JOURNAL
water
pollution control
FEDERATION

POLYCHLORINATED BIPHENYLS IN TREATMENT PLANT EFFLUENTS

Douglas J. Dube, Gilman D. Veith, and G. Fred Lee

MAY 1974

Polychlorinated biphenyls in treatment plant effluents

DOUGLAS J. DUBE, GILMAN D. VEITH, AND G. FRED LEE

As METHODS of detection for chlorinated hydrocarbon pesticides have improved, polychlorinated biphenyls (PCB's), which are mixtures of chlorinated biphenyl compounds that have various percentages of chlorination, have been found in the environment. Interest in PCB's has increased because some of the physiological effects of the PCB isomers were thought to be similar to those of the chlorinated pesticides.

In Wisconsin, Veith [1] found PCB's in samples of the Milwaukee River near the city of Milwaukee. The concentrations of these PCB's (identified as Aroclor 1260) ranged from 0.02 to 0.25 μg/l. The PCB's were also found in selected wastewater treatment plant effluents along the Milwaukee River at concentrations of equivalent Aroclor 1254 from 0.12 to 0.25 μg/l.[1]

This study of wastewater treatment plant efflents was conducted in order to determine the degree of contamination in other wastewaters in southeastern Wisconsin.

STUDY AREA

Samples were collected at municipal treatment plants in 11 southeastern Wisconsin cities (Figure 1). Factors used to select these cities were population (1,500 to 100,000), volume of waste flow [140,000 gal/day to 13 mgd (530 to 49,205 cu m/day)], type of treatment, number and types of industries present, and type of receiving water. The characteristics of each municipality investigated are presented in Table I.

METHODS

Sampling. Glass containers were used throughout the study to minimize the possibility of sample contamination.

The samples were collected by immersing 2.5-l bottles in the waste stream at its entrance to the treatment plant, in the primary settling tank, in the trickling filter effluent, and in the final effluent of the treatment plant. The samples were conveyed to the State Laboratory of Hygiene, Madison, Wis., and extracted within 24 hr.

Extraction. The samples were batch extracted with redistilled hexane in separatory funnels. The samples were not filtered because they contained small amounts of solids. Hexane (100 ml) and the sample (800 ml) were placed in the funnel. After vigorous agitation for 1 min, the sample was passed to another funnel that also contained hexane (100 ml) and was again agitated for 1 min. The water portion was then discarded. This procedure was followed until 2,400 ml of the sample had been extracted. The extracts were combined and concentrated to 10 ml for cleanup.

Cleanup. The sample cleanup was done by means of liquid-solid chromatography of florisil.[2-7] The florisil column used was a 0.5-in. (1.27-cm) OD glass column with a 200-ml vessel on the top. The column was fitted with a fritted glass and Teflon stopcock at the bottom. The column was filled with 0.5 in. (1.27 cm) of anhydrous sodium sulfate (Na_2SO_4) and 19 g of florisil that had been activated at 105°C. The column was then covered with another 0.5 in. (1.27 cm) of anhydrous Na_2SO_4 to prevent deactivation from water in the sample extract.[4] The columns were prewetted with hexane, and the extracts (10 ml) were placed on the column and eluted with hexane ether mixture (200 mg, 94.6 percent) at 3 to 5 ml/min.[7] This procedure was designed to remove fats, waxes, oils, and pigments from the eluate.

In order to separate the PCB's from other pesticides, the eluate was concentrated to 2 ml and passed through a second florisil column. This column consisted of florisil in a 9-mm ID glass column with 65 ml of hexane as the eluate.[1] The extracts were then concentrated to appropriate volumes for analysis of the samples on the gas-liquid chromatograph.

Instrumentation. Analyses of the cleaned extracts to determine the presence of PCB's were made by means of gas-liquid chromatography (GLC) with an electron-capture detector. Gas chromatographic analyses were conducted on a gas chromatograph * equipped with a concentric tube, electron-capture detector (^{90}Sr). The columns used were 6 ft by 0.25 in. (18.3 m by 0.635 cm) glass coils packed with OV-101/Qf-1 (2:2 percent) and OV-101/DC-200 (2:3 percent) coated on Gas Chrom Q (80/100 mesh). The carrier gas (purified nitrogen) was maintained at a flow rate of 28 ml/min; and the injector, column, and detector temperatures were 210°, 200°, and 270°C, respectively.

