New Jersey	3	0.53 ± 0.09 (3)	0.37–0.68	0.01 ± 0.01 (2)	ND–0.02	0.01 ± 0.01 (2)	ND–0.02	0.01 ± 0.00 (2)	0.01–0.02	0.55 ± 0.01 (3)	0.54–0.56
Delaware	1	0.67 ± 0.00	—	ND		ND		ND		0.80 ± 0.00	—
Maryland	2	0.22 ± 0.07 (2)	0.15–0.29	ND		ND		0.01 ± 0.00 (1)	ND–0.01	0.29 ± 0.04 (2)	0.25–0.33
Virginia	2	0.18 ± 0.02 (2)	0.16–0.19	ND		ND		ND		0.21 ± 0.02 (2)	0.19–0.22
West Virginia	1[1]	0.23 ± 0.00	—	ND		ND		0.01 ± 0.00	—	0.57 ± 0.01	—
North Carolina	1[1]	0.15 ± 0.00	—	ND		ND		ND		0.15 ± 0.00	—
South Carolina	1	0.37 ± 0.00	—	ND		ND		0.01 ± 0.00	—	1.00 ± 0.00	—
Georgia and Florida	1[1]	0.11 ± 0.00	—	ND		ND		ND		0.45 ± 0.00	—
MALLARDS, ATLANTIC FLYWAY											
Maine	1[1]	0.21 ± 0.00	—	0.02 ± 0.00	—	ND		ND		0.28 ± 0.00	—
Vermont	1[1]	0.09 ± 0.00	—	0.02 ± 0.00	—	ND		ND		0.14 ± 0.00	—
New Hampshire	1[1]	0.20 ± 0.00	—	0.01 ± 0.00	—	ND		ND		0.27 ± 0.00	—
Massachusetts	2	0.33 ± 0.12 (2)	0.21–0.45	0.02 ± 0.01 (2)	0.01–0.02	0.02 ± 0.00 (2)	0.02–0.02	0.05 ± 0.03 (2)	0.02–0.07	0.05 ± 0.03 (2)	0.02–0.07
Connecticut	1	0.14 ± 0.00	—	ND		ND		ND		1.17 ± 0.00	—
Rhode Island	1	0.58 ± 0.00	—	0.03 ± 0.00	—	0.01 ± 0.00	—	0.04 ± 0.00	—	0.98 ± 0.00	—
New York	2	0.48 ± 0.26 (2)	0.41–0.55	0.03 ± 0.00 (2)	0.03–0.03	ND		0.02 ± 0.00 (2)	0.02–0.02	0.79 ± 0.09 (2)	0.70–0.87
Pennsylvania	3	0.23 ± 0.02 (3)	0.20–0.28	0.01 ± 0.01 (2)	ND–0.02	ND		0.01 ± 0.00 (1)	ND–0.01	0.49 ± 0.15 (3)	0.28–0.77
New Jersey	2	0.47 ± 0.06 (2)	0.41–0.52	0.02 ± 0.01 (2)	0.01–0.02	0.01 ± 0.00 (2)	0.01–0.01	0.02 ± 0.01 (2)	0.01–0.02	0.55 ± 0.61 (2)	0.44–0.65
Delaware	2	0.57 ± 0.15 (2)	0.42–0.71	ND		ND		0.01 ± 0.00 (2)	0.01–0.01	0.41 ± 0.03 (2)	0.38–0.43
Maryland	2	0.12 ± 0.01 (2)	0.11–0.13	ND		ND		0.01 ± 0.00 (2)	0.01–0.01	0.21 ± 0.06 (2)	0.15–0.27
Virginia	3	0.15 ± 0.05 (3)	0.08–0.25	0.01 ± 0.00 (1)	ND–0.02	ND		0.01 ± 0.01 (1)	ND–0.01	0.29 ± 0.08 (3)	0.15–0.44
West Virginia	1[1]	0.23 ± 0.00	—	ND		ND		ND		0.38 ± 0.00	—
North Carolina	2	0.13 ± 0.03 (2)	0.10–0.15	ND		ND		0.02 ± 0.01 (2)	0.01–0.03	0.87 ± 0.75 (2)	0.12–1.62
South Carolina	2	0.15 ± 0.08 (2)	0.07–0.23	0.01 ± 0.01 (1)	ND–0.01	ND		0.28 ± 0.27 (2)	0.01–0.55	0.14 ± 0.08 (2)	0.06–0.21
Georgia	2	0.37 ± 0.20 (2)	0.17–0.57	ND		ND		0.01 ± 0.01 (1)	ND–0.01	0.12 ± 0.04 (2)	0.08–0.15
Florida	1[1]	0.02 ± 0.00	—	0.02 ± 0.00	—	ND		ND		0.09 ± 0.00	—

