SPECIAL REPORT ON POLYCHLORINATED BIPHENYLS (PCBs)

Polychlorinated biphenyls are chemical mixtures of chlorinated biphenyl isomers and find wide industrial application requiring heat stable, non-flamable liquids. PCBs in the USA are marketed as the Aroclor®-1200 series.

Residues of PCBs occur globally in fish and wildlife. In fish, residues of PCBs are principally the result of exposure to low levels of four Aroclor formulations: Aroclor® 1242 (used as a hydraulic fluid), Aroclor® 1248 (used in electronic and industrial electrolytic capacitors), Aroclor® 1254 (used in heat exchangers and dielectrics in large electrical transformers) and Aroclor® 1260 (a plasticizer). The routes by which these materials enter aquatic ecosystems are not well known.

Research problems receiving our immediate attention are: 1) PCB interferrence in analytical determinations for pesticide residues; 2) unknown biological effects of PCB exposures to aquatic organisms as well as significance of PCB residues in fish, and 3) the as yet undefined potential for PCB-pesticide interactions in fish and invertebrates.

Chemical Studies on PCBs

Analysis: The composition of the various Aroclor® formulations is best illustrated in Figures 9 and 10. The number above the chromatographic peak designates the number of chlorine atoms substituted on the biphenyl ring. The chromatograms were obtained by separating the Aroclor® formulations with a support-coated, open tubular capillary column in our Perkin-Elmer 270 gas chromatograph-mass spectrometer.

Techniques for the separation and analysis of PCB and pesticide residues were evaluated. The most satisfactory approach at present is to

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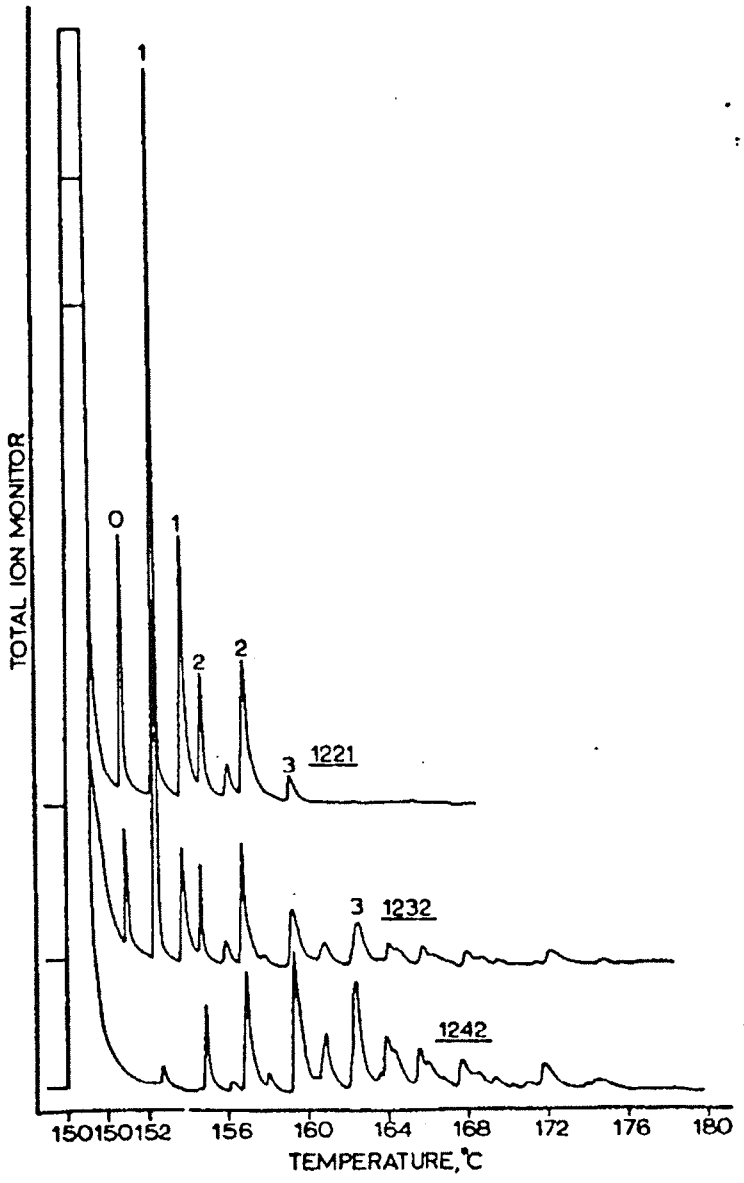

Figure 9. GC-MS of Aroclor® PCBs. SCOT GC-MS separation of Aroclor materials. The underlined numbers designate the Aroclor formulation and numbers above the peaks designate the number of chlorine atoms in the compound(s) determined from the mass spectrum. Temperature program rate 2° C/min, He 9 psig, 50' x 0.020" SE-30 SCOT column, PE-270 GC-MS.

