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CHLOROBIPHENYLS (PCBs) IN THE MILWAUKEE RIVER

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Abstract—The analyses of water from the Milwaukee River indicated that isomers of chlorinated biphenyl similar to those used in industry were present in the river from West Bend to Lake Michigan. Analyses of municipal sewage treatment plant effluents, industrial discharges, and the Milwaukee River water near combined sewer outfalls presented evidence that chlorobiphenyls (PCBs) were discharged to natural waters through municipal and industrial wastes. PCBs concentration at the $\mu g\,l^{-1}$ level suggested that PCBs in large ecosystems such as Lake Michigan have resulted, in part, through water transport from metropolitan areas.

INTRODUCTION

THE CHLORINATED biphenyls (PCBs) are a class of chlorinated hydrocarbons which have industrial importance as plasticizers, dielectrics, lubricants, and flame retardants (HUBBARD, 1964; MONSANTO Co., undated). The PCBs are produced commercially by Monsanto Company under the trade name, Aroclor, and exist as mixtures of isomers with chlorine contents of 21, 32, 42, 48, 54, 60 and 62 per cent by weight. In general, the chemical stability of the mixture increases with increasing chlorine content while the volatility decreases in the more highly chlorinated mixtures.

Many of the industrial applications of PCBs depend largely on the chemical stability of the mixtures. Their uses as dielectrics in transformers and capacitors and as additives to hydraulic fluids restrict the chlorinated biphenyls to closed systems. However, possible uses of PCBs in paints, varnishes, waxes, synthetic polymers, inks, dust-inhibitors, and pesticide formulations may lead to direct contamination of natural waters through industrial and sanitary waste dischargers. Also, the stability of the more highly chlorinated mixtures to low temperature flames may result in aerial transport of the PCBs from industrial and municipal solid waste incinerators to natural waters.

The presence of PCBs in the environment has been detected only recently and reviews of the current knowledge of PCBs have been presented (HUBBARD, 1964; VEITH and LEE, 1970a; PEAKALL and LINCER, 1970). In general, PCBs have been found in organisms associated with natural waters which receive wastes from urban centers. Concentrations of PCBs (as Aroclor, 1254) in excess of 250 $\mu g\,l^{-1}$ have been reported (DUKE *et al.*, 1970; HOLDEN, 1970) in industrial discharges while those in municipal sewage treatment plant effluents and receiving streams typically range from the low $ng\,l^{-1}$ to the low $\mu g\,l^{-1}$ levels where detectable.

The PCBs are similar to many chlorinated pesticides in that higher concentrations are found in organisms representative of the higher trophic levels. Concentrations of the PCBs in the predator food chain range from at or near the determinable limit in water to 75–100 $\mu g\,g^{-1}$ in fish-eating birds. Consequently, the chronic effects of the PCBs in higher organisms and the levels of PCBs in water supplies are of concern and require evaluation. The presence of PCBs in fish from the Milwaukee River at concentrations exceeding 100 $\mu g\,g^{-1}$ on a whole fish basis indicated that this tributary of Lake Michigan receives comparatively large quantities of PCBs. This paper presents the results of a study of PCB sources in the Milwaukee River drainage basin.

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The Milwaukee River originates in the Kettle Moraine area of southern Fond du lac and Sheboygan counties, Wisconsin, and flows in a southerly direction for approximately 95 stream miles into Lake Michigan at Milwaukee. FIGURE 1 presents the Milwaukee River watershed and the major industrial and sewage treatment plant (STP) outfalls into the river. The major municipalities along the river include West Bend, Saukville, Grafton, Cedarburg, Thiensville and Milwaukee, all of which discharge municipal and industrial wastes to the river. The major physical alterations of the natural river have been the construction of a total of 22 dams and spillways for

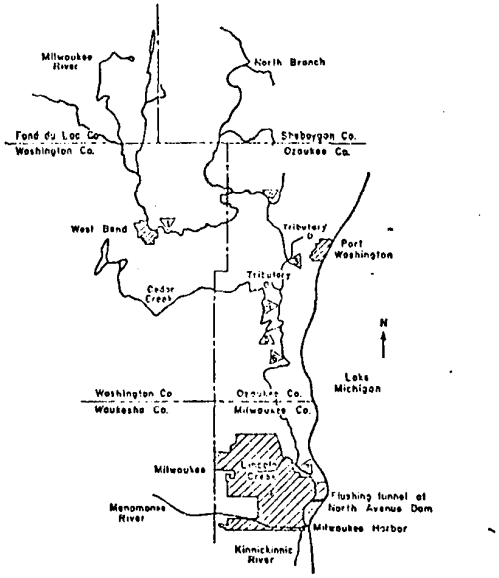

FIG. 1. MILWAUKEE RIVER WATERSHED (MILWAUKEE RIVER STUDY COMMITTEE, 1968)—Municipal STP* Outfall.