MALLARDS, MISSISSIPPI FLYWAY											
Minnesota	4	0.10 ± 0.03 (4)	0.04–0.15	0.00 ± 0.00 (1)	0.00–0.01		ND	0.00 ± 0.00 (1)	ND–0.01	0.08 ± 0.02 (4)	0.04–0.14
Wisconsin	5	0.10 ± 0.02 (5)	0.06–0.18		ND		ND		ND	0.12 ± 0.02 (5)	0.07–0.20
Michigan	5	0.16 ± 0.03 (5)	0.10–0.29		ND		ND	0.00 ± 0.00 (2)	ND–0.01	0.20 ± 0.04 (5)	0.10–0.31
Iowa	6	0.09 ± 0.01 (6)	0.08–0.11		ND		ND	0.03 ± 0.02 (4)	ND–0.12	0.07 ± 0.03 (6)	0.02–0.20
Illinois	5	0.15 ± 0.05 (5)	0.06–0.34	0.000 ± 0.00 (1)	ND–0.02		ND	0.01 ± 0.00 (4)	ND–0.02	0.16 ± 0.08 (5)	0.03–0.45
Indiana	3	0.26 ± 0.09 (3)	0.12–0.43	0.02 ± 0.02 (1)	ND–0.05	0.01 ± 0.00 (1)	ND–0.02	0.00 ± 0.00 (1)	ND–0.01	0.16 ± 0.05 (3)	0.08–0.25
Ohio	3	0.17 ± 0.02 (3)	0.12–0.20	0.00 ± 0.00 (1)	ND–0.01		ND	0.01 ± 0.01 (2)	ND–0.02	0.51 ± 0.09 (3)	0.35–0.64
Missouri	5	0.06 ± 0.02 5)	0.02–0.12		ND		ND	0.00 ± 0.00 (1)	ND–0.01	0.03 ± 0.01 (5)	0.01–0.06
Kentucky	2	0.09 ± 0.07 (2)	0.02–0.15		ND		ND	0.01 ± 0.00 (2)	0.01–0.01	0.12 ± 0.06 (2)	0.06–0.18
Arkansas	7	0.15 ± 0.03 (7)	0.07–0.27	0.01 ± 0.00 (4)	ND–0.01		ND	0.01 ± 0.00 (7)	0.01–0.02	0.03 ± 0.01 (6)	ND–0.06
Tennessee	4	0.09 ± 0.02 (4)	0.04–0.12	0.00 ± 0.00 (1)	ND–0.01		ND	0.02 ± 0.01 (4)	0.01–0.03	0.07 ± 0.02 (4)	0.02–0.10
Louisiana	6	0.08 ± 0.01 (6)	0.05–0.12	0.00 ± 0.00 (1)	ND–0.01		ND	0.01 ± 0.00 (4)	ND–0.01	0.03 ± 0.00 (6)	0.02–0.04
Mississippi	5	0.21 ± 0.03 (5)	0.11–0.26	0.03 ± 0.01 (4)	ND–0.05	0.01 ± 0.01 (3)	ND–0.05	0.02 ± 0.00 (5)	0.01–0.03	0.04 ± 0.01 (5)	0.02–0.05
Alabama	4	0.85 ± 0.29 (4)	0.29–1.48	0.13 ± 0.03 (4)	0.09–0.21	0.09 ± 0.03 (4)	0.02–0.17	0.31 ± 0.29 (4)	0.01–1.18	0.14 ± 0.03 (4)	0.11–0.22
MALLARDS, CENTRAL FLYWAY											
Montana (eastern)	4	0.04 ± 0.01 (4)	0.04–0.10		ND		ND		ND	0.04 ± 0.01 (4)	0.02–0.07
North Dakota	6	0.05 ± 0.01 (6)	0.04–0.08	0.00 ± 0.00 (1)	ND–0.01		ND		ND	0.04 ± 0.02 (6)	0.02–0.12
South Dakota	4	0.08 ± 0.02 (4)	0.05–0.12	0.02 ± 0.01 (2)	ND–0.05		ND		ND	0.06 ± 0.04 (4)	0.04–0.10
Wyoming (eastern)	4	0.06 ± 0.02 (4)	0.04–0.11	0.01 ± 0.01 (1)	ND–0.02		ND	0.01 ± 0.01 (1)	ND–0.02	0.05 ± 0.01 (4)	0.03–0.07
Nebraska	8	0.06 ± 0.01 (8)	0.03–0.14		ND		ND	0.01 ± 0.01 (2)	ND–0.05	0.02 ± 0.01 (5)	ND–0.06
Colorado (eastern)	6	0.09 ± 0.02 (6)	0.04–0.18	0.01 ± 0.00 (4)	ND–0.02		ND	0.02 ± 0.00 (6)	0.01–0.02	0.12 ± 0.02 (6)	0.05–0.18
Kansas	5	0.04 ± 0.01 (5)	0.03–0.05		ND		ND		ND	0.01 ± 0.00 (3)	ND–0.02
New Mexico (eastern)	3	0.16 ± 0.05 (3)	0.06–0.24		ND		ND		ND	0.10 ± 0.02 (3)	0.05–0.14
Oklahoma	7	0.11 ± 0.18 (7)	0.04–0.17	0.00 ± 0.00 (1)	ND–0.01		ND	0.00 ± 0.00 (2)	ND–0.01	0.06 ± 0.01 (7)	0.03–0.11
Texas	7	0.28 ± 0.11 (7)	0.04–0.69	0.02 ± 0.02 (3)	ND–0.11	0.00 ± 0.00 (1)	ND–0.02	0.00 ± 0.00 (1)	ND–0.01	0.07 ± 0.02 (7)	0.02–0.14
MALLARDS, PACIFIC FLYWAY											
Washington State	9	0.24 ± 0.07 (9)	0.10–0.77	0.02 ± 0.01 (7)	ND–0.06	0.00 ± 0.00 (1)	ND–0.01	0.01 ± 0.00 (5)	ND–0.01	0.04 ± 0.00 (8)	ND–0.11
Oregon	4	0.57 ± 0.22 (4)	0.18–1.20	0.02 ± 0.01 (3)	ND–0.05		ND	0.00 ± 0.00 (1)	ND–0.01	0.08 ± 0.01 (4)	0.05–0.11
Idaho	8	0.28 ± 0.07 (8)	0.13–0.71	0.02 ± 0.01 (6)	ND–0.05		ND	0.00 ± 0.00 (2)	ND–0.01	0.06 ± 0.01 (8)	0.03–0.12
Montana (western)	5	0.05 ± 0.01 (5)	0.04–0.07		ND		ND		ND	0.02 ± 0.01 (4)	ND–0.04

TABLE 1. (cont'd.). *Organochlorine residues in pools of wings from adult mallards and black ducks, 1979–80*

State	Number of Pools	Residues, ppm Wet Weight									
		DDE		DDT		TDE		Dieldrin		PCBs	
		$\bar{x} \pm$ SE	Range	$\bar{x} \pm$ SE	Range	$\bar{x} \pm$ SE	Range	$\bar{x} \pm$ SE	Range	$\bar{x} \pm$ SE	Range
Wyoming (western)	2	0.08 ± 0.03 (2)	0.05–0.10	ND		ND		ND		0.01 ± 0.00 (1)	ND–0.02
California	6	0.34 ± 0.10 (6)	0.06–0.72	0.01 ±0.00 (3)	ND–0.02	ND		0.01 ± 0.00 (3)	ND–0.02	0.05 ± 0.02 (6)	0.01–0.11
Nevada	2	0.12 ± 0.01 (2)	0.11–0.13	ND		ND		0.01 ± 0.01 (1)	ND–0.01	0.07 ± 0.01 (2)	0.06–0.07
Utah	2	0.31 ± 0.06 (2)	0.25–0.37	0.04 ± 0.03 (2)	0.01–0.06	ND		0.01 ± 0.01 (1)	ND–0.01	0.11 ± 0.07 (2)	0.04–0.18
Colorado (western)	3	0.60 ± 0.12 (3)	0.37–0.72	0.02 ± 0.01 (2)	ND–0.04	ND		0.01 ± 0.00 (2)	ND–0.01	0.05 ± 0.02 (3)	0.02–0.07
Arizona and New Mexico (western)	3	1.22 ± 1.03 (3)	0.16–3.28	0.02 ± 0.01 (2)	ND–0.04	0.01 ± 0.01 (2)	ND–0.03	0.04 ± 0.02 (2)	ND–0.07	0.27 ± 0.21 (3)	0.03–0.69

NOTE: Means and standard error were rounded off if the third place was five or more. Values in parentheses are number of pools that contained the residue. ND = not detected at 0.01 ppm.
[1] One or more of these pools contained fewer than 25 wings.

