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A STUDY OF THE DISTRIBUTION OF POLYCHLORINATED BIPHENYLS IN THE AQUATIC ENVIRONMENT

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Abstract.—Data gathered from monitoring activities and project studies indicate the ubiquitous occurrence and distribution of polychlorinated biphenyls in the aquatic environment. Residues have been detected in samples from 19 States, representing nearly every region of the country. Concentrations ranged from 0.1 to 1.0 μg/l in unfiltered water samples and 5.0 to 3,200 μg/kg in bottom sediments. PCB residues were also found in fish and aquatic plants. Samples were prepared by the same techniques used for general chlorinated insecticide detection, with special attention to cleanup and separation of PCB's from other compounds. Basic identification and quantification were made by dual-column electron-capture gas chromatography and confirmed by gas chromatography—mass spectrometry whenever possible. The sampling program is expected to be broadened geographically in 1973 and increased in successive years in order to more adequately define the distribution of PCB residues in the major drainage basins of the United States.

During the past three years, polychlorinated biphenyls (PCB's) have been recognized as a major environmental contaminant. Their detection has caused widespread concern and has generated intense interest in data relating to the presence and effects of these compounds, particularly in the aquatic environment. First produced about 40 years ago, PCB compounds have become increasingly useful in such industrial applications as components in transformers and capacitors, heat exchangers, paints, inks, dyes, and dust control agents.

While much attention has been focused on the estimation of levels and potential hazards of PCB's in aquatic organisms, few data are available on the occurrence of PCB's in water and bottom sediments. The U.S. Geological Survey, through its water-quality-monitoring activities and water-resources-assessment projects, has been alert to the PCB problem since it was first reported by Widmark (1967). Although the Geological Survey has no nationwide PCB assessment program, sufficient data have accumulated from pesticide-residue programs to permit a preliminary assessment of PCB contamination of the Nation's hydrologic environment. The purpose of this paper is to present data gathered from these activities, showing the widespread occurrence of PCB's in significant concentrations in unfiltered surface water and ground water, bottom sediments, flora, and fauna.

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ANALYTICAL TECHNIQUES

PCB residues were analyzed by the multiple-pesticide residue methods for water, suspended sediment, and bottom material, as described by Goerlitz and Brown (1972). The analytical procedures include not only chlorinated pesticides, but also the general class of organochlorine compounds. Special attention was given to cleanup and separation of PCB's from coextractives.

Extraction of water, sediment, and biota

One-liter unfiltered water samples were collected in precleaned glass bottles and were extracted three times with hexane. The hexane portions were combined, dried with anhydrous Na_2SO_4, and concentrated to 1 ml before cleanup and analysis by electron-capture gas chromatography (ECGC).

Fifty-gram sediment samples (dry-weight basis) were extracted with an acetone-hexane solvent. The sediment is dispersed first in acetone, and hexane is added to recover the acetone together with the desorbed material. The extract is washed with distilled water, dried over Na_2SO_4, and concentrated to 5 ml for cleanup before ECGC analysis.

The two extraction procedures used for biota are described in an analytical manual issued by the Food and Drug Administration (1971). Fish samples were extracted with petroleum ether in a blender, whereas aquatic plants were extracted with acetonitrile. The chlorinated hydrocarbon fraction was partitioned between petroleum ether and acetonitrile, dried, and concentrated to a final volume of 5 ml.

Separation

Bottom-sediment, fish, and plant extracts were cleaned up with a technique developed by Law and Goerlitz (written commun., 1971). This technique requires less time and smaller

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volumes of solvents for elution than other widely used [illegible]. Liquid-solid column chromatography was employed, by use of two different types of semimicro columns in sequence, as shown in figure 1. Hexane extracts were first passed through an alumina column, and one fraction was further chromatographed on silica gel to separate PCB's from chlorinated insecticides. Successive chromatography on alumina and silica gel results in a simultaneous cleanup and separation of PCB's from the common insecticides, except dieldrin, and a slight overlap of pp' DDE. To achieve a reduction in background interference, mercury was added to remove sulfur from bottom-sediment extracts before they were applied to the silica column.