1-West Bend
2-Fredonia
3-Saukville
4-Grafton
5-Cedarburg
6-Thiensville
7-Milwaukee Combined Sewer Outfalls
*STP—Sewage Treatment Plant.

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Field sampling

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power (MARTIN, 1965), the dredging of the river from the mouth to the Milwaukee North Avenue dam, and the construction of a flushing tunnel just below the North Avenue dam to flush the wastes from the lower river with water from Lake Michigan.

EXPERIMENTAL PROCEDURES

Field sampling

The collection of water was conducted with allglass systems to preclude possible interaction of the sample with rubber, plastic, or polyvinyl chloride surfaces. Samples were collected from the river by submerging a weighted, glass carboy (20 l.) at a depth of 0.2 m in the center of the main channel. Sewage treatment plants (STP) effluents were sampled by submerging a glass bottle (4 l.) directly into the effluent. Preservatives were not added, as samples were cooled and extracted within 24 h of collection.

Extraction

Water samples (20 l.) were batch-extracted with hexane in 2 l. separatory funnels. Hexane (400 ml) was placed in 6 funnels and 1600 ml portions of the sample were introduced into the first 3 funnels. After repeated shaking and settling, the aqueous layers were drained into the 3 remaining funnels. The process was repeated until the 20-l. sample was extracted twice. The hexane portions were combined, dried with anhydrous Na_2SO_4, and concentrated to 15 ml for cleanup in a gentle air stream.

Liquid chromatography

The cleanup of extracts for gas chromatographic analysis was conducted with liquid chromatography on Florisil as described by REYNOLDS (1969) and HUGHES *et al.* (1970). The media (Kensington Scientific) was extracted in a Soxhlet extractor for 24 h with an azeotrope of hexane and acetone (41:59) to remove organic impurities. The azeotrope was evaporated from the Florisil at 105°C, and the Florisil was heated to 650 C for 2.5 h for activation.

The Florisil column for preliminary cleanup was prepared by vibrating 19 g of Florisil into a 25 mm o.d. glass column which was fitted with a glass frit and Teflon stopcock. The column was topped with 10 g anhydrous sodium sulfate to prevent deactivation of the Florisil by traces of water in the extract. The extracts were placed on the column and eluted with hexane (200 ml) to recover DDE, heptachlor, aldrin, toxiphene, strobane, and PCBs, if present. After changing the receiving flask, the column was eluted with 20 per cent ethyl ether in hexane (200 ml) to obtain DDT, DDD, dieldrin, heptachlor epoxide, and lindane, if present. With some samples, particularly those from STP effluents, it was necessary to rechromatograph the hexane eluate from the 25 mm o.d. Florisil on a smaller diameter Florisil column (9 mm i.d.) to isolate the PCBs from organic interferences. If necessary, the PCBs may be separated from the DDT group of pesticides through chromatography on silicic acid (ARMOUR *et al.*, 1970; REINERT, 1970).

Instrumentation

The analyses of water extracts were conducted on an Aerograph 1745-20 gas chromatograph equipped with concentric tube electron capture detectors (^3H, 250 mCi) and a 50:50 effluent splitter for simultaneous analysis with electron capture and

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flame ionization detectors. Analytical GLC columns consisted of 2.0 m × 1.8 mm glass coils which were packed with either OV-101 (3 per cent), OV-101/XE-60 (3:3 per cent), or OV-101/QF-1 (3:4.5 per cent) coated onto Gas Chrom Q (720/140 mesh). The carrier gas (purified N_2) was maintained at 21 ml min^{-1}; and the injector, column, and detector temperatures were 250°C, 180°C, and 220°C, respectively.

Analysis

The commercially prepared PCBs in the U.S.A. (Monsanto Company, St. Louis, Mo.) exist as seven complex mixtures under the name "Aroclor", which range in chlorine content from 21 to 62 per cent. When the PCB mixtures are chromatographed with GLC, the mixtures of isomers produce both resolved and superimposed peaks and are somewhat characterized by the GLC fingerprint presented as relative peak heights and retention times. Because of the complexity of the mixtures, determinations have been quantitatively defined by comparing the area of a sample chromatogram to the area of a known quantity of the commercial mixture which most closely resembles that of the sample. However, some of the samples contained PCBs which appeared to be mixtures of the Aroclor mixtures and were not representative of a single commercially prepared mixture. Estimates of PCBs in these samples were made by visually comparing the chromatograms to mixtures of standards prepared from the Aroclor mixtures.