(Table 2). The highest level of dieldrin was 1.18 ppm in a pool from Alabama (Table 1). PCBs were detected in all pools from the Atlantic Flyway and were found in at least 90% of the pools from the other three flyways (Table 2). This is a significant increase ($P < 0.05$) in the percentage occurrence of PCBs over that reported for the 1976–77 hunting season (Table 2). The highest residues of PCBs were 1.80 ppm in a pool of black duck wings from New York and 1.62 ppm in a pool of mallard wings from North Carolina. Three pools from the Pacific Flyway, two from the Central Flyway, and one from the Mississippi Flyway did not have PCB residues at the 0.01-ppm limit of detection (Table 1).

In addition to the organochlorine compounds listed in Table 1, heptachlor epoxide, chlordane isomers, and hexachlorobenzene (HCB) were found in duck wings, but less frequently. Residues of these three compounds seldom exceeded 0.1 ppm, so these data were not included in Table 1. The percentage occurrence of these three compounds and the percentage occurrence of mirex and endrin are presented in Table 2 and compared with the 1976–77 wing data. Hexachlorocyclohexane, lindane, and toxaphene residues were found in only three pools at the 0.01-ppm level.

Means of DDE, DDT, TDE, dieldrin, and PCBs in the 1976 and 1979 collections are presented by flyways in Table 3. To compare these residues with the data pre-

TABLE 2. *Comparison of the percent occurrence of organochlorine residues in duck wings by flyway for the two collection periods of 1976–77 and 1979–80*

Species	Year of Collection	No. of Pools	Organochlorine Residues, ppm Wet Weight [1]									
			DDE	DDT	TDE	Dieldrin	PCBs	Heptachlor Epoxide	Mirex	Endrin	HCB	Chlordane Isomers
ATLANTIC FLYWAY												
Black duck	1976–1977 [2]	32	100_a [3]	69_a	66_a	84_a	100_a	34_a	19_a	3_a	16_a	59_a
Black duck	1979–1980	24	100_a	38_b	29_b	58_b	100_a	4_b	13_a	0_a	21_a	58_a
Mallard	1976–1977	20	100_a	60_a	50_a	85_a	100_a	50_a	50_a	5_a	10_a	55_a
Mallard	1979–1980	29	100_a	52_b	17_b	62_b	100_a	14_b	3_b	3_a	3_b	48_b
MISSISSIPPI FLYWAY												
Mallard	1976–1977	69	100_a	87_a	38_a	78_a	61_a	45_a	29_a	4_a	7_a	22_a
Mallard	1979–1980	64	100_a	28_b	13_b	64_b	98_b	28_b	2_b	8_b	2_b	16_a
CENTRAL FLYWAY												
Mallard	1976–1977	56	100_a	79_a	45_a	64_a	13_a	48_a	14_a	2_a	9_a	14_a
Mallard	1979–1980	54	100_a	22_b	2_b	22_b	90_b	30_b	0_b	0_a	4_b	7_b
PACIFIC FLYWAY												
Mallard	1976–1977	50	100_a	92_a	58_a	62_a	14_a	32_a	4_a	0_a	24_a	14_a
Mallard	1979–1980	44	100_a	57_b	7_b	39_b	93_b	23_b	0_a	0_a	23_a	5_b

[1] Detection limit = 0.01 ppm.
[2] Data taken from White *(8)*.
[3] 1979–80 percent occurrence is significantly different ($P < 0.05$) than 1976–77 percent occurrence where subscript letters (a or b) differ.

TABLE 3. *Means and standard errors of organochlorine residues in waterfowl wing pools by major flyway, 1976 and 1979*

Species	Flyway	Year	No. of Pools	Residues, ppm Wet Weight				
				DDE	DDT	TDE	Dieldrin	PCBs
Black duck	Atlantic	1976 [1]	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)
		1979	24	0.32 ± 0.04 (24)	0.02 ± 0.00 (9)	0.04 ± 0.03 (7)	0.03 ± 0.01 (14)	0.63 ± 0.09 (24)
Mallard	Atlantic	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)
		1979	29	0.27 ± 0.03 (29)	0.02 ± 0.01 (15)	0.01 ± 0.00 (5)	0.05 ± 0.03 (18)	0.45 ± 0.07 (29)
Mallard	Mississippi	1976	69	0.25 ± 0.04 (69)	0.07 ± 0.01 (60)	0.05 ± 0.03 (26)	0.05 ± 0.01 (54)	0.23 ± 0.03 (42)
		1979	64	0.17 ± 0.03 (64)	0.05 ± 0.01 (18)	0.05 ± 0.02 (8)	0.05 ± 0.03 (41)	0.11 ± 0.02 (63)
Mallard	Central	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)
		1979	54	0.10 ± 0.02 (54)	0.03 ± 0.01 (12)	0.02 ± 0.00 (1)	0.02 ± 0.00 (12)	0.06 ± 0.01 (49)
Mallard	Pacific	1976	50	0.22 ± 0.04 (50)	0.06 ± 0.01 [2] (46)	0.03 ± 0.00 (29)	0.02 ± 0.00 (31)	0.16 ± 0.04 (7)
		1979	44	0.35 ± 0.08 (44)	0.02 ± 0.01 (25)	0.02 ± 0.01 (3)	0.02 ± 0.00 (17)	0.07 ± 0.02 (41)

NOTE: Values in parentheses are actual number of pools containing residues; means were calculated using these values.
[1] Data taken from White *(8)*.
[2] Significant difference ($P < 0.05$).

sented from the 1976 collection (*8*), the author calculated the mean values by using only the wing pools that contained the residues. A trend toward lower mean values for most of these residues in both the mallard and black duck wings was not significant ($P > 0.05$).

The only significant decline ($P < 0.05$) was DDT residues in mallard wings from the Pacific Flyway (Table 3). Residues of DDT, TDE, and dieldrin were all low in the four flyways, and the percentage occurrence of these contaminants has declined significantly ($P < 0.05$) since 1976. PCB residues were low in mallard wings from the Mississippi, Central, and Pacific Flyways, but their percentage occurrence increased significantly ($P < 0.05$) above the 1976 level (Table 2).

Conclusions

Mean values of DDE residues in mallard and black duck were not significantly ($P > 0.05$) lower than those reported for 1976 in all flyways. DDT, TDE, and dieldrin residues in duck wings have declined significantly ($P < 0.05$) in the percentage occurrence in all flyways. The decline of PCB residues in mallard wings from all flyways was not significant ($P > 0.05$). PCBs, however, occurred in a significantly ($P < 0.05$) larger percent of the 1979–80 pools than in the 1976 pools.