From the gas chromatograms, preliminary identification of the PCB's was made by comparing chromatograms of standard Aroclors with the chromatograms of the samples to determine which Aroclor the sample most resembled. The determination of the concentration present was made by measuring the height of the most prominent peaks in each of the Aroclor standards

* Barber Coleman 5460 Pestalyzer, Barber-Coleman Co., Rockford, Ill.

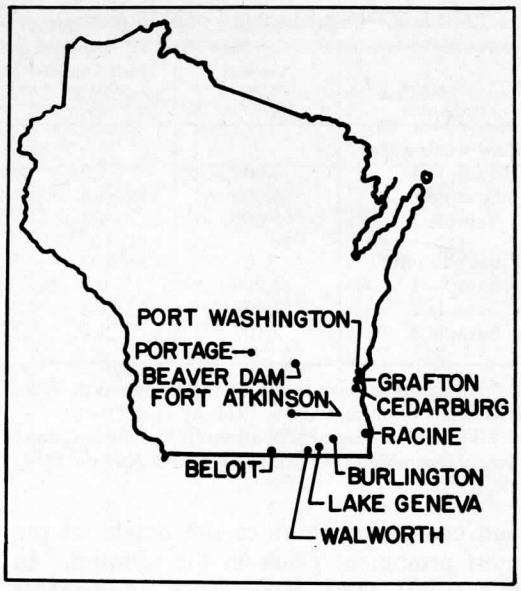

FIGURE 1.—Location of sampling sites in southeastern Wisconsin.

TABLE I.—Characteristics of Municipalities Investigated in this Study

Municipality	Population	Dominant Types of Industries	Flow (mgd)	Type of Treatment*
Beaver Dam	15,000	Paint, glass, foundry, metal fabricators	0.25	TF, C
Beloit	35,000	Printing, tool and die, chemical formulators, heavy equipment	5	AS, C
Burlington	6,000	Cement, metal work, abrasives, paint, fiberglass, electrical equipment	1.5	AS, C
Cedarburg	5,000	Casting, plastics, tool and die, printing, paint	1	TF, C
Fort Atkinson	8,000	Tool and die, printing, electrical equipment, paint	1.3	AS, C
Grafton	4,000	Steel products, welding and cutting, casting, printing, plastics, electrical equipment	0.8	AS, C
Lake Geneva	5,000	Plastics, electric fixtures, rubber products, tool and die	0.7	TF, C
Port Washington	8,500	Foundries, chemicals, clothes manufacturing	1	Pr, C
Portage	8,000	Concrete products, plastics, hosiery, reproducing paper	0.7	TF, C
Racine	100,000	Die and molding, precision stamping, casting, foundry, printing, electrical products, chemical treatment and formulators	11	AS, C
Walworth	1,500	None	0.14	TF

* TF = trickling filter; C = chlorination; D = digestors; AS = activated sludge; Pr = primary.
Note: Mgd × 3,785 = cu m/day.

TABLE II.—Reproducibility of PCB Analysis

Sample*	Volume Extracted (ml)	PCB Concentration† (μg/l)
Raw wastewater		
Sample 1	3,000	1.5
Sample 2	3,000	1.4
Sample 3	3,000	1.4
Final effluent		
Sample 1	2,500	0.9
Sample 2	2,400	1.1
Sample 3	2,400	1.0

* All samples were taken at the Cedarburg, Wis., treatment plant on Oct. 6, 1971, at 11:30 hours.

† The chromatograms of all samples collected most closely resembled the chromatogram of Aroclor 1254.

and comparing these to the height of the most prominent peaks in the samples. In this study, these peaks (PCB components numbers 4 and 7) lay on either side of the first doublet peak (isomer components numbers 5 and 6 in Figure 2). The difficulty of this method is apparent when a sample contains a mixture of two or more Aroclors and more detailed study is needed.

Recoveries of the samples used to test the precision of the Aroclor 1254 analyses are summarized in Table II. The analyses of the raw wastewater samples varied 7 percent from 1.4 μg/l, while analyses of the final effluent samples varied 10 percent from 1.0 μg/l.