In order to insure reproducible chromatographic conditions, the activity of the adsorbents was carefully controlled. Water extracts were cleaned up on a deactivated alumina microcolumn (Law and Goerlitz, 1970). When PCB's were detected in the cleaned-up water extracts, they were also separated on a semimicro silica gel column.

Identification

Basic identification was made by dual-column ECGC (DC-200 and QF-1/OV-17) and confirmed by gas chromatography–mass spectrometry (GC–MS) when sample size and concentrations were sufficient. The amount of PCB's was

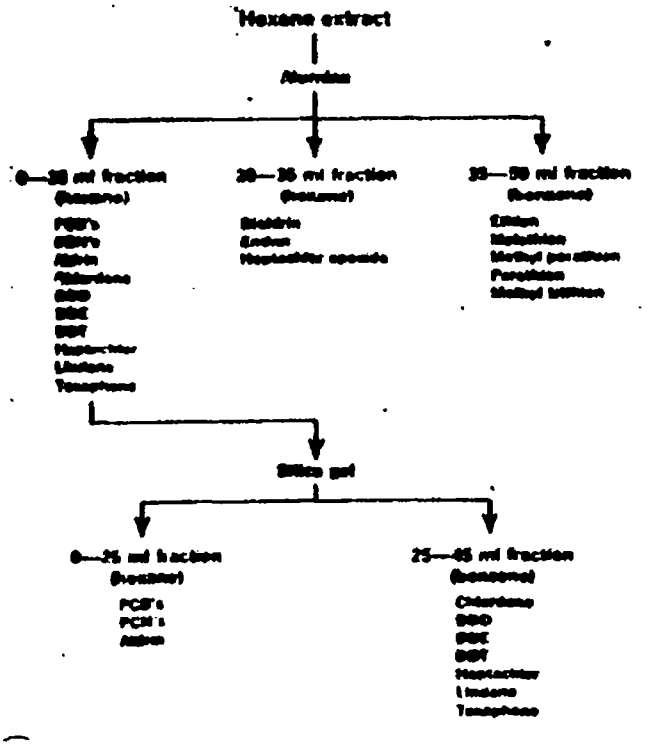

Figure 1.—Scheme for separating polychlorinated biphenyls (PCB's) and polychlorinated naphthalenes (PCN's) from pesticides.

determined by matching the unknown peaks on the chromatogram to the nearest fitting commercial formulation and measuring the areas of four corresponding peaks. Retention time and peak-area measurements were made with a digital electronic integrator. The lower detection limit for PCB residues was 0.1 μg/l in water and 5.0 μg/kg in bottom sediment. Reported levels are subject to considerable error because of the complexity of multiple peaks, some peak alteration, and the occasional presence of mixtures of PCB's in environmental samples. At best, reported values are estimates that may be as much as 50 percent in error.

DATA DESCRIPTION

Occurrences of pesticide residues in the aquatic environment have been documented over a period of years through monitoring programs of several Federal agencies. As early as 1957, studies of chlorinated hydrocarbon pesticides in major river basins were made by the Federal Water Pollution Control Administration, now a part of the Environmental Protection Agency, by use of the carbon-adsorption technique (Breidenbach and others, 1964). In 1964, interagency cooperation in pesticide-monitoring programs culminated in a proposal to begin a national monitoring program. The original program for water was described in 1967 in the first issue of the Pesticides Monitoring Journal (Green and Love, 1967). The purpose of this program, revised in 1971 (Felts and others, 1971), is to provide continuing information on the levels of pesticide residues in the water resources of the Nation and to identify possible problem areas. Because PCB's are analyzed by the multiple-pesticide residue techniques, routine reporting of these compounds has been incorporated into current pesticide programs. At present, samples from 20 of the 161 proposed network sites are collected and analyzed by the Geological Survey. All the samples are collected from sites located west of the Mississippi River and provide continuity with a network established to evaluate the quality of water used for irrigation (Brown and Nishioka, 1967; Manigold and Schulze, 1969). Budgetary restrictions have prevented further implementation of the network.