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HUMANS

Organochlorine Pesticide Residues in Human Milk Samples from Comarca Lagunera, Mexico, 1976

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ABSTRACT

Milk samples were obtained from 15 nursing mothers in the agricultural region of Comarca Lagunera, Mexico, and were analyzed for organochlorine pesticide residues. Nine different types of residues were found. Of these, p,p'-*DDE,* p,p'-*DDT, and β-BHC occurred most frequently. All samples had concentrations of DDT-derived compounds higher than the practical limit recommended by the U.N. Food and Agriculture Organization/World Health Organization for DDT in cows' milk. Residues of other chlorinated hydrocarbons were present at levels similar to those found in human milk in other developing countries.*

Introduction

In the developing countries, organochlorine pesticides are used in large quantities to control agricultural pests and the vectors of endemic diseases. Although there have been few studies to determine organochlorine residues in human milk samples, some studies have been carried out in Guatemala (*20, 28*), Portugal (*12*), and Argentina (*10*).

In spite of high production, import, and use of these compounds in Mexico, there had been no studies of their presence in human milk. The present study is a preliminary evaluation of those residues in human milk from Comarca Lagunera. This is an important agricultural region of Mexico, on the border of the states of Durango and Coahuila, where the principal crop is cotton.

Comarca Lagunera was selected because previous analyses have shown consistently high levels of organochlorine pesticide residues in foodstuffs and animal feeds (*3, 4*) and in human adipose tissue (*2*).

Methods and Materials

All solvents were distilled twice in all-glass systems and checked by a 100-fold concentration test. Florisil was standardized for oil retention ability and activity. Before use, all reagents were checked for electron-capturing impurities.

Fifteen human milk samples were collected during March 1976 from voluntary donors at the University Hospital in Torreón, the main city of Comarca. All donors had lived in the area for 4 or more years. Four donors were from medium-income homes and 11 were from low socioeconomic levels. Seven lived in urban areas and eight lived in rural areas of Comarca. Donors' ages ranged from 16 to 30 years, with infants ranging in age from 1 to 29 days. All samples were manually expressed directly into wide-mouth jars that had been thoroughly cleaned. Jars were closed with Teflon-lined caps and stored in a refrigerator until samples were analyzed.

Lipids were extracted at the School of Medicine in Torreón immediately after sampling was completed. The volume of each sample was measured and the lipids were extracted with a BD-1 solution (*15*) at 3:2 (v/v) sample:solution ratio. Extracted lipids were carefully transferred to clean vials and weighed. Extractable lipids averaged 1.91% ± 0.97%. Lipids were frozen and taken to the CIEA-IPN laboratories in Mexico City, where they were kept at −20°C until analysis.

Three sets of analyses were carried out; each was comprised of five samples. Along with each set, a blank and a sample of milk lipids fortified with 1 ppm β-BHC

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and 3.5 ppm *p,p'*-DDE (lipid basis) were also analyzed. Recoveries ranged from 96% to 103%.

The lipids were dissolved in *n*-hexane and transferred to a chromatographic column prepared with 10 g Florisil deactivated with 2% water. The column was eluted with 100 ml of a 70:30 (v/v) mixture of petroleum ether–CH_2Cl_2 (*7*). The eluate was concentrated carefully and the residue was dissolved in *n*-hexane for gas-liquid chromatographic (GLC) analysis. No further cleanup was necessary.

Identification and quantitation were carried out by GLC under the following conditions:

Chromatographs:	Varian Aerograph, Models 1440 and 2440
Detectors:	electron-capture tritium and scandium tritiide
Columns:	glass, 6-ft long by 2-mm ID, packed with either (a) 3% OV-101 or (b) 3% OV-210, both on 100–120-mesh Gas-Chrom Q
Temperatures:	column (a) 170°C column (b) 150°C
Carrier gas:	high-purity nitrogen flowing through (a) at 40 ml/min and through (b) at 35 ml/min

Qualitative identification was accomplished by comparison of retention times with those of known standards provided by the U.S. Environmental Protection Agency. Quantitation was based on relative peak heights of individual standard solutions of each compound. The minimum detectable level was 0.005 μg/g (extractable-lipid basis) for all compounds.

Identity was confirmed routinely by the multicolumn technique (*11*), using a column packed with a mixture of 2% QF-1 and 2% SE-30 on 100–120-mesh Gas-Chrom Q. Column temperature was 150°C and carrier gas was nitrogen flowing at 35 ml/min. All samples containing more than 0.5 μg/g (extractable-lipid basis) of *p,p'*-DDE and *p,p'*-DDT were confirmed by chemical derivation (*8*) and by thin-layer chromatography (TLC) (*7*). Samples containing above 0.2 μg β-BHC/g were confirmed only by TLC.

Results and Discussion

The number of chlorinated hydrocarbon residues per sample ranged from five to nine, with five to six compounds per sample occurring most often.

The following compounds were identified: hexachlorobenzene, α-BHC, β-BHC, *p,p'*-DDE, *p,p'*-TDE, *p,p'*-DDT, dieldrin, endrin, and heptachlor epoxide. Those found more frequently in concentrations higher than 0.01 μg/g were β-BHC, *p,p'*-DDE, and *p,p'*-DDT. However, *p,p'*-DDT was found in only 11 samples, whereas *p,p'*-DDE was present in all samples. Hexachlorobenzene and *p,p'*-TDE occurred at concentrations above 0.01 μg/g in only four and five samples, respectively; dieldrin, heptachlor expoxide, α-BHC, and endrin were found only in trace concentrations—below 0.01 μg/g. Among these, the most frequent was dieldrin, which was identified in 13 samples, and heptachlor epoxide, which was present in 7. These data are summarized in Table 1.

The means, ranges, and standard deviations for these compounds are presented in Table 2. These data are calculated both on an extractable-lipid basis (μg/g) and in whole milk (μg/ml). Only the results from samples with more than 0.01 μg/g of a given compound were considered for these calculations. Total equivalent DDT was obtained by multiplying the values for *p,p'*-DDE and *p,p'*-TDE by the appropriate factors before addition.

Among the compounds with high percent occurrences, *p,p'*-DDE was found at the highest mean concentration,

TABLE 1. *Occurrence of organochlorine pesticide residues in human milk samples from Comarca Lagunera, Mexico, 1976*

Compound	Total Positive Samples		Samples with Residue Levels Above 0.01 μg/g	
	n/N	%	n/N	%
Hexachlorobenzene	9/15	60	4/15	27
α-BHC	4/15	27	—	—
β-BHC	15/15	100	15/15	100
Dieldrin	13/15	87	—	—
Endrin	2/15	13	—	—
Heptachlor epoxide	7/15	47	—	—
p,p'-DDE	15/15	100	15/15	100
p,p'-DDT	15/15	100	11/15	73
p,p'-TDE	15/15	100	5/15	33

NOTE: n = number of positive samples; N = total number of samples.

