

POLYCHLORINATED NAPHTHALENES, BIPHENYLS, DIBENZO-*p*-DIOXINS, AND DIBENZOFURANS AS WELL AS POLYCYCLIC AROMATIC HYDROCARBONS AND ALKYLPHENOLS IN SEDIMENT FROM THE DETROIT AND ROUGE RIVERS, MICHIGAN, USA

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Abstract—Sediment from the upper Detroit and lower Rouge Rivers in southeastern Michigan, USA, were analyzed to examine the distribution of polychlorinated naphthalenes (PCNs), biphenyls (PCBs), dibenzo-*p*-dioxins (PCDDs), and dibenzofurans (PCDFs) as well as polycyclic aromatic hydrocarbons (PAHs) and alkylphenolic compounds such as butylphenol, octylphenol, and nonylphenol (NP). Sediments from a non-point source location in Lake Michigan were also analyzed for target compounds. Concentrations of target compounds in the upper Detroit and lower Rouge Rivers varied considerably among locations, and notable spatial variation existed. Concentrations of PCNs and PCDDs/PCDFs in sediments from the upper Detroit and lower Rouge Rivers ranged from 0.08 to 187 ng/g and 69 to 1420 pg/g dry weight, respectively. Total PCBs, PAHs, and NP concentrations ranged from 8 to 25,000, 17 to 44,000, and <10 to 60,000 ng/g dry weight, respectively. Concentrations of all target compounds except PCNs were significantly correlated with total organic carbon content of sediments. Similarly, concentrations of PCBs, PCDDs, and PCDFs were significantly correlated with each other. The distribution of organic contaminants in the upper reaches of the Detroit River and lower Rouge River suggested the presence of localized, but multiple, sources of contamination for each compound class. Connors Creek combined sewer overflow has been identified as one of the potential sources for the upper Detroit River, where the highest concentrations PCBs and PCDDs/PCDFs were found. Polycyclic aromatic hydrocarbon and NP concentrations were consistently high in sediment from the lower Rouge River. Analysis of data from selected locations suggested that PCNs contributed a greater proportion of the dioxin-like activity than PCBs and PCDDs/PCDFs contributed.

Keywords—Organochlorines Polychlorinated naphthalenes Polychlorinated dibenzo-*p*-dioxins/dibenzofurans Sediment

INTRODUCTION

The Detroit and Rouge Rivers of southeastern Michigan, USA, have historically suffered from the stress of pollutant loading from a variety of sources, including hazardous waste from manufacturing facilities and abandoned dumps, sewage from combined sewer overflows, dredged materials, and urban runoff. High concentrations of organic contaminants such as polychlorinated biphenyls (PCBs) and polycyclic aromatic hydrocarbons (PAHs) have impacted the health of benthic organisms, including fish, in the Detroit River [1–3]. For instance, brown bullheads (*Ameiurus nebulosus*) collected from Trenton Channel in the Detroit River had a higher prevalence of morphological abnormalities such as lip and skin lesions and of physiological effects such as cytochrome P450 enzyme induction, liver neoplasms, and carcinomas than those collected from relatively less-polluted, upstream river sites [3]. In vitro studies of cytotoxicity and genotoxicity have demonstrated increased DNA repair in bullheads exposed to Detroit River sediment extract [4].

The Detroit River connects Lake St. Clair to the western basin of Lake Erie and is one of the four major channels joining the Great Lakes. The river is 51 km in length, with an average southerly discharge rate of 5,200 m³/s. The lower portion of

the river has a significant deposition of fine-grained sediments; therefore, sediments in the lower portion contain significant concentrations of organic contaminants, especially along the Michigan mainland shoreline [1,5,6]. Studies have reported the distribution of organic contaminants in the lower reaches of the Detroit River, including the Trenton Channel, but little information is available regarding contamination in the upper Detroit River. A significant spatial heterogeneity in the distribution of contaminants within the river exists [1,7,8]. Similarly, to our knowledge, concentrations of organic pollutants in the Rouge River, which drains through the intensely urbanized areas of Detroit, have not been previously reported. The Rouge River drainage basin is approximately 1,139 km² and is located in Wayne and portions of Oakland and Washtenaw counties. Overall, more than 50% of the land use in the Rouge River basin is residential, commercial, or industrial. The remaining area is primarily farmland or undeveloped. The eastern portion of the catchment is intensely urbanized and includes the city of Detroit. The sediments were collected from the heavily industrial area of the lower Rouge River, the turning basin to its junction with the Detroit River. The present study was undertaken to evaluate the distribution of PCBs, PAHs, and alkylphenols such as butylphenol (BP), octylphenol (OP), and nonylphenol (NP) in sediment from the upper Detroit and lower Rouge Rivers. Concentrations of non-*ortho* coplanar PCBs as well as polychlorinated naphthalenes (PCNs), diben-

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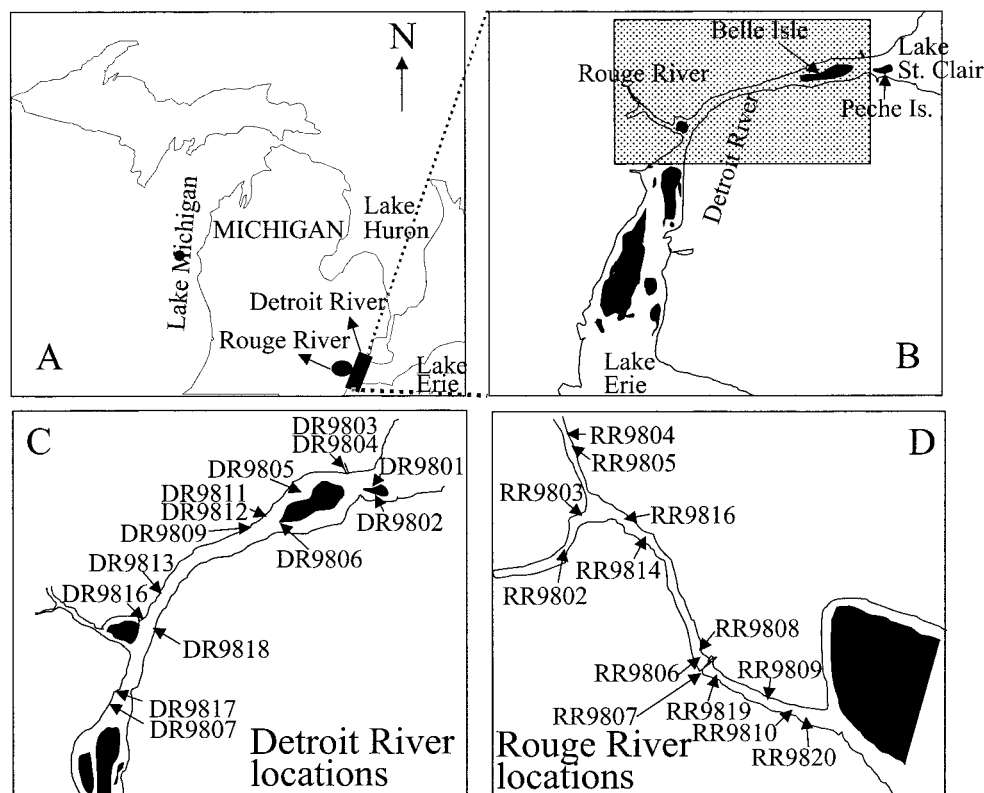