Because of possible complications caused by the presence of more than one Aroclor and because of the possible interference of DDE, identification of some of the samples was confirmed using mass spectrometry. Confirmation was made on nine of the peaks from three of the samples.

The mass spectra were obtained at the Environmental Protection Agency's Southeast Water Laboratory in Athens, Ga. Analyses were made on a double focusing instrument † interfaced to a gas chromatograph ‡ with a separator.§ A constant accelerating voltage of 70 ev was used. The mass spectra were manually reduced.

† Hatachi Perkin Elmer RMU-7, Perkin-Elmer Corp., Norwalk, Conn.

‡ PE-900, Perkin-Elmer Corp., Norwalk, Conn.

§ Watson-Bieman.

RESULTS AND DISCUSSION

The analysis of the mass spectra of three water extracts confirmed that the PCB mixtures present were the same as those indicated by the gas chromatograph. Because the judgments made from chromatograms were confirmed by mass spectrometry and because all samples were analyzed on the gas chromatograph under similar conditions, judgments made on the remaining samples were assumed to be qualitatively correct. However, the occurrence of materials other than PCB's in the rest of the samples is not precluded. The waste treatment plant at Beaver Dam was the only site where possible interference was noted. On the gas chromatograms from this site, PCB's could be detected, but the peaks on the graphs were obscured in such a way that the PCB concentrations present could not be determined.

The samples analyzed in this study indicate that Aroclor 1254 is the most common PCB in the wastewater effluents. Table III shows that PCB's were detected in all samples at concentrations that ranged from < 0.05 μg/l at Beaver Dam to 2.8 μg/l at Lake Geneva.‖ The mass transport (average pounds per day) of equivalent Aroclor 1254 ranged from less than $0.2 \times 10^{3-}$ to $142 \times 10^{3-}$ lb/day ($0.9 \times 10^{4-}$ to $64.5 \times 10^{3-}$ kg/day) at Beaver Dam and Racine, respectively.

Port Washington is not as highly industrialized as Grafton; however, the effluents from both cities contained approximately the same concentrations of PCB's. The concentrations ranged from 0.12 to 0.23 μg/l which, based on this study, is typical for cities with little or no industry.

Cedarburg is an industrialized municipality whose effluents contained concentrations of equivalent Aroclor 1254 of approximately 1.0 μg/l. Because the concentrations of PCB's for this city were high, the fluctuations in concentration throughout a 24-hr period were determined. The

‖ The determinable level for PCB's in water is approximately 0.05 μg/l with this method.

TABLE III.—PCB Concentrations in Wisconsin Treatment Plant Effluents

City	Sampling		PCB Concentrations* (μg/l)	Flow (mgd)	Estimated Mass Transport† (10^{8-} lb PCB/day)
	Date (1971)	Time			
Beaver Dam	1/20	6:30	<0.05	1.59	<0.2
	2/19	6:30	<0.05	4.33	—
	3/22	6:30	<0.05	3.50	—
	10/6	6:30	<0.05	2.34	—
Port Washington	1/20	8:30	0.14	0.70	—
	2/19	8:30	0.12	1.27	—
	3/22	8:30	0.22	1.46	2.7
	10/6	8:30	0.19	1.80	—
Grafton	1/9	9:30	0.12	0.84	0.8
	2/19	9:30	0.13	1.00	1.1
	3/22	9:30	0.23	0.78	1.5
	10/6	9:30	0.07	0.84	—
Cedarburg	1/20	10:30	0.48	1.05	4.2
	2/19	10:30	0.28	1.17	2.7
	3/22	10:30	0.97	2.57	—
	10/6	10:30	0.91	1.95	15
	10/6	10:30	1.1	1.95	18
	10/6	10:30	1.0	1.95	16
Racine	1/20	8:30	0.72	16.45	—
	2/19	12:00	0.60	25.06	—
	3/22	12:00	0.76	23.01	—
	10/6	12:00	0.83	20.51	142
Burlington	1/20	9:30	0.14	1.74	—
	2/19	13:00	0.09	2.61	—
	3/22	13:00	0.08	2.50	1.7
	10/6	13:00	0.12	1.35	—
Lake Geneva	1/20	10:30	2.5	0.56	—
	2/19	14:00	2.2	0.66	—
	3/22	14:00	2.8	0.78	18
	10/6	14:00	2.4	0.54	—
Walworth	1/19	11:00	0.17	—	—
	2/20	14:30	0.21	—	—
	3/22	14:30	0.34	—	—
	10/6	14:30	0.18	—	—
Beloit	1/19	12:30	0.11	3.89	—
	2/20	16:00	0.07	11.75	—
	3/22	16:00	0.06	7.56	3.8
	10/6	16:00	0.14	4.42	5.2
Fort Atkinson	1/19	2:00	0.15	1.24	—
	2/20	18:00	0.07	2.48	—
	3/22	18:00	0.10	1.85	1.5
	10/6	18:00	0.08	1.30	—
Portage	5/20	10:00	42	0.79	—
	9/20	10:00	38	1.00	—
	10/6	10:00	32	0.78	—