After development of the technique to separate PCB's from pesticide residues, examination for the presence of PCB's in water and suspended- and bottom-sediment samples collected for the national monitoring program began in January 1971. Funding has been requested to increase the number of network stations to 50 in 1973, and to 100 stations in 1974, allowing a better assessment of PCB's and pesticides in major drainage basins throughout the United States. Analysis of 194 water samples and 33 bottom-sediment samples revealed no positive identifications of PCB's; however, these data are not truly representative of the entire Nation because of the limited number of sites sampled.

In 1968, the Geological Survey began operation of a bench-mark network to provide basic hydrologic data on

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selected stream basins throughout the United States that are expected to remain in their present natural condition or are not expected to be significantly altered by man. Locations of the 57 bench marks established in 37 States are shown in figure 2.

To insure minimum interference by man, many of the hydrologic bench marks are in national parks, wilderness areas, State parks, national forests, and areas set aside for scientific study. A detailed description of the network basins, including drainage, climate, topography, geology, vegetation, hydrology, water quality, and manmade influences, can be found in a report by Cobb and Biesecker (1971). Data gathered from 46 of these sites are presented in table 1. Despite the careful screening for pristine location of bench-mark sites, two bottom-sediment samples analyzed in the 1972 water year contained PCB residues. A value of 5.2 µg/kg was measured in the sample from South Fork Rocky Creek near Briggs, Tex., and 8.8 µg/kg in the sample from Upper Twin Creek at McGaw, Ohio.

Table 1.—*Summary of PCB residue data, national hydrologic bench-mark network, January 1971–June 1972*

Type of sample		No. of samples	Occurrences	Concentration
Water	µg/l	54	0	.....
Bottom sediment	µg/kg	51	2	5.2, 8.8

The majority of the Geological Survey's water resources studies are conducted in cooperation with State water resources and pollution-control agencies, or in response to requests from other Federal agencies. PCB data from these programs in 35 States are presented in tables 2, 3, and 4. Water samples alone, because of the low water solubility of PCB's, are not a good indicator of the widespread occurrence of the compounds, and show an incidence of slightly over 5 percent. Unfiltered water samples from 12 of the 35 States had PCB concentrations ranging from 0.1 to 4.0 µg/l. However, a significant number of suspected traces of PCB's were not reported because of several analytical limitations. Generally, resampling of areas where PCB's were first detected revealed that the compounds were still present several months later.

Bottom sediments were collected concurrently with many of the water samples reported in table 2. These samples were taken from lakes and streams that drain a variety of land-use areas generally located away from industrial centers. The data in table 3 show that the bottom-sediment samples may be used as an indicator of PCB contamination in the Nation's hydrologic environment. Significantly, of samples collected at random from 16 States, 13 contained PCB's in the range 5.0–2,400 µg/kg. Across the Nation, one of every five bottom-sediment samples examined contained PCB's.

Data available from Florida (table 4) merit special attention, because they reveal the distribution of residues in several environmental components. Only 12 of 231 unfiltered water