Explicit chemical confirmations for the presence of PCBs in each sample were not possible in this study. PCBs with similar retention volumes and relative peak heights were confirmed in the fish from the Milwaukee River using i.r. and mass spectrometry. Thus, from the i.r. and mass data, GLC retention data under multiple column conditions, and the stability of the extract mixtures to dehydrohalogenation and nitration, the components in the chromatograms were presumed to be PCB isomers. However, the analysis do not preclude the possible presence of other chemicals which may have similar chemical properties such as the chloronaphthalenes.

The analytical procedures for PCBs in natural waters were evaluated using Aroclor 1260 which contains 60 per cent chlorine. Six replicates of unfiltered Lake Mendota water (4.0 l.) were "spiked" with 4.0 μg of Aroclor 1260 as a 50 ml acetone solution. The water was aerated for 5 min and incubated at room temperature for 2 days. The recovery of PCBs from water at the 1.0 $\mu g\ l^{-1}$ level was found to vary with the degree of chlorination of PCB components. If the major component of Aroclor 1260 which eluted at 12.8 min on the OV-101/QF-1 column was used as a reference, 82.3 ± 6.3 per cent of the Aroclor 1260 mixture was removed. If the major component of Aroclor 1260 which eluted at 6.4 min was used, the recovery was 80.0 ± 8.2 per cent of the quantity added.

When the component eluting at 4.1 min which is a major component of Arclor 1242 was used as a reference, only 69.0 ± 6.5 per cent of the mixture was recovered. The recovery of the minor component of Aroclor 1242 eluting at 1.3 min was slightly less than 50 per cent, and the minor component eluting at 0.7 min could not be detected in any of the 6 replicates. Since the "spiking" procedure may be of questionable reliability when applied to nonelectrolytes, the recovery data must be regarded as estimates which indicate that the precision and accuracy of the analytical procedures are satisfactory for the analysis of natural waters. The data also indicate that the com-

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position of the PCB mixtures may be altered during analysis if care is not taken to minimize loss of the more volatile PCB components.

RESULTS AND DISCUSSION

Sections of the Milwaukee River were sampled on August 23 and 25, 1969, to determine the levels of PCBs in the river system. In addition, selected tributaries, municipal sewage treatment plants (STP) effluents, and industrial discharges were sampled on March 26, 1970.

The water quality characteristics of the river on the August, 1969, sampling dates are presented in TABLE 1. In general, because of photosynthesis of plankton in the impoundments and less pollutional loading in the upper river, the dissolved oxygen (DO), pH, and suspended solids were higher in the upper river above dams than in the lower river within the city of Milwaukee. For example, above the dam at Grafton the water contained 10.0 mg l^{-1} DO, 60.5 mg l^{-1} suspended solids, and a pH of 8.7. In contrast, the water at the Buffalo Avenue bridge in Milwaukee contained 4.2 mg l^{-1} DO, 14.7 mg l^{-1} suspended solids, and a pH of 7.7. The decreases in alkalinity and conductivity from 196 mg l^{-1} and 642 $\mu\Omega$ cm^{-1}, respectively, at the North Avenue dam to 118 mg l^{-1} and 420 $\mu\Omega$ cm^{-1} at the harbor reflect the input of Lake Michigan water below the dam through the flushing tunnel.

The estimates of PCBs in the Milwaukee River water are presented in TABLE 2. The GLC analyses indicated that PCB mixtures similar to Aroclor 1260 (predominately the later-eluting PCBs) were present above the dam at Grafton at approximately 0.05 μg l^{-1}. Tributary "O", the receiving stream for a plastics manufacturing firm, was not a source since PCBs could not be detected in the water near the firm. Thus, a PCB source(s) upstream from Grafton was indicated.

Possible sources upstream from Grafton were examined through the analyses of selected outfalls to the river. The data, which are presented in TABLE 3, show that the STP at West Bend, Fredonia, Saukville, and Grafton were discharging PCBs. The highest concentration observed in effluents was 2.5 μg l^{-1} Aroclor 1242 observed in a chemical plant effluent several miles upstream from Grafton.