* The chromatograms from all cities except for Portage most closely resembled the chromatogram of Aroclor 1254; the chromatogram from the Portage samples most closely resembled the chromatogram of Aroclor 1248.

† Mass transport estimates were made by dividing the number of pounds of PCB's discharged by the plant per day by the average flow of wastes into the plant per day.

Note: Mgd × 3,785 = cu m/day; lb × 0.454 = kg.

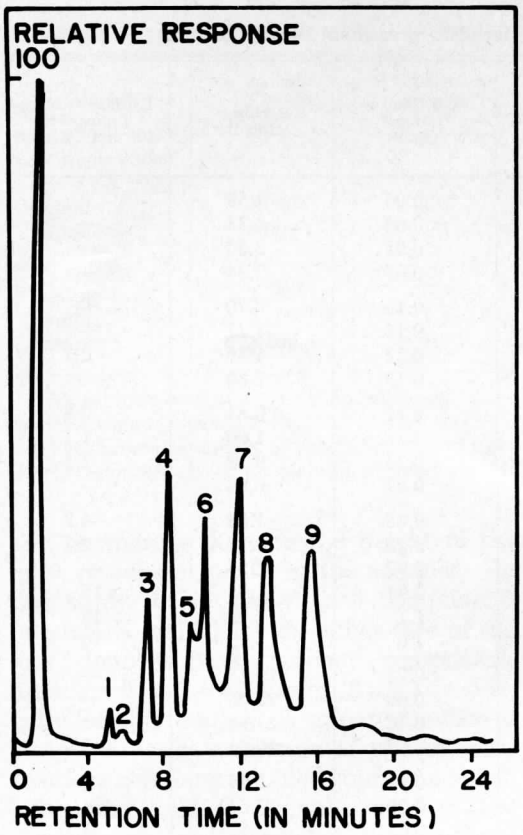

FIGURE 2.—Chromatogram of Aroclor 1254.

concentration of PCB's in raw wastewater began to increase at the beginning of the working day (8:00) from 0.54 μg/l to a maximum of 3.1 μg/l at 16:00 hours (Figure 3).

The concentration of PCB's in the final effluent seems to begin increasing from 0.33 μg/l at 0:00 (midnight) to a maximum of 0.77 μg/l at 14:00. The PCB concentration in both raw and final wastewaters increased and decreased simultaneously throughout the day.

The PCB concentration in the effluent is approximately 30 percent of that in the influent, and it is likely that the primary and secondary treatment plant was removing in excess of 70 percent of the PCB's.

The analysis of PCB's in the sludge presented in Table IV indicates that the sludges contain 1,000 times higher concentrations than does the water effluent of Cedarburg.

Racine is highly industrialized and has a high flow [11 mgd (41,635 cu m/day)] in its wastewater treatment plant. The PCB concentrations varied from 0.60 μg/l on February 19 to 0.83 μg/l on October 6. Because of the comparatively high flow, the mass transport of PCB's from the Racine plant is greater than 0.1 lb/day (0.05 kg/day) compared with approximately 0.02 lb/day (0.009 kg/day) from the Cedarburg treatment plant.