TABLE 2. *Concentrations of organochlorine pesticide residues in human milk samples from Comarca Lagunera, Mexico, 1976* [1]

Compound	Concentrations of Residues μg/g	
	Extractable Lipid	Whole Milk
	$\bar{x} \pm$ SD (Range)	$\bar{x} \pm$ SD (Range)
Hexachlorobenzene	0.21 ± 0.23 (ND–0.48)	0.002 ± 0.002 (ND–0.004)
β-BHC	1.63 ± 0.94 (0.46–3.58)	0.030 ± 0.026 (0.007–0.100)
p,p'-DDE	10.35 ± 11.02 (1.36–36.01)	0.202 ± 0.266 (0.013–0.984)
p,p'-DDT	1.98 ± 1.70 (T–6.04)	0.049 ± 0.073 (T–0.243)
p,p'-TDE	0.56 ± 0.37 (T–1.06)	0.015 ± 0.016 (T–0.043)
Total Equiv. DDT [2]	13.18 ± 13.39 (1.51–43.86)	0.266 ± 0.348 (0.020–1.198)

NOTE: $\bar{x}$ = mean concentration; SD = standard deviation; ND = <0.005 μg/g extractable lipids; T = Trace (0.01 μg/g >T>0.005 μg/g extractable lipids).

[1] Calculations based on samples with residues >0.01 μg/g extractable lipids.

[2] DDT + 1.115 DDE + 1.11 TDE.

followed by *p,p'*-DDT and β-BHC. Total equivalent DDT ranged from 1.21 to 35.09 times the practical limit (1.25 μg/g, lipid basis) recommended by FAO/WHO for DDT alone or combined with TDE and DDE in cows' milk (*26*); the mean concentration of *p,p'*-DDT was 1.98 μg/g, 1.58 times the FAO/WHO limit. The concentrations of *p,p'*-DDE ranged from 1.08 to 28.81 times the limit. Therefore, concentrations of DDT-derived compounds in all samples were higher than the FAO/WHO practical limit. The mean concentration of β-BHC (1.63 μg/g) was equivalent to 8.15 times the limit of 0.2 μg/g recommended by FAO/WHO for the δ-isomer (lindane) in cows' milk (*26*). β-BHC was above this limit in all samples.

The finding of residues of the cyclodienic compounds dieldrin, heptachlor epoxide, and endrin in the human milks analyzed, although at low levels, is a matter of concern. These pesticides are being increasingly used in Mexico, even though their persistence and toxicological effects have caused their use to be severely restricted in other countries.

Also noteworthy is the presence of hexachlorobenzene residue, which heretofore has only been reported in developed countries (*1, 17, 22, 23*).

The mean value (lipid basis) of *p,p'*-DDE calculated as DDT (11.81 μg/g) represented 89.60% of the average total equivalent DDT. This could indicate that most of the DDT-derived material in the human milks analyzed originated in the food chain due to excessive past use of DDT in the region (*5*).

In general, the organochlorine residue levels found in the present study of human milk would be unacceptable in cows' milk in other countries.

The results of the present study and similar surveys in other countries are presented in Table 3. It is evident that the higher values for *p,p'*-DDE, β-BHC, and total equivalent DDT in human milk correspond to levels found in other developing countries such as Guatemala, Portugal, Argentina, and Chile.

Several other studies (*9, 19*) have indicated that high concentrations of organochlorine residues in human milk may adversely affect neonates. Other investigators have shown the effects of the chronic ingestion of low levels of some pesticides are more severe in young and malnourished animals (*6, 16*).

Mother's milk is an important source of nutrition for infants in the region studied, especially in the low socioeconomic groups in which malnourishment of mother and child is also frequent. In view of the high values obtained for organochlorine pesticide residues in human milk in the present study, further related research in this region and throughout Mexico is essential.

Acknowledgments

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TABLE 3. *Average concentrations of some organochlorine pesticide residues in human milk from various countries, 1965–79*

Country	Year	Concentrations in Whole Milk, μg/ml			
		β-BHC	*p,p'*-DDE	*p,p'*-DDT	Total Equiv. DDT
United States (*21*)	1965	—	—	0.08	0.12
Holland (*25*)	1971	0.004	0.03	0.016	—
Australia (*23*)	1975	—	0.080	0.015	—
Sweden (*27*)	1972	—	0.059	0.020	—
United States (*14*)	1977	0.003	0.035	0.008	—
Canada (New Brunswick) (*18*)	1974	—	0.035	0.013	—
Canada (*17*)	1979	0.002	0.035	0.006	—
New Guinea (Sepik) (*13*)	1972	—	0.096	0.181	—
New Guinea (Saidor) (*13*)	1972	—	0.002	0.001	—
Portugal (Lisbon) (*12*)	1974	—	0.223	0.100	0.323
Portugal (Bragança) (*12*)	1974	—	0.040	0.023	0.063
Guatemala (La Bomba) (*20*)	1973	—	1.02	1.00	2.15
Guatemala (La Bomba) (*20*)	1976	—	—	—	0.587
Guatemala (Guatemala City) (*??*)	1976	—	—	—	0.233
Argentina (*10*)	1974	0.042	0.092	0.046	0.140
Chile (*24*)	1978	—	0.15	0.092	0.25
Mexico (This Study)	—	0.030	0.202	0.049	0.266

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WATER

1,2-Dibromo-3-chloropropane Residues in Water in South Carolina, 1979–80[1]

George E. Carter, Jr., and Melissa B. Riley [2]

ABSTRACT

During 1979–80, a total of 236 water samples were collected from 205 sites in South Carolina. Well water, surface water (lakes, ponds, and rivers), and municipal water were sampled and analyzed for the soil fumigant 1,2–dibromo–3–chloropropane (DBCP). DBCP levels ranged from nondetectable to 0.05 μg/liter (ppb) in an area of nonuse (background). No municipal water samples in the state exceeded the background level. In the area of high use of DBCP, 37% of the surface water samples exceeded the background level, but none exceeded 0.4 μg/liter. Twenty-seven percent of the well water samples from the high-use area exceeding the background level, and 10.2% of the samples exceeded 1 μg/liter. All samples exceeding 1 μg/liter came from a small area within one county. The possible mode of contamination was not determined.

Introduction

Soil fumigation for nematode control is a key factor in a program against peach tree short life, a condition that has decimated southeastern peach orchards (*1, 5*). Both pre- and postplant treatments are required for growing healthy peach trees (*Prunus persica* (L.) Batsch) (*3*). 1,2-Dibromo-3-chloropropane (DBCP) is the postplant nematicide used to control ring (*Macroposthonia xenoplax Raski*) and root-knot (*Meloidogyne spp.*) nematodes. Peach trees have no resistance to either nematode, DBCP is the only pesticide cleared for postplant treatment of orchards, and no other pesticide has been effective for controlling the nematodes well enough to prevent premature death of peach trees. Low concentrations of DBCP have been reported in California groundwater samples (*4*), which led to questions of groundwater contamination in South Carolina. The purpose of the present study was to determine the levels of DBCP present in water samples collected in South Carolina.