Fig. 1. Sampling locations in the Detroit and Rouge rivers and in Lake Michigan (MI, USA). **A.** Map of Michigan showing the locations of the Detroit and Rouge rivers. **B.** Study area (shaded) of the Detroit and Rouge Rivers. **C.** Detroit River sampling locations. **D.** Rouge River sampling locations. (See Table 1 for details of locations.)

zo-*p*-dioxins (PCDDs), and dibenzofurans (PCDFs) were measured in a few selected samples of sediments. Data regarding the concentrations and patterns of different classes of organic contaminants in the upper Detroit River were evaluated to identify the domestic or industrial sources of these chemicals. Concentrations of target contaminants in sediments from these rivers were compared with those collected off of Muskegon, Lake Michigan (43°N, 86°W).

MATERIALS AND METHODS

Sampling

Surface (0–30 cm) and subsurface sediments (>30) were collected using a Ponar grab or core sampler from 35 locations in the Detroit and Rouge Rivers (Fig. 1) during June 1998. Sediment samples were collected as a part of a joint sediment-assessment project between the Michigan Department of Environmental Quality and the U.S. Environmental Protection Agency. Samples were transferred to a solvent-cleaned glass jar and stored at –20°C until extraction. Details of the sampling locations are given in Table 1 and Figure 1.

Chemical Analysis

PCBs, PAHs, and alkylphenols. Concentrations of PCBs, PAHs, and alkylphenols were analyzed according to methods described elsewhere [9], with some modifications. Wet sediments were homogenized with sodium sulfate to remove moisture and Soxhlet extracted with methylene chloride and hexane (3:1 v/v, 400 ml) for 12 h. Extracts were concentrated to 10 ml by rotary evaporation and treated with acid-activated copper granules to remove sulfur. Extracts were then fractionated and purified by eluting through 10 g of activated Florisil® (ITC,

Hunt Valley, MD, USA) packed in a glass column (inner diameter, 10 mm). The first fraction (F1), which was eluted with 100 ml of hexane, contained PCBs. Polycyclic aromatic hydrocarbons were eluted in the second fraction (F2) using 100 ml of 20% dichloromethane in hexane (v/v). Nonylphenol, OP, and BP were eluted in the third fraction (F3) with 100 ml of 50% dichloromethane in methanol. Polychlorinated biphenyls and PAHs were quantified using a gas chromatograph with a ⁶³Ni electron-capture detector and a mass spectrometer, respectively. A solution containing 100 individual PCB congeners with known composition and content was used as a standard, and concentrations of 100 individually resolved peaks were summed to obtain total PCB concentrations [10]. The PAH standard (AccuStandard, New Haven, CT, USA) consisted of 16 priority pollutant PAHs as identified by the U.S. Environmental Protection Agency (Method 8310). The mass spectrometer was operated under selected ion monitoring (SIM) mode using the molecular ions selective for individual PAHs [9]. Alkylphenols were quantified using a reverse-phase, high-pressure liquid chromatograph with fluorescence detection. Fraction 3 extracts and standards were injected (10 μl) by a Perkin-Elmer Series 200 autosampler (Perkin-Elmer, Norwalk, CT, USA) onto an analytical column (ProdigyTM ODS (3), 250 × 4.6 mm; Phenomenex, Torrance, CA, USA), which was connected to a guard column (Prodigy ODS (3), 30 × 4.6 mm; Phenomenex) and eluted with a flow of acetonitrile (ACN) and water at a gradient from 50% ACN in water to 98% ACN in water delivered by a Perkin-Elmer Series 200 pump for 20 min. Detection was accomplished using a Hewlett-Packard (Wilmington, DE, USA) 1046A fluorescence detector with an excitation wavelength of 229 nm and an emis-

Table 1. Description of sediment sampling locations in the upper Detroit and lower Rouge rivers and in Lake Michigan, Michigan, USA^a

Station ID	Location	Remarks ^b
DR9801	North Peche Island	
DR9802	South Peche Island	
DR9803	Connors Creek—Inner	Combined sewer overflow
DR9804	Connors Creek—Outer	Combined sewer overflow
DR9805	Scott middle ground	
DR9806	Belle Isle South	
DR9807	Great Lakes Steel shoal	
DR9809	Penn Dixie	Adjacent to the boat slip in the upper Detroit River
DR9811	Coast Guard boat slip	Near former Uniroyal tire facility
DR9812	Coast Guard boat slip	Near former Uniroyal tire facility
DR9813	U.S. ACE—Inner	U.S. Army Corps of Engineers boat slip (downstream of Revere Copper and Brass industrial plant)
DR9814	U.S. Ace—South	U.S. Army Corps of Engineers boat slip
DR9815	Powerline—Inner	Delray-Edison boat slip above Rouge River Cutoff Canal
DR9816	Powerline—Mid	Delray-Edison boat slip above Rouge River Cutoff Canal—middle portion
DR9817	Great Lakes Steel—A	Near Great Lakes Steel Company
DR9818	Powerline—Ontario	Delray-Edison boat slip above Rouge River Cutoff Canal—Ontario shore
RR9802	Upper Rouge	
RR9803	Turning Basin	Near Ford Motor Company
RR9804	Ford Slip—A	Near Ford Motor Company boat slip in the Rouge River
RR9805	Ford Slip—B	Near Ford Motor Company boat slip in the Rouge River; near Rouge steel
RR9806	Shell—Upper	Near Shell Oil Company
RR9807	Shell oil dock	Near Shell Oil Company
RR9808	Cement Dock	American Cement Company
RR9809	Jeff—Upper	Jefferson Street Bridge over the Rouge River—Upstream (Detroit Sewage Treatment Plant)
RR9810	Jeff—Lower	Jefferson Street Bridge over the Rouge River—Downstream (upstream of American Oil Company)
RR9814	Fordson—Mid	Fordson Island on the Rouge River (Baby Creek storm sewer outfall)
RR9814	Fordson—Mid	Fordson Island on the Rouge River
RR9814	Fordson—Mid	Fordson Island on the Rouge River
RR9814	Fordson—Mid	Fordson Island on the Rouge River
RR9816	Dix Nav A	Dix Road bridge—Navigation Channel; near Ford Motor/Edward Levy
RR9819	Shell—Nav	Near Shell Oil Company
RR9820	Jeff—Nav	Jefferson Street Bridge over the Rouge River (near American Oil Company)
LM1	43°54'N, 86°94'W	(off Muskegon, MI)
LM2	43°54'N, 86°94'W	(off Muskegon, MI)
LM3	43°45'N, 86°94'W	(off Muskegon, MI)
LM4	43°09'N, 86°81'W	(off Muskegon, MI)
LM5	43°09'N, 86°81'W	(off Muskegon, MI)

^a DR = Detroit River; LM = Lake Michigan; RR = Rouge River; U.S. ACE = U.S. Army Corps of Engineers.