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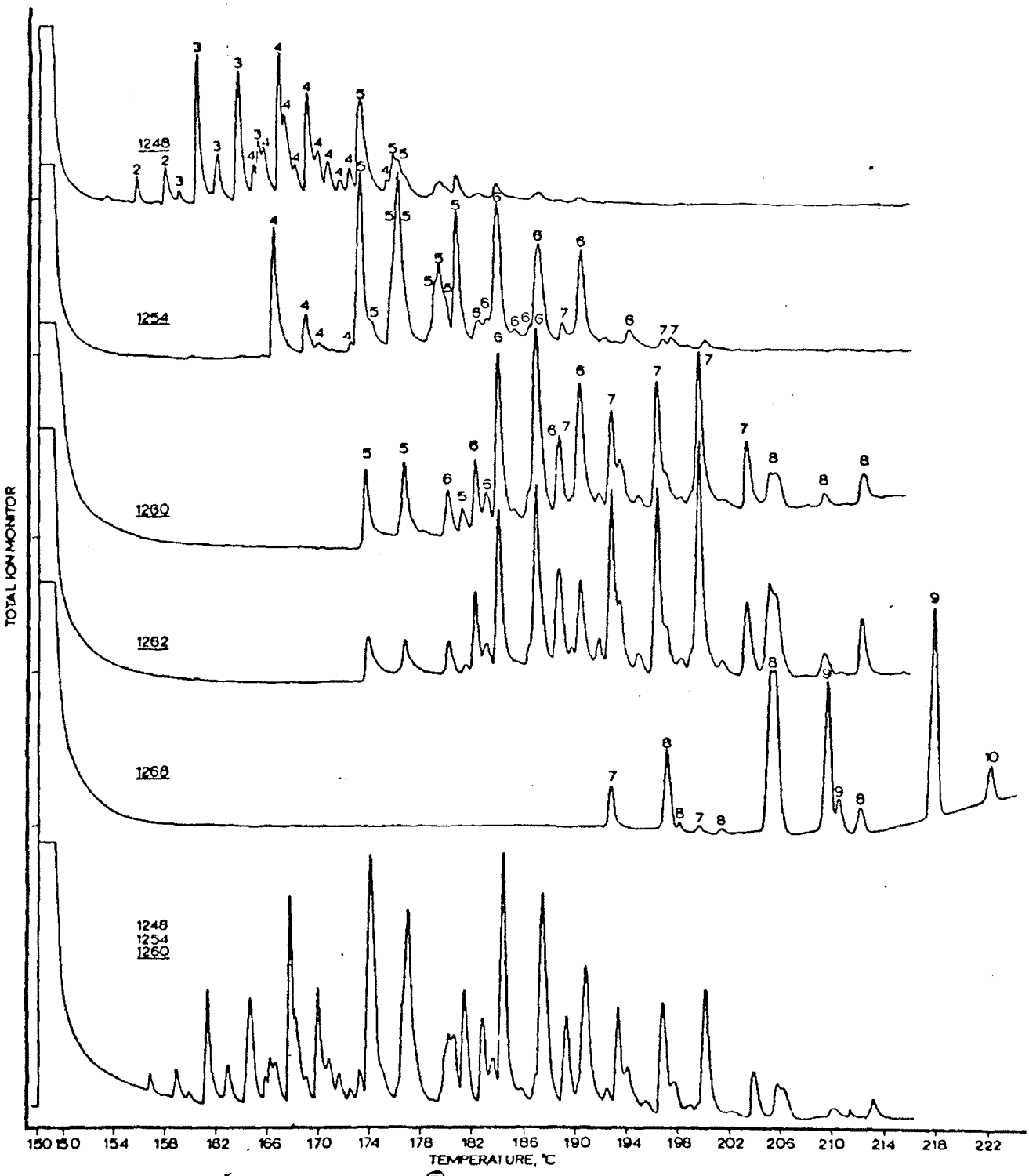