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Materials and Methods

WATER SAMPLE COLLECTION

Three areas of South Carolina were selected for their DBCP usage: (1) Piedmont area, non-use; (2) Coastal area, scattered agricultural use; and (3) Sandridge area, extensive agricultural use. During 1979–80, three types of water samples were collected from each area as follows: well water from privately owned wells; surface water from ponds, rivers, and lakes; and water from homes supplied by municipal sources. Samples were collected in new canning jars which were discarded after one collection. Jars were rinsed with glass-distilled, pesticide grade ethyl acetate, covered with ethyl acetate-rinsed aluminum foil, and closed with jar caps and rings. Jars were filled to the top from home taps (well and municipal) or by submerging into ponds, rivers, and lakes, leaving no head space, and were placed in ice immediately after collection. The location of the sample and any information on the agricultural practices of the area were recorded at the time of collection. Sites yielding samples containing over 1 ppb DBCP were resampled to verify results.

EXTRACTION

This procedure was obtained from the California Department of Food and Agriculture (*2*) and was modified by the addition of a centrifugation step. Five glass beads, rinsed with ethyl acetate, were combined with a 160-ml water sample and 10-ml glass-distilled, pesticide-grade ethyl acetate in a round-bottom boiling flask that was attached to a modified Stark and Dean trap and condenser. The flask was placed in a heating mantle; full voltage was applied until the mixture began to boil and then was reduced to one-third maximum. The mixture was allowed to reflux 15 minutes or until the ethyl acetate was distilled over to the trap. The

heating mantle was turned off and the condenser was washed with distilled water. After 5 minutes, the distillate was removed and centrifuged 10 minutes at 17, 500g in a Sorvall RC2-B refrigerated centrifuge. The ethyl acetate layer was transferred to an ethyl acetate-washed, screw-cap tube to which a small amount of anhydrous sodium sulfate was added. An aluminum foil liner rinsed with ethyl acetate was placed between the test tube and the screw cap. Samples were kept in the freezer after extraction and before gas chromatographic analysis.

Glassware blanks were run by placing 30 ml ethyl acetate in the boiling flask of the extraction apparatus and refluxing it 15 minutes. A 10-ml quantity was then collected to be used as a glassware blank. Glassware was cleaned by placing it overnight in sodium dichromate–sulfuric acid cleaning solution, and then rinsing it three times with distilled water and ethyl acetate.

GAS CHROMATOGRAPHY

The concentration of DBCP in water samples was determined by use of a Varian 3700 gas chromatograph connected to a CDS111 chromatography data system and recorder. Instrument parameters and operating conditions were as follows:

Detector:	^{63}Ni electron-capture
Column	2 m by 2 mm glass, packed with 10% OV-101 on 80–100-mesh Chromosorb W-HP
Temperatures:	column: 100°C for 3 min, then increased column: 4°/min for 7 min, then increased column: 18°/min for 5.66 min, and then held column: at 230°C for 4.33 min injector 220 C detector 280°C
Carrier gas:	nitrogen flowing at 30 ml/min
Retention time:	5.75 minutes for DBCP
Detection limit:	0.008 ppb

Recovery percentage was determined from the mean value of four fortified samples (50 ng DBCP added to 160 ml distilled, deionized water). This value, 88%, was used to calculate DBCP present in the samples. Levels of DBCP were calculated by the data system, using an external standard method of calibration.

DBCP standards were prepared in ethyl acetate, using a 99.6% pure analytical standard (AMVAC Chemical Corp.); standards and sample extracts were kept in different freezers. The gas chromatograph was calibrated using a 5 pg DBCP/µl standard as the first sample every day. Ethyl acetate blanks were run after every sample containing DBCP.

Either of the following apparatus and operating conditions was used to confirm the presence of DBCP:

Column	2 m by 2 mm glass, packed with 3% OV-210 on 80–100-mesh Chromosorb W-HP
Temperatures, °C	column 75 injector 270 detector 250
DBCP retention time:	2.1 min
OR	
Column:	2 m by 2 mm glass, packed with 2% DEGS on 80–100-mesh Chromosorb W, A/W
Temperatures, °C	column 100 injector 250 detector 250
DBCP retention time:	1.2 min
Carrier gas (both columns):	nitrogen flowing at 40 ml/min
Detection limit (both)	0.008 ppb

MASS SPECTROMETRIC ANALYSIS FOR DBCP

Selected samples were taken to Research Triangle Institute in Research Triangle Park, North Carolina, for analysis. Methane-enhanced negative ion chemical ionization mass spectrometric analysis was conducted on one of two gas chromatograph-mass spectrometers under the following conditions:

GC/MS:	LKB 2091
Column:	25-m WCOT SE-30 capillary
Temperatures, °C:	column: 100°C for 4 min, then 8° min to 240°C injector 210 ion source 210
Electron energy:	50 eV
Box current:	250 µA
Accelerating voltage:	3.5 kV
OR	
GC MS:	Finnigan Model 4000/PPNICI
Column:	25-m SP2100 capillary
Temperatures, °C:	column 70° for 1 min, then 8°/min to 250°C injector 250 ion source 250
Electron energy:	70 eV

The appearance of the characteristic ions (m/z 79, 81, 158, 160, and 162) in the correct retention window was used to confirm the presence of DBCP in the samples. Tentative confirmation was based on the observation of the m/z 79 and 81 ions in the correct retention window. Selected samples were concentrated before analysis by placing the sample in ice with a stream of nitrogen flowing over it.