^b Refer to a nearby facility for identification.

sion wavelength of 310 nm. Detection limits for NP, OP, and BP were 10 ng/g dry weight. Sample extracts were injected into a gas chromatograph equipped with a mass-selective detector for the confirmation of NP, OP, and BP by SIM mode [9]. Further details of the fractionation procedure and instrumental analyses have been described elsewhere [9]. Florisil column fractionation resulted in the elution of PCNs, PCDDs, and PCDFs in all three fractions at different proportions. Therefore, these compounds were analyzed separately, as described below.

Polychlorinated naphthalenes. The PCNs were analyzed in selected samples according to the method described by Kannan et al. [11], with slight modification. A portion of the Soxhlet extract of the sediment was cleaned on a acidic silica/silica gel column by elution with hexane. The hexane extract was concentrated to 1 ml and transferred to a carbon column packed with 1 g of activated carbon-impregnated silica gel. The PCNs were eluted with 200 ml of toluene and analyzed by a high-resolution gas chromatograph connected to a high-resolution mass spectrometer. A Hewlett-Packard 6890 gas chromatograph interfaced with a Jeol (Peabody, MA, USA) JMS-700 high-resolution mass spectrometer was used. Details of the instrumental conditions for PCN analysis have been described elsewhere [12]. The PCNs were separated on a DB-1701 capillary column coated at 0.25 μ m (length, 30 m; inner diameter,

0.25 mm). The column head pressure was kept at 120 kPa. The column oven temperature was programmed to increase from 80°C (1 min) to 160°C at a rate of 40°C/min, to 170°C at 10°C/min, to 250°C at 4°C/min, to 280°C at 6°C/min, and to 296°C at 4°C/min, which was then held for 10 min. Injector and transfer-line/ion-source temperatures were held at 260 and 250°C, respectively. The mass spectrometer was operated at an electron impact energy of 70 eV, and the ion current was at 600 μ A. The PCN congeners were monitored by SIM at the two most intensive ions at the molecular ion cluster. Calculated concentrations were reported as being less than the limit of detection if the observed isotope ratio was not within $\pm 20\%$ of the theoretical ratio or the peak area was not greater than the threshold amount (i.e., threefold greater than the noise). The detection limits of individual PCN congeners varied from 0.1 to 1 pg/g, depending on the sample size and relative responses. Recoveries of PCN congeners have been reported elsewhere [11].

PCDDs, PCDFs, and coplanar PCBs. A portion of the Soxhlet extract of the sediment was spiked with ¹³C-labelled, 2,3,7,8-substituted tetra- through octa-chlorinated dibenzo-*p*-dioxin and dibenzofuran congeners and cleaned with concentrated sulfuric acid. The extract was then passed through 2 g of silica gel packed in a glass column and eluted with 130 ml of 10% dichloromethane in hexane. The extract was then

Table 2. Concentrations of polychlorinated biphenyls (PCBs) polycyclic aromatic hydrocarbons (PAHs) in sediments from the upper Detroit River (DR) and lower Rouge River (RR) and Lake Michigan (LM), Michigan, USA, in June 1998

Station ID	Location	Description	TOC (%) ^a	PCBs (ng/g dry wt)	PAHs (ng/g dry wt)
DR9801	North Peche Island	Surface	0.22	32	17.5
DR9802	South Peche Island	0–30 cm	1.14	57	394
DR9803	Conners—Inner	0–30 cm	4.02	NA ^b	15,000
DR9804	Conners—Outer	0–30 cm	3.73	25,000	9,770
DR9805	Scott middle ground	0–30 cm	1.31	28.4	555
DR9806	Belle Isle South	0–35 cm	0.47	8	1,140
DR9807	Great Lakes Steel shoal	Ponar	0.65	250	12,700
DR9809	Penn Dixie—A	0–30 cm	2.69	4,660	17,800
DR9811	Coast Guard—B	0–30 cm	3.08	2,150	24,000
DR9812	Coast Guard—A	Ponar	4.48	460	NA
DR9813	U.S. ACE—Inner ^c	0–30 cm	2.87	13,400	8,240
DR9814	U.S. ACE—South	0–30 cm	2.34	14,100	13,800
DR9815	Powerline—Inner	0–30 cm	1.79	54	5,750
DR9816	Powerline—Mid	0–30 cm	2.87	5,880	35,400
DR9817	Great Lakes Steel—A	Ponar	2.59	5,600	36,200
DR9818	Powerline—Ontario	0–30 cm	1.69	160	3,640
RR9802	Upper Rouge—B	Ponar	3.92	670	24,200
RR9803	Turning Basin	0–30 cm	2.25	810	20,100
RR9804	Ford Slip—A	0–30 cm	2.67	3,660	24,100
RR9805	Ford Slip—B	0–30 cm	3.75	4,300	34,500
RR9806	Shell—Upper	0–30 cm	4.14	10,900	22,500
RR9807	Shell Oil dock	0–30 cm	4.52	NA	17,500
RR9808	Cement Dock	Ponar	2.05	470	7,450
RR9809	Jeff—Upper	0–30 cm	4.17	1,080	12,100
RR9810	Jeff—Lower	0–30 cm	4.28	1,380	13,000
RR9814	Fordson—Mid	151–162 cm	7.51	NA	NA
RR9814	Fordson—Mid	91–150 cm	8.08	NA	NA
RR9814	Fordson—Mid	0–30 cm	3.04	1,780	43,800
RR9814	Fordson—Mid	31–90 cm	5.28	NA	33,000
RR9816	Dix Nav—A	Ponar	4.6	890	27,400
RR9819	Shell—Nav	Ponar	4.32	1,610	13,700
RR9820	Jeff—Nav	Ponar	4.04	640	10,700
LM1	43°54'N, 86°94'W		0.68	9.6	160
LM2	43°54'N, 86°94'W		0.61	1	400
LM3	43°54'N, 86°94'W		0.72	23	84
LM4	43°09'N, 86°81'W		0.68	7.3	33
LM5	43°09'N, 86°81'W		0.61	18	70

^a TOC = total organic carbon.

^b NA = not analyzed.