Figure 10. GC-MS of Aroclor® PCBs. SCOT GC-MS separation of Aroclor materials. The underlined numbers designate the Aroclor formulation and numbers above the peaks designate the number of chlorine atoms in the compound (s) determined from the mass spectrum. Temperature program rate 2° C/min, He 9 psig, 50' x 0.020" SE-30 SCOT column, PE-270 GC-MS.

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separate pesticides and Aroclor® formulations by silicic acid chromatography. We carefully evaluated the procedure developed by Armour and Burke (J.A.O.A.C. 53, No. 4, 761-763, 1970) and are satisfied that separation of PCBs and pesticides is adequate.

The response of two chlorine specific GC detectors, the electrolytic conductivity or microcoulometric, can be calibrated in ug or ng of compounds when the molecular weight of the component is known. Thus, the concentration of an Aroclor® component can be calculated when no standards are available using the following equation:

$$\mu g \text{ PCB component} = \frac{\text{MW}}{\text{No. of Cl}} \cdot \frac{\mu g \text{ Cl}}{35.5}$$

Determination of the amounts of Aroclor® 1248, 1254, and 1260 in residue extracts is possible because each Aroclor® formulation contains two major components which are not present in the next higher eluting Aroclor® formulation. This technique requires cleaned-up extracts. Pesticides should not be present in these extracts unless mass spectrometry is employed to confirm GC peak identity.

Standardization of various laboratory methods remains undefined for analysis and reporting residues of Aroclor® formulations in samples which contain more than one formulation or for samples in which the isomer composition is radically altered.

Preparation of ^{36}Cl-radiolabeled PCBs:--Radiolabeled ^{36}Cl PCB were developed and utilized in developing analytical methodology and in studies of biological uptake and metabolism. One-gram quantities of ^{36}Cl-radioactive labeled Aroclor® 1248 and 1254 were prepared by neutron irradiation in a nuclear reactor. These irradiated materials were cleaned-up using silicic

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acid chromatography. The radio-labeled materials were identical to the starting materials.

David L. Stalling
James N. Huckins

Biological Studies on PCBs

Acute toxicity of PCBs to fish:--The toxicity of the Aroclor® series was determined using the standard 96-hr static bioassay and cutthroat trout. Additional tests were also made with bluegills and channel catfish (Table 14). The solubilities of the Aroclor formulations in water are reported in the range of 0.1-0.3 µg/l.

The results of these tests indicate a decrease in acute toxicity for Aroclor® 1254 and higher. The PCB toxicity indicated by these tests is misleading in that most fish mortalities occurred in the last 24 hours of the test and the concentrations of the test solutions were considerably above the true solubilities. The toxicities of these compounds became more apparent in long term, intermittent-flow bioassays.

Donald V. Swedberg
Harry D. Kennedy

The oral toxicity of Aroclor® 1242 and 1260 to rainbow trout was greater than 1500 mg/kg (given per os for 5 days at 300 mg/kg/day).

Foster L. Mayer, Jr.

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Table 14. Acute toxicity[1] of several Aroclors to selected fishes.

Aroclor®	Species	Temperature (C)	96-Hr TL_{50} (µg/l)
1221	Cutthroat trout	8.9[2]	1,170
1232	" "	8.9	2,500
1242	" "	8.9	5,430
1248	" "	8.9	5,750
1254	" "	8.9	42,500
1260	" "	8.9	60,000
1262	" "	8.9	> 50,000
1268	" "	8.9	> 50,000
4465	" "	8.9	> 50,000
5442	" "	8.9	> 50,000
5460	" "	8.9	> 50,000
1248	Channel catfish	18.3[3]	6,000
1254	" "	18.3	12,000
1248	Bluegills	18.3[3]	278
1254	"	18.3	2,740

1/ Static bioassay

2/ Alkalinity, 150 ppm; pH 7.6

3/ Alkalinity, 35 ppm; pH 7.1

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Chronic toxicity of PCBs to fish:--Fifteen intermittent-flow bioassays were conducted with rainbow trout, channel catfish, and bluegills. The chemicals were Aroclor® 1242, 1248, 1254, 1260 and DDT. The trials were conducted at 20° C. However, Aroclor® 1248 was also tested at 27° C against channel catfish and bluegills (Table 15). Rainbow trout were the most susceptible to the Aroclor® compounds, followed by bluegills and channel catfish. Aroclor® 1248 was more toxic to all species tested than Aroclor® 1254. These tests served in setting guideline concentrations for chronic uptake studies. Further studies are required to establish the time-independent TL_{50}.