Plants in Burlington, Walworth, Beloit, and Fort Atkinson had concentrations

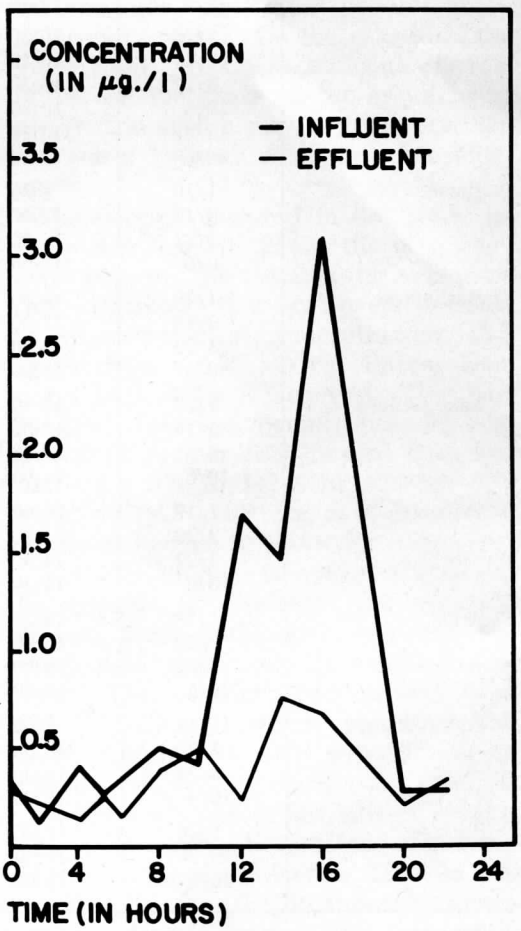

FIGURE 3.—Hourly concentrations of polychlorinated biphenyls in the influent and effluent from the Cedarburg, Wisconsin, treatment plant, April 15, 1971.

above the determinable level but less than 0.40 μg/l. The mass transport of PCB's from the treatment plants in these four cities was less than 0.01 lb/day (0.005 kg/day).

Lake Geneva is a highly industrialized city whose treatment plant effluents had PCB concentrations between 2.2 and 2.8 μg/l. These high PCB concentrations suggested that the contamination is possibly from industrial wastes. The daily discharge of 0.02 lb/day (0.009 kg/day) was comparable to that for the Cedarburg plant.

Although industries in the city of Portage are few, they contributed between 32 and 42 μg/l of equivalent Aroclor 1248 to the sanitary waste flow. A sample of the digester sludge was analyzed at 10:00 and found to contain 5.25 mg/l. It is of interest to note that the city of Portage has reported problems with the operation of their trickling filter, which may partially be the result of the presence of PCB's and other chemicals. With 32 to 42 μg/l equivalent Aroclor 1248 in the waste, it could be toxic to some of the filter fauna. Organic mercury compounds were also found by mass spectrometry on the scum of the trickling filter at concentrations up to 90 mg/l.

Data presented in Figure 3 demonstrate that the time of sampling waste effluents is of major importance in mass transport estimate. For example, if the Cedarburg effluent was sampled at 14:00 on April 15, 1971, the estimated transport of PCB's out of the plant would be approximately twice that estimated from a sample taken at 8:00. It should be noted, however, that the PCB concentration in the effluent from the plant varied considerably less than that in the raw wastes entering the plant. Consequently, the mass transport may be considered as order-of-magnitude estimates.

The sources of the PCB's entering the treatment plants have not been identified in this study or in the literature. It is possible that PCB's could be released through the use of household products such as cleaning compounds and waxes. For example, Veith and Lee [8] found PCB's in several detergents designed for electric dishwashers, aluminum foil, and packaging material. In addition to these possible household sources, PCB's may be released from leaking heat-exchanges, cutting oils, and lubricants. The Monsanto Company, formerly the sole producer of PCB's in the U. S., restricted the sales of PCB's to capacitors, transformers, and heat exchange systems in August 1970, although until April 1971 PCB's were still sold for industrial uses for which suitable replacement chemicals were not immediately available.

Further studies are needed to determine how effective these self-imposed restrictions by Monsanto will be in reducing the quantities of PCB's entering the environment.

TABLE IV.—PCB Concentrations in the Cedarburg, Wisconsin, Treatment Plant*

Sample	PCB Concentration†	
	At 10:00 (mg/l)	At 16:00 (mg/l)
Digester sludge	24	20
Primary settling sludge	69	31

* Samples taken on April 15, 1971.