^c U.S. ACE = U.S. Army Corps of Engineers.

passed through a carbon column packed with 1 g of activated carbon-impregnated silica gel. The first fraction, which was eluted with 20 ml of 25% dichloromethane in hexane, was discarded. The second fraction, which was eluted with 250 ml of toluene, contained 2,3,7,8-substituted PCDDs and PCDFs and non-ortho coplanar PCB congeners 77, 126, and 169. The PCDDs and PCDFs were analyzed using a high-resolution gas chromatograph/high-resolution mass spectrometer. A Hewlett-Packard 6890 gas chromatograph connected to an Autospec Ultima (VG; Micromass, Manchester, UK) was used. Both PCDD and PCDF congeners were separated on a DB-5 capillary column coated at 0.25 μ m (length, 60 m; inner diameter, 0.25 mm). The column oven temperature was programmed to increase from 160°C (3 min) to 200°C at a rate of 40°C/min, with a 2-min hold time, and then to 310°C at 2°C/min, which was held for 1 min. Injector and transfer-line/ion-source temperatures were held at 280 and 250°C, respectively. The mass spectrometer was operated at an EI energy of 40 eV, and the ion current was at 600 μ A. The PCDD/PCDF congeners were monitored by SIM mode at the two most intensive ions at the molecular ion cluster. Recoveries of ¹³C-labelled PCDD and PCDF congeners through the analytical procedure ranged from 63 to 90%. The reported concentrations were not corrected for the recoveries of internal standard. Concentrations of certain

PCDD/PCDF congeners were confirmed by using a DB-17 column (length, 60 m; inner diameter, 0.25 mm; film thickness, 0.25 μ m). Non-ortho coplanar PCBs were separated on a DB-5 capillary column coated at 0.25 μ m (length, 60 m; inner diameter, 0.25 mm) and analyzed using a SIM mode.

The total organic content (TOC) of sediment samples was analyzed at the Plant and Nutrient Analysis Laboratory in Michigan State University (MI, USA). An aliquant of sediment samples were dried to a constant weight at 100°C to estimate moisture content.

RESULTS AND DISCUSSION

Polychlorinated biphenyls

The PCBs were found in all the sediment samples analyzed, and their concentrations ranged from 8 to 25,000 ng/g dry weight (Table 2). Surface sediment collected from Conners Creek contained the highest PCB concentration (25,000 ng/g dry wt). Sediment from southern Peche Island, which is approximately 1 km northwest of the Conners Creek, contained 440-fold less PCB (57 ng/g) than in Conners Creek. These results suggest the presence of point sources of PCBs at Conners Creek, which is a large, combined sewer overflow in the city of Detroit. It can also be inferred that the Lake St. Clair

Table 3. Concentrations and their toxic equivalents of non- and mono-*ortho* polychlorinated biphenyl congeners in sediments from the upper Detroit River (DR) and lower Rouge River (RR), Michigan, USA (pg/g dry wt)^a

Congener	DR9805	DR9812	DR9802	RR9805	RR9803	DR9803	DR9814	RR9807	DR9815	RR9804
81	11.0 (0.021)	17.3 (0.033)	3.4 (0.006)	108 (0.204)	94.3 (0.179)	360 (0.685)	205 (0.39)	118 (0.223)	11.1 (0.021)	227 (0.431)
77	350 (0.006)	503 (0.009)	100.8 (0.002)	3,105 (0.056)	2,634 (0.047)	10,172 (0.183)	5,498 (0.099)	3,823 (0.069)	384.2 (0.007)	4,929 (0.089)
126	16.0 (0.351)	44.7 (0.982)	4.8 (0.106)	79.0 (1.74)	52.2 (1.15)	273.1 (6.01)	179 (3.93)	62.6 (1.38)	22.1 (0.49)	140 (3.07)
169	1.3 (0.001)	2.7 (0.001)	0.5 (<0.001)	5.7 (0.003)	3.2 (0.001)	20.7 (0.01)	12.9 (0.006)	6.1 (0.003)	2.1 (0.001)	8.6 (0.004)
105	1,500 (0.012)	2,300 (0.018)	260 (0.002)	30,000 (0.24)	3,000 (0.024)	NA ^b	71,800 (0.574)	NA	2,100 (0.017)	53,000 (0.424)
118	3,200 (0.019)	5,700 (0.028)	830 (0.006)	81,000 (0.77)	4,800 (0.061)	NA	246,000 (1.21)	NA	4,800 (0.03)	180,000 (0.61)
156	350 (0.019)	510 (0.028)	110 (0.006)	14,000 (0.770)	1,100 (0.061)	NA	22,000 (1.21)	NA	550 (0.03)	11,000 (0.61)
Total TEQs	0.412	1.074	0.123	3.04	1.46	6.89	6.29	1.67	0.56	4.69

^a Toxic equivalency factors of congeners 81, 77, 126, 105, 118, and 156 are 0.0019, 0.000018, 0.022, 0.00047, 0.000008, 0.00000035, 0.000055, respectively [13]. See Table 1 for sample ID definitions. Values in parentheses indicate TEQs.

^b NA = not analyzed.

suspended solids are not a significant source of sediment contamination in the Detroit River. In addition, these results also indicate spatial heterogeneity in PCB distribution, because the concentrations varied by two to three orders of magnitude among the sampling locations. Sediment from the Detroit River locations near Penn Dixie, Coast Guard Shoal, U.S. Army Corps of Engineers boat slip, Great Lakes Steel Company, and Powerline and from the Rouge River locations near Ford Motor Company boat slip, Shell Oil Company, Fordson Island, and Jeff (i.e., Jefferson Street bridge over the Rouge River) contained PCB concentrations greater than 1,000 ng/g dry weight. Although spatial heterogeneity and localized high concentrations may be indicative of specific sources, the location description provided above may not directly indicate potential sources. For instance, the Coast Guard boat slip is not expected to be a direct discharger, but an old Uniroyal Tire facility was operated upstream of the Coast Guard location until the 1980s. The location description provides the nearest industrial or outfall facilities. Many facilities and multiple potential sources on the Detroit River above the Rouge River have influenced sediment contamination. For PCBs, the Conners Creek combined sewer overflow is a potential source in the upper Detroit River. The highest PCB concentration measured in this study was greater than those reported for sediments collected during 1986 and 1987 from the Trenton Channel (14–14,000 ng/g dry wt) in the Detroit River [1] and was also greater than those reported for the Detroit River during the early 1980s [8]. However, to our knowledge, no earlier studies measured PCBs in sediments from Conners Creek.

Penta-, hexa-, and hepta-chlorobiphenyls were the major PCB congeners found in sediments from several locations in the upper Detroit and Rouge Rivers. Sediments from Peche Island and Belle Isle contained a higher proportion of lower chlorinated congeners such as tri- through penta-chlorobiphenyls. Hexa-chlorobiphenyl congeners 138 (2,2',3,4,4',5') and 153 (2,2',4,4',5,5') were the predominant isomers found in sediments from most of the locations, suggesting exposure to technical grade PCB mixtures such as Aroclors 1254 and 1260. The PCBs were also detected in sediments off of Muskegon, Lake Michigan, at concentrations ranging from 1 to 23 ng/g dry weight (Table 2). These concentrations are lower than

those in less-polluted locations in the upper Detroit River such as Peche Island.