Foster L. Mayer, Jr.

Physiological effects of PCBs on fish:--We began studying chronic, sublethal effects of PCBs on fishes only recently and consequently we have limited observations. But, several inferences can be made at present. PCBs in fish food at concentrations known to occur in food organisms may well constitute a hazard to natural populations. For example, growth of lake trout was retarded by Aroclor® 1248 in the diet for 3 months. Concentrations of 1.2, 3.8, and 12 ppm decreased weight gain by 6, 10, and 28%, respectively, below that of controls. Growth of the high-exposure group was only about half that of the controls after 6 months. Conversely, thyroid activity, as indicated by 72-hr radioiodine uptake, was stimulated by PCB exposure (Figure 11). Serum cortisol concentrations ranged from 33 to 46% below that of the controls (see endocrine effects). Depressed growth rates and elevated thyroid activity imply metabolic inefficiency producing a "loading" stress that can adversely effect viability and reproductive success.

Blake F. Grant
Donald Swedberg

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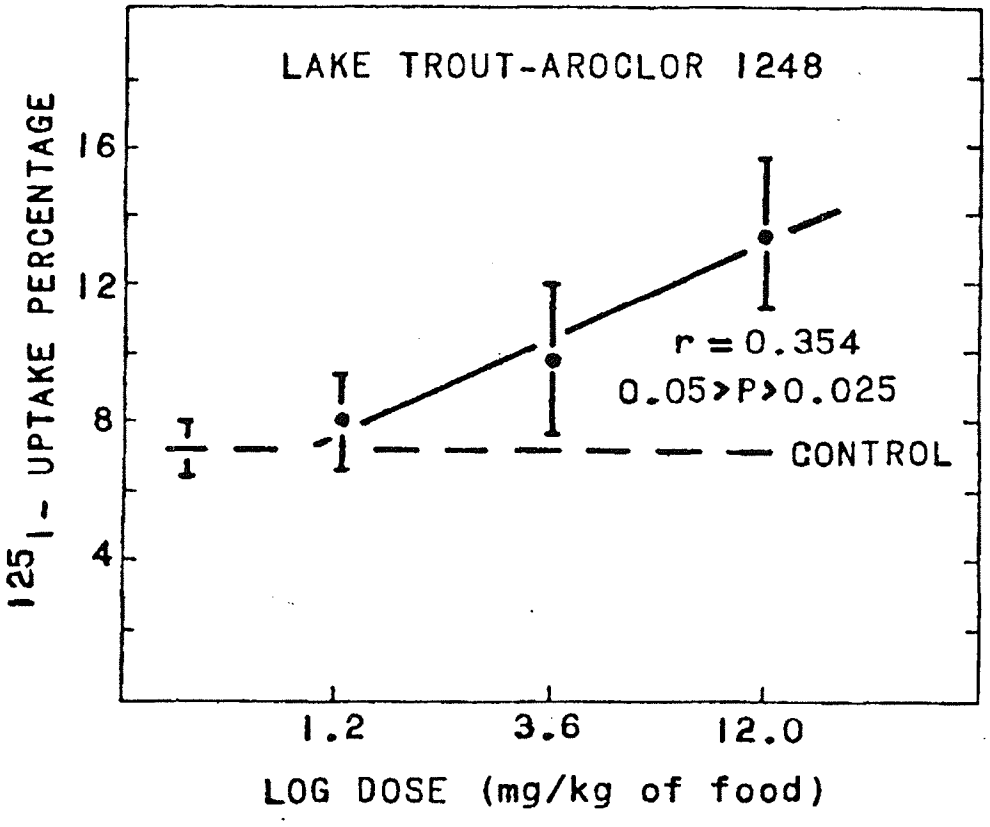

Figure 11. Thyroid stimulation by 6 month dietary exposure to Aroclor® 1248.