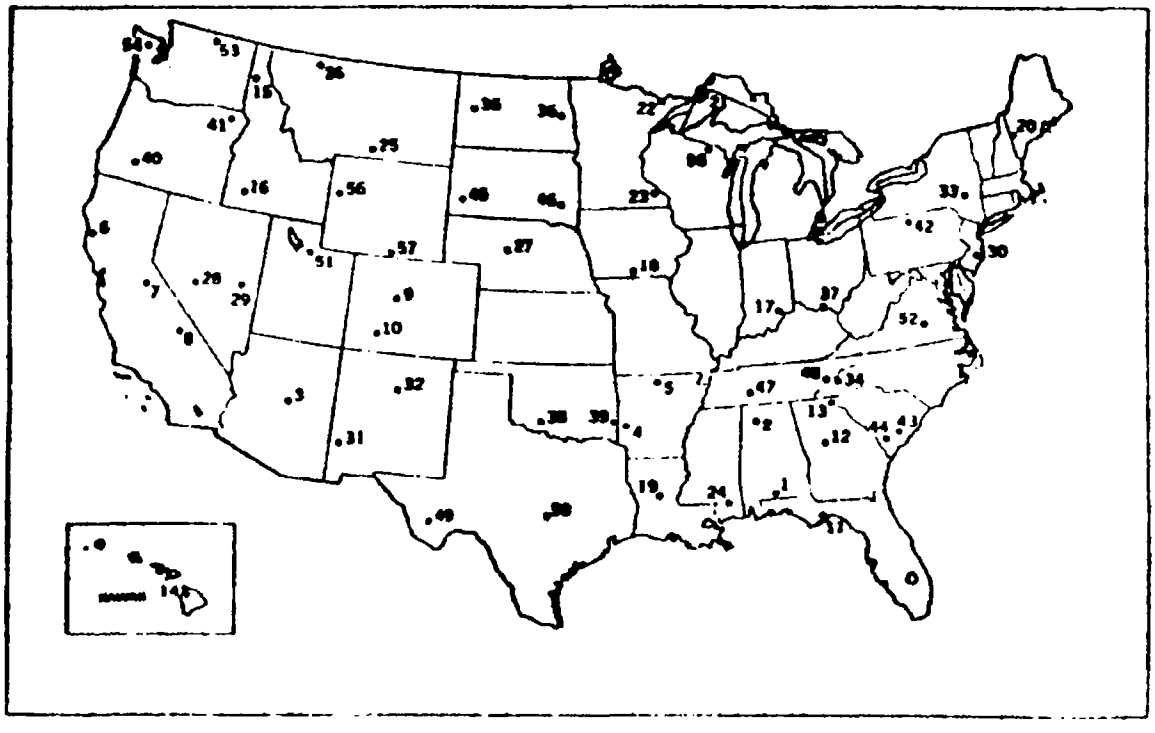

Figure 2.—Map showing location of hydrologic bench-mark stations. Numbers refer to list in Cobb and Biesecker (1971).

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Table 2.—*Summary of PCB residue data for surface and ground water, January 1971–June 1972*

State	No. of samples	Occurrences	Concentration (μg/l)	Median concentration (μg/l)
Alaska	3	0	....	....
Arkansas	8	0	....	....
Arkansas	22	0	....	....
California	161	2	0.1, 0.1	....
Colorado	32	1	.3	....
Connecticut	13	6	.1–.2	0.1
Hawaii	5	0	....	....
Illinois	26	0	....	....
Indiana	10	0	....	....
Kentucky	7	0	....	....
Louisiana	9	0	....	....
Maine	2	0	....	....
Maryland	6	1	.1	....
Massachusetts	5	1	.2	....
Michigan	2	0	....	....
Minnesota	3	2	.1, .3	....
Mississippi	8	0	....	....
Missouri	21	0	....	....
Montana	47	0	....	....
Nebraska	44	0	....	....
New Jersey	11	3	.1	.1
New Mexico	36	0	....	....
New York	223	52	.1–4.0	.3
North Dakota	48	0	....	....
Oklahoma	19	0	....	....
Oregon	13	0	....	....
Pennsylvania	2	1	.2	....
Puerto Rico	7	1	.1	....
South Dakota	18	0	....	....
Texas	660	12	.1–3.0	.4
Utah	4	1	.1	....
Washington	25	0	....	....
West Virginia	4	0	....	....
Wisconsin	3	0	....	....
Wyoming	18	0	....	....