Concentrations of non-*ortho*-substituted coplanar PCBs were four to six orders of magnitude less than those of total PCBs (Table 3). The concentration of PCB congener 77 was the highest in sediment from Conners Creek (10,170 pg/g dry wt), whereas that from Peche Island was the lowest (100 pg/g dry wt). Concentrations of coplanar PCB congeners 77, 126, and 169 in sediments were 0.04 to 0.78%, 0.001 to 0.04%, and 0.00009 to 0.004%, respectively, of the total PCB concentrations. The PCB congener 81 was also found in sediments from all the locations. 2,3,7,8-Tetrachlorodibenzo-*p*-dioxin equivalents (TEQs) of non- and mono-*ortho*-substituted PCB congeners (PCB-TEQs) in sediments were estimated using the H4IIE cell line toxic equivalency factors (TEFs) [13]. The H4IIE TEFs were used because, for other organochlorines such as PCNs, only H4IIE TEFs are available in the literature [14,15]. For comparison of TEQs among different classes of organochlorines, it is necessary to use TEFs derived from a similar bioassay. The PCB-TEQs in sediments ranged from 0.12 to 6.89 pg/g dry weight (Table 3). The PCB congener 126 accounted for 67 to 91% (mean, 78%) of the total PCB-TEQs in sediments.

Polycyclic aromatic hydrocarbons

Concentrations of PAHs in the upper Detroit River and lower Rouge River sediments ranged from 18 to 43,810 ng/g dry weight (Table 2). Polycyclic aromatic hydrocarbon concentrations were greater than 1,000 ng/g dry weight at all the sampling locations except Peche Island and Scott middle ground. In general, sediments from Rouge River locations contained greater PAH concentrations than those from the upper Detroit River. Sediment collected from Fordson Island on the Rouge River contained the highest PAH concentration. Several oil companies, including Marathon Oil, and Baby Creek storm sewer outfall are situated in this location. However, attribution of a single source may be invalid due to the presence of multiple sources. Similar to that observed for PCBs, a large spatial variation was observed for PAH concentrations. Therefore, it is not possible to compare the previously published PAH data on a point-to-point basis. In general, the measured concentra-

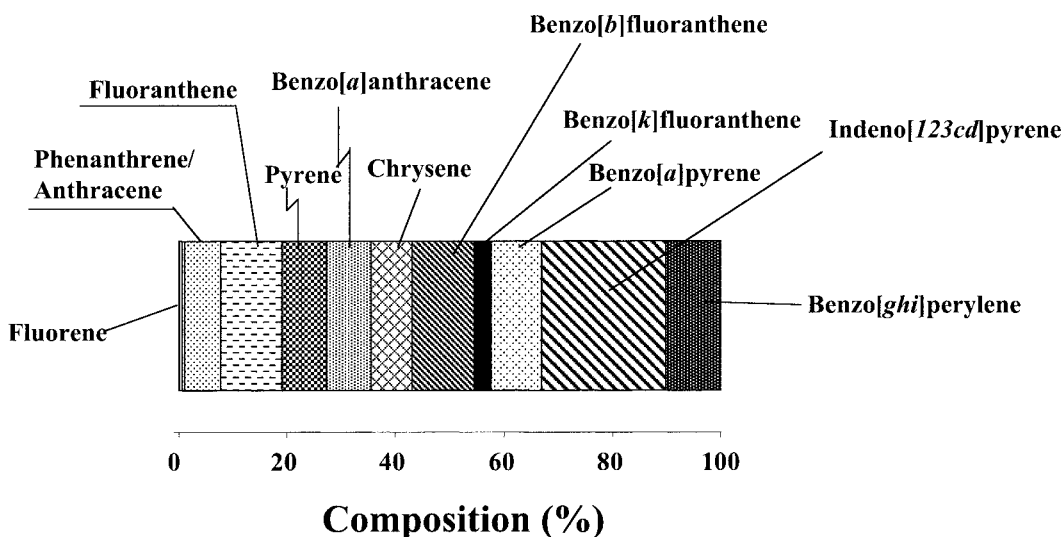


Fig. 2. Composition of polycyclic aromatic hydrocarbons in sediments from the upper Detroit and lower Rouge rivers (MI, USA).

tion ranges of PAHs were similar to those reported for sediments collected during 1986 from the Trenton Channel in the Detroit River (350–130,000 ng/g dry wt). However, the maximum concentration reported for the Trenton Channel sediments was threefold greater than the highest concentration observed in this study [1]. Similarly, surveys conducted by the Michigan Department of Environmental Quality from 1993 to 1996 reported PAH concentrations of as much as 200 µg/g dry weight in sediments from the lower Rouge River [16].

A variety of approaches have been developed and used to derive sediment-quality guidelines for PAHs to protect sediment-dwelling organisms [17–20]. Concentrations of total PAHs in sediments were greater than the suggested threshold effect concentrations (i.e., the concentration below which harmful effects are unlikely to occur) of 1,684 ng/g dry weight in all the locations except those from Belle Isle and Peche Island [19]. Similarly, the probable effect concentration (i.e., the concentration above which harmful effects are likely to occur) for total PAHs in sediment is 22,800 ng/g dry weight [20]. Sediments collected near Coast Guard boat slip, Great Lakes Steel, Powerline, Upper Rouge, Fordslip, Shell Oil Company, Fordson Island, and Dix navigation channel have exceeded the probable effect concentration for PAHs. On the basis of organic carbon-normalized concentrations, the threshold effect concentration for total PAHs is 290 µg/g organic carbon [18]. The organic carbon-normalized concentrations of total PAHs in the Detroit River and Rouge River sediment varied from 8 to 1,440 µg/g organic carbon. All the sediments except those from Peche Island, Belle Isle, and Scott middle ground exceeded the threshold effect concentration. Similar to the situation with PCBs, it is not possible to delineate specific emission sources of PAHs in the Rouge River, because several petroleum-based industries that operate along this river would have contributed to the measured PAH contamination.

The majority of PAHs found in sediments were high-molecular-weight PAHs (four to six rings) (Fig. 2). Indeno[1,2,3(cd)]pyrene accounted for, on average, 23% ± 6% of the total PAH concentrations. This was followed by benzo[b]fluoranthene (11% ± 3%), benzo[ghi]perylene (10% ± 2%), and benzo[a]pyrene (9.7% ± 1.8%). Despite differences in the magnitude of contamination, the relative amount of each PAH was similar across a wide range of absolute concentrations.

This suggests either a single PAH source, multiple sources that are not significantly different from one another (e.g., petroleum industries), or PAHs being well mixed before sedimentary deposition. In addition to being compositionally uniform, the presence of significant amounts of photoreactive PAHs such as anthracene and benzo[a]anthracene [21] in sediments suggests that a PAH source other than combustion-derived atmospheric particles contributes to the observed PAH signal. Some molecular ratios of specific PAH compounds were calculated to evaluate the characteristics of PAHs arising from different sources [22]. The fluoranthene-to-pyrene concentration ratios (Fluo:Py) of less than one are indicative of pyrolytic sources, whereas the values greater than one are indicative of petrogenic sources. The Fluo:Py ratios in surface sediments were generally greater than one for most locations and ranged up to 3.7. This suggests that the major source of PAHs in the upper Detroit and lower Rouge Rivers is petrogenic.