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Table 15. Intermittent-flow bioassays of Aroclors against three fishes.[1/]

Aroclor®	Species	TL_{50} (µg/l) after-- 5 days	10 days	15 days	20 days	25 days	30 days
1242[2/]	Rainbow trout	109	39	-	-	-	-
1248[2/]		51	-	-	-	-	-
1254		156	8	-	-	-	-
1260		-	240	94	21	-	-
DDT	Rainbow trout	2.26	0.87	0.26	-	-	-
1242	Bluegills	154	72	54	-	-	-
1248		307	150	75	10	-	-
1254		-	443	204	135	54	-
1260		-	-	-	245	212	151
1242	Channel catfish	-	174	107	-	-	-
1248		-	255	127	-	-	-
1254		-	-	741	300	113	-
1260		-	-	-	296	166	137
1248[3/]	Bluegills	137	76	-	-	-	-
1248[3/]	Channel catfish	-	94	57	-	-	-

[1/] Temperature, 20°C; alkalinity, 260; pH, 7.4

[2/] Preliminary bioassays

[3/] Temperature, 27°C

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Toxicity of PCBs to Invertebrates:--Tests were conducted to determine the toxicity of PCBs to selected invertebrates. Static and continuous-flow tests with invertebrates did not differ as much as with fish assays. In general, insects are much more resistant to the Aroclors than are crustacea (Table 16).

Herman O. Sanders

Bioconcentration of PCBs by aquatic microorganisms:--Aroclors, like some of the organochlorine insecticides, appear to be rapidly and greatly concentrated by various organisms. For example, preliminary experiments showed that Daphnia magna concentrated ^{36}Cl- Aroclor® 1254 by 45,000 times after only 48 hours of exposure to a concentration of 300 ng/l. These data closely parallel that obtained in DDT and aldrin investigations with Daphnia magna.

B. Thomas Johnson

Bioconcentration of PCBs by aquatic invertebrates:--The potential of 1254 to accumulate in fish-food organisms was investigated by exposing several species of aquatic invertebrates to a ^{36}Cl-labeled formulation of this chemical in a continuous-flow system. All invertebrates exposed to 1254 showed an initial period of rapid uptake and residue magnification many times greater than the concentrations in water. For example, late instar mosquito larvae, Culex tarsalis, which were exposed to 1.5 µg/l of 1254 accumulated a residue of 19 mg/kg within 24 hours. This represents a 12,600-fold increase over the residues in water. The tissue residues contained to accumulate until the seventh day of exposure when the mosquito larvae were transforming into pupae.

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Table 16. Aroclor® and DDT toxicity to invertebrates.

Compound	Organism[1/]	Bioassay type[2/]	Exposure (days)	TL_{50} (µg/l)
Aroclor® 1242	Crayfish	static	7	30
Aroclor® 1254	Crayfish	static	7	100
Aroclor® 1254	Crayfish	continuous-flow	7	80
DDT	Crayfish	static	4	100
Aroclor® 1242	Scud	continuous-flow	4	10
Aroclor® 1242	Scud	continuous-flow	10	5.0
Aroclor® 1248	Scud	static	4	52
Aroclor® 1254	Scud	static	4	2,400
DDT	Scud	static	4	3.2
DDT	Scud	continuous-flow	5	0.6
Aroclor® 1254	Glass shrimp	continuous-flow	7	3.0
DDT	Glass shrimp	static	5	1.0
DDT	Glass shrimp	continuous-flow	5	1.3
Aroclor® 1242	Dragonfly	static	7	800
Aroclor® 1254	Dragonfly	static	7	1,000
Aroclor® 1242	Damselfly	continuous-flow	4	400
Aroclor® 1254	Damselfly	continuous-flow	4	200
DDT	Damselfly	static	4	56

1/ Crayfish (Orconectes nais), Scud (Gammarus fasciatus), Glass shrimp (Palaemonetes kadiakensis), Dragonfly (Macromia sp.), Damselfly (Ischnura verticalis).