Table 3.—*Summary of PCB residue data for bottom sediments, January 1971–June 1972*

State	No. of samples	Occurrences	Concentration (μg/kg)	Median concentration (μg/kg)
Alaska	3	0	....	....
Arkansas	23	4	20–2,600	60
California	13	3	20–190	85
Connecticut	1	1	40	....
Hawaii	4	0	....	....
Georgia	12	10	10–1,300	300
Maryland	11	5	10–1,200	20
Mississippi	8	2	50; 170	....
New Jersey	12	10	8–250	20
Oregon	4	2	15; 140	....
Pennsylvania	16	11	10–50	20
South Carolina	11	8	30–200	50
Texas	293	23	7.9–290	80
Virginia	10	8	5–80	40
Washington	10	0	....	....
West Virginia	2	1	10	....

samples contained PCB's ranging from 0.1 to 2.1 μg/l, but over 40 percent of the associated bottom sediments analyzed during the same period were contaminated with PCB's ranging from 5.0 to 3,200 μg/kg. The median PCB concentrations of 20 μg/kg and 40 μg/kg found in aquatic plants and fish, respectively, follow the scheme of the biological accumulation

Table 4.—*Summary of PCB residue data from selected sampling sites in Florida, January 1971–June 1972*

Type of sample	No. of samples	Occurrences	Concentration range	Median concentration
Water ..... μg/l ...	231	12	0.1–2.1	0.2
Bottom sediment . μg/kg ..	118	59	5–3,200	30
Flora ..... μg/kg ..	16	5	10–50	20
Fauna ..... μg/kg ..	43	36	6–1,000	40

of the DDT family in southern Florida (Feltz and Culbertson, 1972).

DISCUSSION AND EVALUATION

Preliminary data presented in this report indicate that significant concentrations of PCB's are widespread in the water resources of the Nation. However, there are some shortcomings of data compiled from pesticide-residue programs. First, there is the problem of nonrepresentative sampling within States and some repetition of sampling in a given basin. Second, the lower limit of detection for PCB residues on the basis of a one-liter water sample is inadequate for critical evaluation. Trace amounts of less than 0.1 μg/l were detected in a significant number of samples but were excluded from the tabulation because they could not be confirmed. Third, because of the low solubility of PCB's in water, especially the higher chlorinated ones, the bulk of PCB residues in streams are associated with suspended sediment and bottom material. Therefore, PCB concentrations may be expected to vary directly with the suspended-sediment concentration in the cross section of a stream. Most surface-water samples were collected by depth integration at the center of flow, which usually does not provide a representative sample of suspended sediment. Future investigations should be made with a depth-integrating sampler using the equal-transit-rate procedure (Feltz and Culbertson, 1972). In spite of these shortcomings, evidence for the ubiquity of PCB's in the hydrologic environment is clearly established.

As others have pointed out (Goerlitz and Law, 1972), polychlorinated naphthalenes (PCN's) are compounds that have uses similar to PCB's and may possibly be present in environmental samples. They can be separated from chlorinated hydrocarbon insecticides and are eluted in the same fraction as PCB's by alumina–silica gel column chromatography. Analysis of sediment samples collected from a southern Florida drainage ditch contained mixtures of PCN ranging from 1,250 to 5,000 μg/kg, whereas the water samples overlying the sediments averaged 5.7 μg/l. Identification was confirmed by both microcoulometry and GC–MS. This may possibly be the first evidence of the occurrence of PCN's in an environmental sample and illustrates the importance of developing analytical capability for the surveillance of other organochlorine compounds that may behave like chlorinated hydrocarbon pesticides.

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The entrance of PCB's into the aquatic environment is probably related primarily to low-temperature incineration of sulfur wastes, industrial waste disposal into waterways, and sewage outfalls. The highest levels are usually associated with industrial areas and nearby aquatic food chains. In contrast, we have noticed significant concentrations in the bottom sediments of drainage ditches, multipurpose canals, and suburban real estate lakes remote from major industrial and metropolitan areas. The presence of PCB's in real estate lakes was attributed to a variety of construction materials used in the housing industry. PCB's in surface and ground water used for public water supplies were detected through cooperative programs. The highest concentration was 4.0 μg/l in an untreated source for a city in the State of New York.

It is clear that the presence of PCB's and other organochlorine compounds in the aquatic environment merits continuing observation because of the limited evaluation that can be made from the meager data available. It is important to measure baseline levels of PCB's in streams and lakes in order to determine trends. Long-term monitoring on a systematic basis will provide the data necessary to assess the presence of PCB residues and concurrently reveal problem areas.

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