The river downstream from Grafton and Thiensville contained higher concentrations of the isomers corresponding to Aroclor 1260 as well as many early-eluting isomers (GLC) which closely resembled those in Aroclor 1248 or Aroclor 1242. The increase in the concentration of Aroclor 1260 to 0.26 μg l^{-1} and the introduction of other PCB isomers suggested a source(s) between Grafton and Thiensville. The likely source is Cedar Creek in which oil films, petroleum odors, and water discoloration have been a problem in the past (SCHRAUFNAGEL *et al.*, 1968; MCKERSIE *et al.*, 1969).

The PCBs were found at greatest concentrations in the Estabrook Park–East Rivers de Park region of the river in Milwaukee. The concentrations of Aroclor 1242 associated with the water in this region were 2.07 and 2.80 μg l^{-1} in August, 1969, and February, 1970, respectively. The sources of the contamination in this region are likely to be the Milwaukee combined sewer outfalls and contaminated industrial cooling waters which discharge to Lincoln Creek and the Milwaukee River near Estabrook Park.

The presence of μg l^{-1} quantities of chlorinated materials such as the PCBs in natural waters may generate concern in regard to public health. Although standards for PCBs in drinking water supplies have not been established due, in part, to a lack of

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TABLE 1. CHARACTERISTICS OF MILWAUKEE RIVER SURFACE WATER (AUGUST 25, 1969)

Location	Depth of Secchi Water (m)	Depth of Secchi Depth (m)	Temp. (°C)	DO (mg l⁻¹)	pH	Alkalinity (mg l⁻¹ $CaCO_3$)	Conductivity (μΩ cm⁻¹ 20°C)	Suspended solids (mg l⁻¹)
Tributary "O", Grafton	0.3	—	24.5	10.1	8.8	242	670	12.2
200 m above dam, Grafton	1.7	0.4	26.0	10.0	8.7	257	720	60.5
100 m above dam, Thiensville	2.1	0.6	27.5	13.6	8.9	245	720	30.0
Highway 167, (below dam), Thiensville	0.5	—	27.2	10.2	9.2	251	740	24.0
200 m above dam, Glendale	0.8	—	27.0	15.4	—	—	—	—
100 m above dam, Estabrook Park	2.4	0.3	30.0	15.6	9.0	232	745	50.0
100 m below North Avenue Dam	5.4	0.8	26.0	8.5	8.6	196	642	14.6
Milwaukee River Mouth (Buffalo Avenue)	7.0	1.0	28	4.2	7.7	145	505	14.7
Menomonee River Mouth	9.6	1.1	27	3.4	7.2	131	565	10.6
Kinnickinnic River Mouth	10.0	0.7	23	4.1	7.3	127	478	5.0
Harbor Breakwater	10.4	1.7	19	8.7	8.0	118	420	5.6

TABLE 2. C

Location

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Milwaukee Harbor

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TABLE 2. CONCENTRATIONS OF PCBs IN THE MILWAUKEE RIVER AUGUST 23-25, 1969

Location	Estimate of corresponding Aroclor(s) ($\mu g\ l^{-1}$)* Aroclor 1260	Aroclor 1242
Tributary "O", Grafton	†	†
200 m above dam, Grafton	0.05	†
100 m above dam, Thiensville	0.26	0.08
Highway 167 (below dam), Thiensville	0.13	0.03
200 m above dam, Glendale	0.13	†
100 m above dam, Estabrook Park	0.10	2.07
100 m below North Avenue Dam	0.05	0.26
Milwaukee River Mouth (Buffalo Avenue)	0.05	0.13
Menomonee River Mouth	0.03	0.13
Kinnickinnic River Mouth	0.03	0.12
Milwaukee Harbor Entrance	0.02	0.10

* The 1200 series of Aroclors are mixtures of PCBs. The last two numbers pertain to the percent chlorine of the mixture.
† Below determinable limit of approximately 0.02 $\mu g\ l^{-1}$ for A-1242 to 0.01 $\mu g\ l^{-1}$ for A-1260, depending on foil condition.