2/ Temperature, 15.6°C; alkalinity, 35 ppm; pH, 7.1

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In some experiments, we were able to continue the bioassays until an apparent plateau, or equilibrium concentration was reached within the organism. For example, the scud, Gammarus pseudolimnaeus, was exposed continuously to 1.6 µg/l of 1254 in water until residues reached an apparent equilibrium concentration at 14 days; total body residues at this time were 38 mg/kg, a concentration 27,000 times that in water. Once this equilibrium was reached within the organism, no further residue magnification was recorded after an additional 21 days of exposure (Figure 12). In similar experiments, early instar crayfish, Orconectes nais, exposed to 1.2 µg/l of 1254 accumulated residues at a slower rate than other invertebrates investigated. The crayfish were accumulating 1254 at a linear rate when the experiment was terminated after a 28-day exposure (Figure 13).

Herman O. Sanders

Residues:--Scud exposed to 1254 were analyzed by gas-liquid chromatography to investigate potential shifts in the residue composition which may have occurred as a result of metabolism. However, we found no significant alterations in the chemical, but some isomers were accumulated more than others. The most notable shift of residue components was a two-fold increase in concentrations of the lower chlorine isomers (tri- and tetrachlorobiphenyl isomers). The relative concentration of higher chlorinated isomers (penta- and hexachloro biphenyls) were decreased by one half.

David L. Stalling

James L. Johnson

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Analysis of bluegill and channel catfish exposed to Aroclor® 1248 and 1254 revealed the following high concentrations of PCB residues.

	PCB Residues (µg/g whole fish or µg/l water)							
	Aroclor® 1248				Aroclor® 1254			
Exposure (days)	water	channel catfish	water	bluegills	water	channel catfish	water	bluegills
28	13.3	500	4.9	177	4.1	177	6.8	44
60	13.3	958	4.9	312	4.1	312	6.8	87

Residues in bluegills were lower than for channel catfish. Aroclor® 1248 was concentrated to a greater extent than Aroclor® 1254, but no significant changes were observed in isomer composition. Residue concentrations in the fish were 6,300 to 71,400 times the exposure levels after 60 days.

Feeding studies with PCBs are being conducted to determine the significance of dietary uptake and to determine adverse effects on growth and other physiological functions. PCB residue analyses from fish in these studies have yet to be completed.

James M. Huckins

David L. Stalling

PCB-Pesticide Interactions:--No perspective interactions in fish has as yet been generated, but analyses of fish from natural ecosystems show that they contain PCB residues which are 2-5 times greater than the residues of the DDT complex. Research will be conducted to determine whether exposures of fish and invertebrate to PCBs intensifies the effects of PCBs on the chemical kinetics of pesticide uptake and storage. Information on the effects of PCB exposures on fish reproduction and the potential for interaction with certain organochlorine pesticides will be useful in estimating the environmental impact of these materials.

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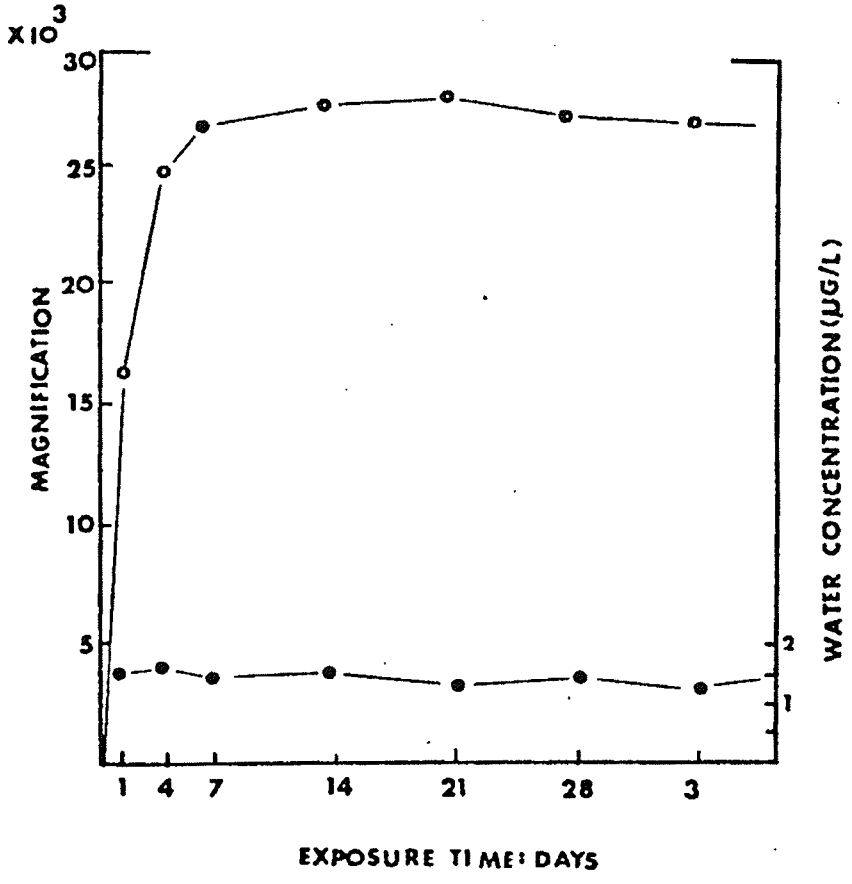