The PAHs were also found in sediment from Lake Michigan at concentrations ranging from 33 to 400 ng/g dry weight. The PAH values in Lake Michigan sediment are 10- to 100-fold greater than those of PCBs in Lake Michigan sediments. The composition of PAHs in sediments from Lake Michigan differed from that in the upper Detroit and lower Rouge Rivers. Four-ring aromatic hydrocarbons dominated in sediments from Lake Michigan. The predominant compounds were pyrene, fluoranthene, benzo[a]anthracene, and chrysene, accounting for 17.2%, 16.9%, 11%, and 13%, respectively, of the total PAH concentrations.

Alkylphenols

Butylphenol, OP, and NP were detected in sediments collected from several locations in the Detroit and Rouge Rivers (Table 4). Nonylphenol was the most predominant among the alkylphenolic compounds analyzed, and its concentration ranged from less than 10 to 60,000 ng/g dry weight. An earlier study reported NP concentrations ranging from 200 to 37,800 ng/g dry weight in sediment from the Detroit River [23]. The highest concentration was found in sediment collected near the Shell Oil Company on the Rouge River. Although a sewage treatment plant is located downstream of this location, a possible source for NP at this location might be the Baby Creek storm sewer outfall, which is located upstream of the location. Concentrations of NP were greater than 1,000 ng/g dry weight in several

Table 4. Concentrations (ng/g dry wt) of alkylphenols in sediments from the upper Detroit River (DR) and lower Rouge River (RR) and Lake Michigan (LM), Michigan, USA, in June 1998

Station ID	Location ^a	Description	Butylphenol	Octylphenol	Nonylphenol
DR9801	North Peche Island	Surface	<10	<10	<10
DR9802	South Peche Island	0–30 cm	50	<10	<10
DR9803	Conners—Inner	0–30 cm	NA ^b	1,080	8,890
DR9804	Conners—Outer	0–30 cm	67	1,520	17,000
DR9805	Scott middle ground	0–30 cm	<10	<10	21
DR9806	Belle Isle South	0–35 cm	<10	<10	<10
DR9807	Great Lakes Steel shoal	Ponar	93	24	1,120
DR9809	Penn Dixie—A	0–30 cm	68	95	3,330
DR9811	Coast Guard—B	0–30 cm	41	240	6,410
DR9812	Coast Guard—A	Ponar	170	69	2,310
DR9813	U.S. ACE—Inner	0–30 cm	36	1,030	3,540
DR9816	Powerline—mid	0–30 cm	68	9.2	82
DR9817	Great Lakes Steel—A	Ponar	37	16	1,950
DR9818	Powerline—Ontario	0–30 cm	<10	<10	130
RR9802	Upper Rouge—B	Ponar	5.6	27	970
RR9803	Turning Basin	0–30 cm	40	160	6,910
RR9804	Ford Slip—A	0–30 cm	170	890	6,200
RR9805	Ford Slip—B	0–30 cm	54	190	3,750
RR9806	Shell—Upper	0–30 cm	240	4,050	60,000
RR9808	Cement Dock	Ponar	<10	100	4,970
RR9809	Jeff—Upper	0–30 cm	<10	310	19,000
RR9810	Jeff—Lower	0–30 cm	<10	350	19,100
RR9814	Fordson—Mid	151–162 cm	<100	<100	<100
RR9814	Fordson—Mid	91–150 cm	<100	<100	<100
RR9814	Fordson—Mid	31–90 cm	340	980	6,000
RR9814	Fordson—Mid	0–30 cm	210	190	5,200
RR9816	Dix Nav—A	Ponar	NA	440	13,100
RR9819	Shell—Nav	Ponar	100	420	21,400
RR9820	Jeff—Nav	Ponar	NA	140	8,000
LM1	43°54'N, 86°94'W		<10	<10	<10
LM2	43°54'N, 86°94'W		<10	<10	<10
LM3	43°54'N, 86°94'W		<10	<10	<10
LM4	43°09'N, 86°81'W		<10	<10	<10
LM5	43°09'N, 86°81'W		<10	<10	<10

^a See Figure 1 for locations. U.S. ACE = U.S. Army Corps of Engineers.

^b NA = not analyzed.

locations of the Rouge River. Low concentrations of NP were found at remote locations such as Peche Island, Belle Isle, and Scott middle ground and in deeper layers (>30 cm) of sediment from Fordson Island. The NP concentrations are higher than those reported in previous studies that analyzed dry sediments from the United States and Europe [24]. Conners Creek combined sewer overflow is a potential source in the upper reaches of the Detroit River. The Detroit and Rouge Rivers also receive effluents from sewage treatment plants in the cities of Detroit and Windsor. Although wastewater treatment plants are located in the lower reaches of the Detroit River, relatively great concentrations of NP in sediment from the upper Detroit River suggest the presence of sources in the upper Detroit River.

A significant correlation existed between the concentrations of NP and OP ($r^2 = 0.69$). This suggests the presence of similar sources for NP and OP, but elimination of the highest concentration resulted in a lack of significant correlation. Furthermore, the ratios of NP to OP varied widely, from 3 in sediment collected near the U.S. Army Corps of Engineers boat slip to 120 in sediments collected near Great Lakes Steel boat slip. The NP:OP ratios in sediment from Conners Creek and Fordslip were also greater than those found at other locations. This suggests the presence of other sources of OP in addition to sewage treatment plant effluents. Use of OP polyethoxylates in industrial applications may have contributed to the greater proportions of OP in certain locations. As observed for OP, the ratios of NP to BP also varied widely, from 1.2 to 250. Relatively greater

ratios of NP to BP in samples collected near Powerline, Coast Guard boat slip, and Great Lakes Steel boat slip suggest the presence of local sources of BP.

Polychlorinated naphthalenes

The PCNs have been used as dielectrics, water repellents, lubricants, and in automobile capacitors. In this study, PCNs were measured in sediments from selected locations (Table 5). Polychlorinated naphthalenes were found in sediments from all the locations, and their concentrations ranged from 0.08 to 190 ng/g dry weight. Sediment collected near Great Lakes Steel shoal contained the greatest concentration, whereas those from Peche Island contained the least. These concentrations were approximately 10-fold lower than the concentrations reported for the Trenton Channel sediments in the Detroit River in 1986 [1]. However, the results of this study are consistent with the lower concentrations of PCNs reported for the locations upstream of the Trenton Channel [1]. These results indicate that the major sources of PCNs are located in the Trenton Channel. Despite this, the measured concentrations of PCNs were greater than those reported for sediment from the Polish coast of the Baltic Sea [25] and for Tsurumi River, Dokay Bay, and Tokyo Bay in Japan [12,26].