TABLE 3. CONCENTRATIONS OF PCBs IN OUTFALLS INTO THE MILWAUKEE RIVER ON MARCH 26, 1970

Location	Estimate of PCB concentration ($\mu g\ l^{-1}$)	Corresponding Aroclor mixture
West Bend STP* effluent	0.25	Aroclor 1254
Fredonia STP effluent	0.12	Aroclor 1254
Tributary "D" at Fredonia	0.04	Aroclor 1260
Saukville STP effluent	0.13	Aroclor 1260
Chemical plant effluent, Saukville	2.50	Aroclor 1242
Grafton STP effluent	0.04	Aroclor 1254

* STP- Sewage Treatment Plant.

toxicological data, reviews by VEITH and LEE (1970a) and PEAKALL and LINCER (1970) have concluded that the PCBs appear to be less toxic to many organisms on an acute basis than is pp'DDT. Since the permissible limit for pp'DDT in public water supplies in the U.S.A. has been established at 42 $\mu g\ l^{-1}$ (FEDERAL WATER POLLUTION CONTROL ADMINISTRATION, 1968), it is unlikely that the observed levels of PCBs in the Milwaukee River system pose an immediate health hazard. This conclusion is substantiated by the fact that much of the PCBs found in the water are associated with suspended solids in the water and are removed during the water treatment and filtration processes.

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However, the presence of PCBs at the $\mu g\ l^{-1}$ level in natural waters may pose a threat to aquatic organisms and the food chains sustained by them. RISEBROUGH *et al.* (1968) and ANDERSON *et al.* (1969) have demonstrated and discussed the induction of hepatic hydroxylating enzymes by PCBs which is similar to that observed from chlorinated pesticides. This enzyme induction effect has been proposed as the factor leading to egg shell thinning and reproductive failures in avian communities. More specifically, DUKE (1970) found that 1 $\mu g\ l^{-1}$ of Aroclor 1254 killed juvenile shrimp in the laboratory. Also, STALLING (1970) found that 1 $\mu g\ l^{-1}$ of PCBs caused adverse physiological effects to bluegills, channel catfish, and trout, and that 10 $\mu g\ l^{-1}$ caused 50 per cent mortalities. VEITH and LEE (1970b) reported that the goldfish in the Estabrook Park region of the Milwaukee River contained as great as 405 $\mu g\ l^{-1}$ of PCBs (as Aroclor 1242) on a whole fish basis. This evidence indicates that the 1 $\mu g\ l^{-1}$ concentration of PCBs may endanger aquatic communities either by direct exposure to the water or by feeding on high-lipid organisms which partition the PCBs from the water at concentration factors of approximately 100,000.

Of particular interest were the relative variations of PCB isomers within the river system. The results of the analyses of water repeatedly indicated a more rapid decrease in the concentrations of the lesser-chlorinated biphenyl isomers with respect to the more highly chlorinated isomers. For example, in TABLE 2 the apparent Aroclor 1242 concentration in the lower river decreased from approximately 2 $\mu g\ l^{-1}$ at Estabrook Park to approximately 0.3 $\mu g\ l^{-1}$ just below the North Avenue dam. In the same reach of river the the more highly chlorinated components which are predominant in Aroclor 1260 decreased from 0.10 to 0.05 $\mu g\ l^{-1}$ at the respective sampling sites. Similar results were obtained from the February sampling of the river.

The relative variations of the composition of PCBs in the river suggest that the lesser-chlorinated isomers may be removed from the river water through preferential vaporization or co-distillation arising from their greater volatility than the heavier isomers (MONSANTO Co., 1959) and/or through the more rapid degradation of the lesser-chlorinated isomers. The chemical stability of the PCB isomers toward nucleophilic and electrophilic substitution has been found to increase with increasing chlorine content (VEITH, 1970). Consequently, the environmental data reported in this paper may be viewed as an indication that similar trends exist toward microbial degradation whereby the lesser-chlorinated isomers in Aroclors 1232 and 1242 are selectively removed from natural waters. Experiments aimed at verifying these indications are in progress.

SUMMARY

The PCBs present in Milwaukee River water were seldom comparable to a single Aroclor mixture. The data are reported as mixtures of Aroclor 1260 and Aroclor 1242, and the respective assignments imply the presence of components which elute later than those of Aroclors 1254 and 1248 in GLC analyses and the presence of components which elute earlier than Aroclor 1248.

The low-level PCB concentrations in all sampling regions and in the STP of small communities suggest that PCBs may be discharged in municipal wastes in addition to industrial wastes. The introduction of PCBs into the Milwaukee River by both large and small municipalities throughout the river basin may reflect the widespread use of the PCBs in products of advanced technology and indicates a need for the examination of PCB levels in ecological studies are needed.

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examination of PCB levels in common consumer-products. Comprehensive toxicological studies are needed to fully evaluate the significance of PCBs in the environment.

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