Figure 12. Biological magnification by scud, Gammarus pseudolimnaeus of ^{36}Cl-Aroclor® 1254 from water during 35 days exposure.

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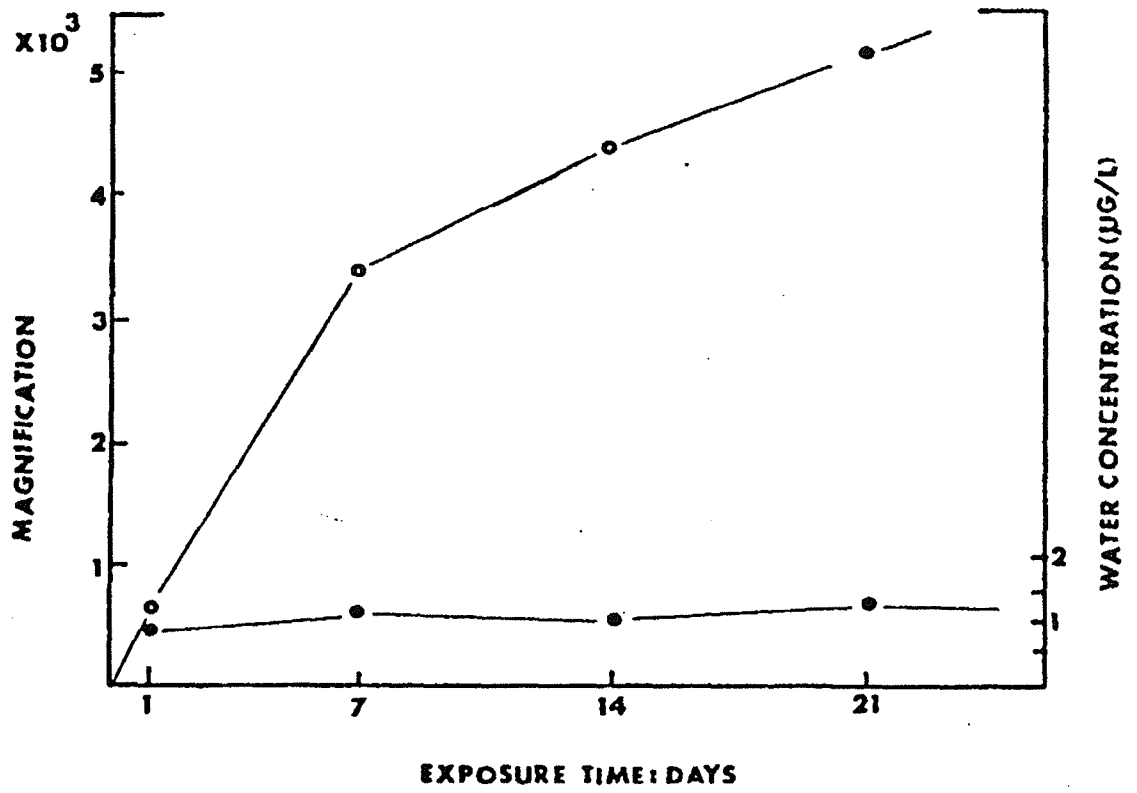

Figure 13. Biological magnification by crayfish Orconectes nais of ^{36}Cl-Aroclor® 1254 from water during 21 days of exposure.

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