The pattern of relative concentrations of PCN isomers and congeners varied among locations, suggesting the presence of multiple sources. On average, penta- and hexa-chloronaphthalenes accounted for 60% of the total PCN concentrations in

Table 5. Concentrations (ng/g dry wt) of polychlorinated naphthalenes in sediments from the upper Detroit River (DR) and lower Rouge River (RR) and Lake Michigan (LM), Michigan, USA, in June 1998

Station ID	Location	Description	Tri-CN ^a	Tetra-CN	Penta-CN	Hexa-CN	Hepta-CN	OCN ^b	Total
DR9801	North Peche Island	Surface	0.002	0.025	0.01	0.024	0.017	<0.001	0.08
DR9802	South Peche Island	0–30 cm	0.28	0.58	0.76	1	0.64	0.59	3.85
DR9805	Scott middle ground	0–30 cm	1.84	4.01	6.56	5.49	1.27	1.29	20.5
DR9806	Belle Isle South	0–35 cm	0.02	0.051	0.056	0.028	0.027	<0.001	0.18
DR9807	Great Lakes Steel shoal	Ponar	9.11	43	73	47	12	2.6	187
DR9809	Penn Dixie—A	0–30 cm	1.89	3.65	6.94	7.89	2.07	1.07	23.5
DR9811	Coast Guard—B	0–30 cm	7.15	13.2	35	44	6.58	1.011	107
DR9815	Powerline—Inner	0–30 cm	0.78	5.61	26.3	33.1	3.75	0.72	70.3
DR9818	Powerline—Ontario	0–30 cm	0.57	1.75	3.2	3.07	0.86	0.49	9.94
RR9802	Upper Rouge—B	Ponar	1.37	2.6	6.07	6.08	1.81	0.247	18.2
LM3	43°54'N, 86°94'W		<0.001	0.07	0.23	0.31	0.17	0.007	0.787
LM4	43°54'N, 86°94'W		<0.001	0.06	0.22	0.28	0.13	0.01	0.7
LM1	43°54'N, 86°94'W		<0.001	0.02	0.08	0.14	0.06	0.01	0.31

^a CN = chloronaphthene.

^b OCN = octachloronaphthene.

sediments. In sediments collected from Peche Island, Belle Isle, and Great Lakes Steel shoal, tri- through penta-chlorinated naphthalenes were relatively higher in concentration than in sediments from other locations. Profiles of PCN congener composition in selected locations representing high, medium, and low concentrations are presented in Figure 3. The PCN congeners 71 and 72 (124568- and 124578-HxCN) were the most abundant in sediment from several locations, followed by PCNs 59 (12458-PeCN) and 69 (123578-HxCN), which collectively accounted for 20 to 30% of the total PCN concentrations. Sediment collected near Peche Island contained greater proportions of congeners 66 and 67 (123467- and 123567-HxCN) and of congeners 52 and 60 (12357- and 12467-PeCN), which collectively accounted for 20% of the total PCN concentrations. Sediment collected near Belle Isle contained greater proportions of hepta-chloronaphthalene congener 73 (1234567). The presence of great proportions of congeners 59,

71, and 72 suggest Halowaxes as the main source of PCNs in sediments from the Detroit and Rouge Rivers; the presence of congener 54, which was absent from Halowaxes, suggests the existence of other PCN sources [27]. Particularly, the presence of congeners 54, 44, and 29 in sediments suggests contribution from incineration-related sources [26]. The PCNs were also found in sediments from Lake Michigan at concentrations ranging from 0.31 to 0.79 ng/g dry weight.

Several of the PCN congeners elicit toxic effects similar to those of 2,3,7,8-tetrachlorodibenzo-*p*-dioxin through the Ah receptor-mediated mechanism [14,15]. These include induction of aryl hydrocarbon hydroxylase and ethoxyresorufin-*O*-deethylase, chloracne, and liver damage [28]. The TEFs (i.e., relative potency of a congener to that of 2,3,7,8-tetrachlorodibenzo-*p*-dioxin) have been reported for several chlorinated naphthalene congeners based on in vitro responses of H4IIE cell lines [14,15]. The TEQs were estimated using an additive

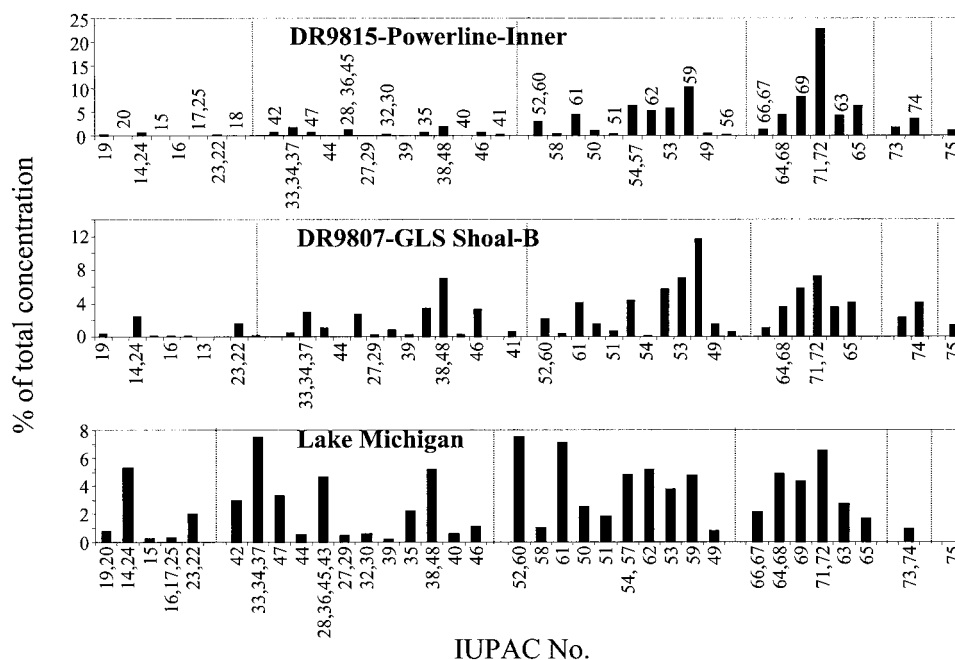


Fig. 3. Relative concentrations of polychlorinated naphthalene (PCN) isomers and congeners in sediments from selected locations in the upper Detroit and lower Rouge rivers and Lake Michigan (MI, USA). Concentrations were normalized relative to that of the most abundant congener, which was treated as 100. Samples were selected to represent low, moderate, and high PCN concentrations. IUPAC = International Union of Pure and Applied Chemists.

Table 6. Concentrations (ng/g dry wt) of dioxin-like polychlorinated naphthalenes and their toxic equivalents (TEQs; pg/g dry wt) in sediments from the upper Detroit River (DR) and lower Rouge River (RR) and Lake Michigan (LM), Michigan, USA, in June 1998^a