Results and Discussion

Distribution of the 236 water samples is shown in Table 1. Samples from the Piedmont area (non-use of DBCP) appeared to contain a background level of DBCP or a compound indistinguishable from DBCP at levels from 0.008 ppb (limit of detection) to 0.05

TABLE 1. *Distribution of water samples analyzed for DBCP in South Carolina, 1979–80*

Area	Type of Water	No. of Sites	No. of Samples
Piedmont (Non-use)	well	8	8
	surface	15	18
	municipal	3	3
Sandridge (High use)	well	49	63
	surface	46	60
	municipal	8	8
Coastal (Scattered use)	well	24	24
	surface	33	33
	municipal	19	19

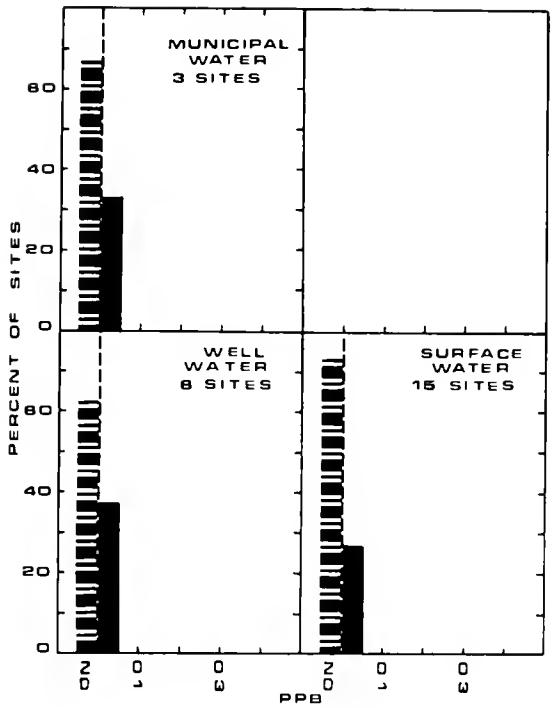

FIGURE 1. *Percentage of sites showing DBCP contamination (ppb) in Piedmont area of South Carolina. Detection limit = 0.008 ppb. ND represents no detectable residue of DBCP.*

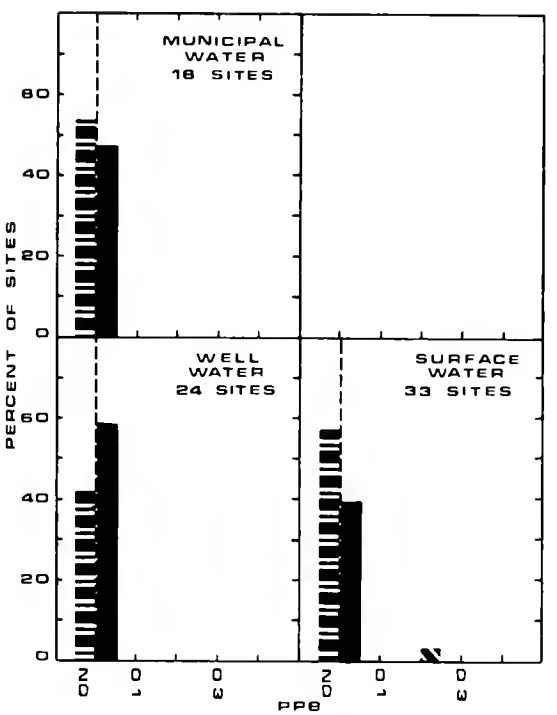

FIGURE 2. *Percentage of sites showing DBCP contamination (ppb) in Coastal area of South Carolina. Detection limit = 0.008 ppb. ND represents no detectable residue of DBCP.*

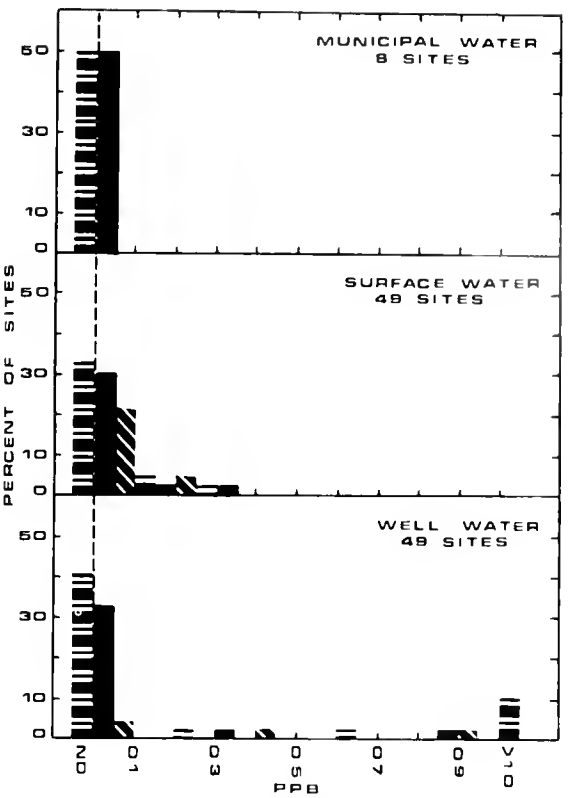

FIGURE 3. *Percentage of sites showing DBCP contamination (ppb) in Sandridge area of South Carolina. Detection limit = 0.008 ppb. ND represents no detectable residue of DBCP.*

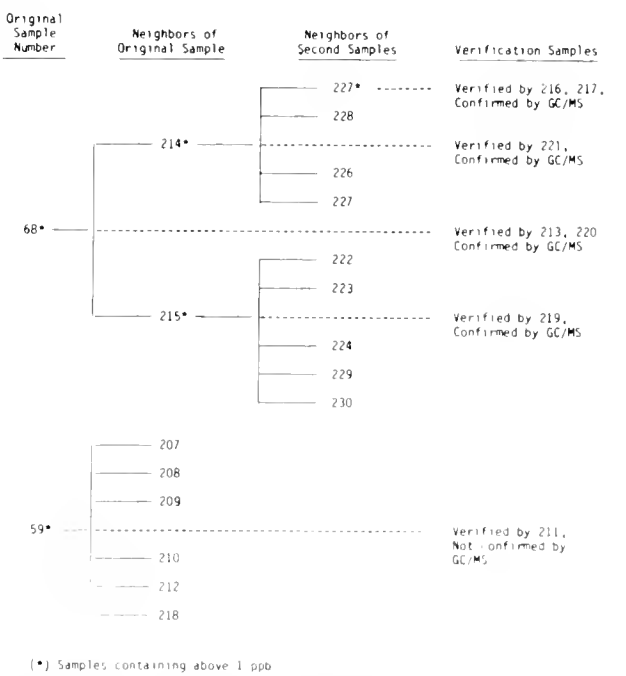

FIGURE 4. *Treatment of original water samples containing above 1 ppb DBCP (numbers indicate sample numbers).*

ppb (Figure 1). Although the compound was tested under two sets of gas chromatographic conditions and at significantly different polarities, and on the mass spectrometer, the low level prevented positive identification. Levels of DBCP up to 0.05 ppb were therefore considered to be background levels.

In the coastal area of South Carolina (scattered use of DBCP), no well water or municipal water sample and only one surface water sample exceeded the background level (Figure 2). Samples were obtained in the Sandridge area of South Carolina (high use of DBCP) showed a greater variability in DBCP concentrations (Figure 3). No municipal water sample exceeded the background level, but surface and well water samples varied from none to more than 1 ppb. Seventeen surface water samples in the Sandridge area contained DBCP, but none were above 0.04 ppb, and 10 were below 0.1 ppb.