† The chromatograms of the samples most closely resembled the chromatogram of Aroclor 1254.

SUMMARY AND CONCLUSIONS

The results of this study indicate that 6 of the 11 wastewater treatment plants in the study had effluent concentrations in the range of 0.1 to 0.5 μg/l of a compound whose chromatogram appeared to match the chromatogram of Aroclor 1254. Two sites had effluent concentrations greater than 1.0 μg/l of equivalent Aroclor 1254. One city had a maximum concentration of 42 μg/l of equivalent Aroclor 1248 in the effluent waters and 5.2 mg/l of equivalent Aroclor 1248 in the digester sludge.

Data from the Cedarburg treatment plant show that the time of collection is important because the concentration can vary greatly. The data show that the minimum concentrations of PCB's in the Cedarburg plant are probably 0.13 to 0.30

μg/l of equivalent Aroclor 1254, while maximum concentrations range from 1.5 to 3.1 μg/l. Because of hourly fluctuations, it is difficult to determine precisely the total amount of PCB's being discharged into receiving waters without hourly sampling of the effluent at a given site.

Of the various samples of waste effluents collected, the estimated mass transport of PCB's varied from $< 0.2 \times 10^{3-}$ to $142 \times 10^{3-}$ lb/day ($0.9 \times 10^{4-}$ to $64.5 \times 10^{3-}$ kg/day). At Racine, an equivalent of 41.1 lb PCB/yr (18.7 kg/yr) flowed into the near shore waters of Lake Michigan.

Based on the study at the Cedarburg plant, it seems that the treatment of domestic waters removes 70 percent or more of the PCB's (Aroclor 1254) present in incoming wastes. The fact that most of the PCB's are removed by treatment is also evident in the comparatively high concentration of PCB's found in the digester and primary settling sludges.

ACKNOWLEDGMENTS

Credits. The authors wish to acknowledge the aid of Jackie Zoch for her assistance in the analyses, Joe Ball for his assistance in sample collection, and Wayne Garrison and his staff from the EPA Southeast Water Laboratory in Athens, Ga., for their help on mass spectral analyses.

This investigation was funded by the Wisconsin Department of Natural Resources and by the Department of Civil and Environmental Engineering, University of Wisconsin, Madison. Additional support was provided by the University of Texas, Dallas.

Authors. Douglas J. Dube is research chemist, Department of Natural Resources, Madison, Wis. Gilman D. Veith is scientist, EPA National Water Quality Laboratory, Duluth, Minn. G. Fred Lee is director, Institute Environmental Science, University of Texas, Dallas.

REFERENCES

1. Veith, G. D., "Environmental Chemistry of the Chloro-Biphenyls in the Milwaukee River." Ph.D. thesis, Univ. of Wisconsin, Madison (1970).
2. Burchfield, H. P., and Johnson, D. E., "The Analysis of Pesticide Residues." U. S. Dept. of Health, Education, and Welfare, Washington, D. C. (1965).
3. Hughes, R. A., "Studies on the Persistence of Toxaphene in Treated Lakes." Ph.D. thesis, Univ. of Wisconsin, Madison (1970).
4. Risebrough, R. S., *et al.*, "Current Progress in the Determination of the Polychlorinated Biphenyls." *Bull. Environ. Contam. Toxicol.*, **4**, 192 (1969).
5. Stalling, D. L., and Huckins, J. N., "Gas-Liquid Chromatography—Mass Spectrometry Characterization of Polychlorinated Biphenyls (Aroclors) and ^{36}Cl-Labeling of Aroclors 1248 and 1254." *Jour. Assn. Offic. Anal. Chem.*, **54**, 801 (1971).
6. Veith, G. D., "Role of Lake Sediments in the Water Chemistry of Toxaphene." M.S. thesis, Univ. of Wisconsin, Madison (1968).
7. "Pesticide Analytical Manual." Food and Drug Admin., Dept. of Health, Education, and Welfare, Washington, D. C. (1971).
8. Veith, G. D., and Lee, G. F., Unpublished data. Water Chemistry Program, Univ. of Wisconsin, Madison (1970).