Five well water samples contained greater than 1 ppb DBCP. All of these samples were verified by resampling at a later date. Two of the sites were located in a random survey, and the remaining three were found when the nearest neighbors to the original samples were sampled, as shown in Figure 4. When the samples containing more than 1 ppb DBCP were tested by mass spectrometry, four of the five were confirmed to contain DBCP.

This study indicates that low levels of a material that is indistinguishable from DBCP may exist in groundwater where no agricultural use has occurred. This possibility must be considered when data concerning trace amounts of DBCP are analyzed. One must consider whether the material is authentic DBCP and, if so, whether it resulted from agricultural use.

Most samples from the high-use area did not exceed the background levels found in samples from the non-use area, but several well water samples from the high-use locality did exceed the background levels. Hydrology of the area, the nature of well construction, and use patterns of DBCP in the vicinity of the wells were not studied. Therefore, it is impossible to conclude that contamination in this area was due to agricultural application of products containing DBCP. Further study is necessary to identify the source of contamination in these five wells.

Acknowledgments

Authors appreciate the assistance of Edo Pellizzari and Ken Tomer of the Research Triangle Institute in conducting the mass spectrometer analyses.

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APPENDIX

Chemical Names of Compounds Discussed in This Issue

LACHLOR	2-Chloro-2',6'-diethyl-*N*-(methoxymethyl)acetanilide
LDRIN	Hexachlorohexahydro-*endo, exo*-dimethanonaphthalene 95% and related compounds 5%
ROCLOR 1016 or 1242	PCB, approximately 42% chlorine
ROCLOR 1242	PCB, approximately 42% chlorine
ROCLOR 1246	PCB, approximately 46% chlorine
ROCLOR 1254	PCB, approximately 54% chlorine
TRAZ'NE	2-Chloro-4-(ethylamino)-6-(isopropylamino)-*s*-triazine
HC (Benzene Hexachloride)	1,2,3,4,5,6-Hexachlorocyclohexane (mixture of isomers)
HLORDANE	Technical: 60% octachloro-4,7-methanotetrahydroindane and 40% related compounds
ANAZINE	2-[[4-Chloro-6-(ethylamino)-*s*-triazin-2-yl]amino]-2-methylpropionitrile
DE	Dichlorodiphenyldichloroethylene (degradation product of DDT)
DT	Dichloro diphenyl trichloroethane. Principal isomer present (*p,p'*-DDT; not less than 70%): 1,1,1-trichloro-2,2,-bis(*p*-chlorophenyl)ethane
IELDRIN	Hexachloroepoxyoctahydro-*endo,exo*-dimethanonaphthalene 85% and related compounds 15%
NDRIN	Hexachloroepoxyoctahydro-*endo,endo*-dimethanonaphthalene
CB	Hexachlorobenzene
EPTACHLOR EPOXIDE	1,4,5,6,7,8,8-Heptachloro-2,3-epoxy-3a,4,7,7a-tetrahydro-4,7-methanoindan
INDANE	*Gamma* isomer of benzene hexachloride (BHC)
IREX	Dodecachlorooctahydro-1,3,4-metheno-1*H*-cyclobuta[cd]pentalene
CBs (Polychlorinated Biphenyls)	Mixtures of chlorinated biphenyl compounds having various percentages of chlorine
DE	Dichloro diphenyl dichloroethane (1,1-dichloro-2,2-bis (*p*-chlorophenyl)ethane, principal component)
OXAPHENE	Technical chlorinated camphene (67-69% chlorine)

ERRATUM

Pesticides Monitoring Journal, Volume 15, Number 2, page 78, of the article "Chlorinated Hydrocarbon Pesticides in Blood of Newborn Babies in India" by M. K. J. Siddiqui et al. Line 9 in the right column and Tables 1–3 should be corrected to read as follows:

There was a significant difference ($P < 0.005$) in total DDT residues by area of residence, but a slightly higher concentration of DDE was estimated in urban subjects, . . .

TABLE 1. *Organochlorine pesticides detected (ppb) in cord blood collected at term from 100 pregnant women, by age group*

Pesticides Detected	Women 18–25 Years Old (58 Cases)			Women 26–34 Years Old (42 Cases)		
	Range	Arithmetic Mean	SE	Range	Arithmetic Mean	SE
Total BHC	6.9–278.3	32.97	16.89	2.0–507.84	45.79	5.90
Lindane*	1.28–78.69	10.27	2.18	3.10–175.73	14.99	1.23
p,p'-DDE	1.02–850.0	12.33	1.98	2.05–78.14	23.10	4.75
p,p'-DDD	ND–48.21	5.84	1.25	ND–48.21	8.01	2.85
p,p'-DDT**	ND–140.0	7.30	2.32	ND–57.52	22.13	2.37
ΣDDT[1]	2.73–1029.85	59.65	25.51	4.59–149.62	51.18	8.51

*, ** Statistically significant ($P<0.05$ and 0.005, respectively).
[1] ΣDDT=total DDT equivalent.

TABLE 2. *Organochlorine pesticides detected (ppb) in cord blood collected at term from 100 pregnant women, by dietetic habit*

Pesticides Detected	Vegetarian Diet (36 Cases)			Nonvegetarian Diet (64 Cases)		
	Range	Arithmetic Mean	SE	Range	Arithmetic Mean	SE
Total BHC	6.9–278.43	38.3	7.29	2.0–507.84	35.64	3.13
Lindane	1.28–78.68	12.47	0.34	1.8–175.73	11.41	1.10
p,p'-DDE	1.02–850.0	15.33	3.26	1.9–150.0	20.53	4.39
p,p'-DDD	ND–48.21	6.55	1.85	0.89–32.09	8.49	1.80
p,p'-DDT	ND–55.56	14.89	3.05	1.78–140.0	17.08	3.55
ΣDDT	4.03–1029.85	62.22	8.50	2.73–240.41	50.07	7.78

TABLE 3. *Organochlorine pesticides detected (ppb) in cord blood collected at term from 100 pregnant women, by area of residence*

Detected Pesticides	Urban Population (48 Cases)			Rural Population (52 Cases)		
	Range	Arithmetic Mean	SE	Range	Arithmetic Mean	SE
Total BHC*	2.0–507.84	47.38	13.87	3.0–76.97	27.06	2.31
Lindane**	1.28–175.73	16.94	0.72	1.8–33.43	8.88	1.63
p,p'-DDE	1.02–257.50	22.81	7.05	2.2–850.0	15.48	4.38
p,p'-DDD	ND–48.21	7.33	3.88	ND–32.09	6.25	1.43
p,p'-DDT	0.5–50.23	13.71	2.19	ND–140.0	17.08	4.43
ΣDDT***	2.73–338.43	41.60	10.88	7.14–1029.85	68.23	13.84

*, **, *** Statistically significant ($P<0.05$, 0.05, and 0.005, respectively).

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).

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