IUPAC ^b no.	TEF ^c	DR9805	DR9809	DR9811	DR9807	DR9802	DR9801	RR9802	DR9815	DR9806	DR9818	LM1	LM3	LM4
54	0.00017	0.04 (0.007)	0.12 (0.20)	5 (0.85)	0.24 (0.041)	0.018 (0.003)	<0.001	1.08 (0.18)	4.42 (0.75)	0.011 (0.002)	0.067 (0.011)	0.02 (0.003)	0.027 (0.005)	0.021 (0.004)
56	0.000049	0.04 (0.002)	0.11 (0.005)	<0.001	0.97 (0.048)	0.012 (0.001)	<0.001	<0.001	0.11 (0.005)	<0.001	0.03 (0.001)	<0.001	<0.001	<0.001
57	0.0000037	0.92 (0.003)	0.94 (0.003)	5 (0.019)	7.9 (0.029)	0.074 (0.001)	<0.001	1.08 (0.004)	4.42 (0.016)	0.011 (0.001)	0.35 (0.001)	0.021 (0.001)	0.037 (0.001)	0.03 (0.001)
60	1.42E-05	1.14 (0.016)	0.93 (0.013)	4.39 (0.062)	4.01 (0.057)	0.17 (0.002)	0.01 (0.001)	0.503 (0.007)	2.13 (0.03)	0.006 (0.001)	0.396 (0.006)	0.036 (0.001)	0.051 (0.001)	0.053 (0.001)
63	0.002	0.49 (0.98)	0.91 (1.82)	4.38 (8.76)	6.58 (13.2)	0.068 (0.14)	<0.001	0.73 (1.46)	2.89 (5.78)	<0.001	0.43 (0.86)	0.01 (0.02)	0.012 (0.024)	0.01 (0.020)
66	0.0024	0.84 (2.02)	0.49 (1.18)	1.66 (3.98)	1.85 (4.44)	0.51 (1.22)	0.016 (0.038)	0.36 (0.86)	0.93 (2.23)	<0.001	0.47 (1.13)	0.012 (0.029)	0.016 (0.038)	0.027 (0.065)
68	0.0015	0.77 (1.16)	0.94 (1.41)	4.5 (6.75)	6.4 (9.6)	0.13 (0.2)	0.008 (0.012)	0.78 (1.17)	3.12 (4.68)	0.007 (0.11)	0.47 (0.71)	0.028 (0.042)	0.038 (0.057)	0.024 (0.036)
69	0.002	1.05 (2.1)	1.55 (3.1)	7.15 (14.3)	11 (22)	0.12 (0.24)	<0.001	1.34 (2.68)	5.69 (11.4)	0.014 (0.028)	0.53 (1.06)	0.013 (0.026)	0.018 (0.036)	0.021 (0.042)
70	0.0095	<0.001	<0.001	<0.001	0.053 (0.50)	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001
73	0.001	0.91 (0.91)	0.71 (0.71)	1.51 (1.51)	4.13 (4.13)	0.57 (0.57)	0.017 (0.017)	1.02 (1.02)	1.2 (1.2)	0.02 (0.02)	0.43 (0.43)	0.008 (0.008)	0.007 (0.007)	<0.001
Total TEQs		7.19	8.26	36.2	54	2.37	0.068	7.39	26.1	0.06	4.2	0.129	0.168	0.167

^a See Table 1 for sample ID. Values in parentheses indicate TEQs.^b IUPAC = International Union of Pure and Applied Chemists.^c TEF = toxic equivalency factor.

Table 7. Concentration (pg/g dry wt) of 2,3,7,8-substituted polychlorinated dibenzo-*p*-dioxins (PCDDs) and polychlorinated dibenzofurans (PCDFs) in sediments from the upper Detroit River (DR) and lower Rouge River (RR; MI, USA) sediments

	DR9805	DR9812	DR9802	RR9805	RR9803	DR9803	DR9814	RR9807	DR9815	RR9804
PCDDs										
2,3,7,8-	0.84	0.8	0.42	2.9	3.5	15.1	5.25	4.91	0.66	3.7
1,2,3,7,8-	1.48	1.79	0.52	6.41	6.43	13.1	8.34	9.89	0.85	8.34
1,2,3,4,7,8-	1.16	1.66	0.42	4.15	2.14	6.56	5.15	4.07	0.66	3.67
1,2,3,6,7,8-	2.66	4.54	0.72	31.8	28.3	50.5	51.6	42.2	2.05	43.1
1,2,3,7,8,9-	0.78	2.48	0.44	9.66	5.66	1.67	1.66	2.63	0.7	5.31
1,2,3,4,6,7,8-	15.7	53.9	8.3	175	46.7	142	70.3	36.1	15.0	97
OCDD ^b	69.4	11.2	45.9	66.7	26.4	1,020	290	114	75.7	137
ΣPCDDs	92.0	76.5	56.8	297	119	1,250	432	214	95.6	299
PCDFs										
2,3,7,8-	4.72	4.16	2.1	6.59	1.87	50.3	14.8	5.03	1.96	10.4
1,2,3,7,8-	2.05	2.23	0.83	4.29	0.94	15.4	5.4	11.6	0.81	6.44
2,3,4,7,8-	2.18	2.84	0.84	6.23	2	42.2	10.9	4.42	1.73	8.42
1,2,3,4,7,8-	2.3	4.05	1.24	11.5	3.57	32.5	16.1	7.16	1.57	15.4
1,2,3,6,7,8-	1.19	3.27	0.55	8.06	2.99	13.3	8	4.47	0.44	9.62
2,3,4,6,7,8-	0.84	3.68	0.45	8.58	2.93	3.82	<0.1	2.14	0.62	7.71
1,2,3,7,8,9-	0.05	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	0.55
1,2,3,4,6,7,8-	8.22	10.1	3.17	10.6	1.25	5.03	12.9	6.27	3.31	3.86
1,2,3,4,7,8,9-	0.33	1.72	0.27	5.75	1.52	2.41	1.96	0.88	0.26	6.93
OCDF ^c	6.09	0.64	2.46	2.6	0.93	6.31	23.9	6.01	3.61	4.5
ΣPCDFs	28	32.7	11.9	64.1	18	171	94.0	48	14.3	73.8
ΣPCDD/PCDFs	120	109	68.7	361	137	1,420	526	262	110	372

^a See Table 1 for sample ID.

^b OCDD = octachlorodibenzo-*p*-dioxin.

^c OCDF = octachlorodibenzofuran.

model by multiplying concentrations of dioxin-like PCN congeners with their corresponding TEFs and then summing the products. The TEQs contributed by PCNs in sediments ranged from 0.06 to 54 pg/g dry weight (Table 6). The lowest concentrations of PCN-TEQs were found in sediment from Belle Isle, whereas the highest concentration was found in sediment collected near Great Lakes Steel shoal.

PCDDs and PCDFs

Concentrations of 2,3,7,8-substituted PCDDs and PCDFs in sediments from selected locations are presented in Table 7.

The greatest concentration (1,415 pg/g dry wt) was found in sediment from Conners Creek, whereas the lowest (69 pg/g dry wt) was found in Peche Island sediments. To our knowledge, no earlier reports of PCDD or PCDF concentrations in sediment from the Detroit and Rouge Rivers are available for comparison. Concentrations of PCDDs were greater than those of PCDFs in sediments. Both octachlorodibenzo-*p*-dioxin and octachlorodibenzofuran are the predominant congeners found in sediments from most locations, which are similar to that found in pentachlorophenol.

Concentrations of TEQs estimated for 2,3,7,8-substituted

Table 8. Toxic equivalents contributed by 2,3,7,8-substituted polychlorinated dibenzo-*p*-dioxins (PCDDs) and polychlorinated dibenzofurans (PCDFs) in the upper Detroit River (DR) and Rouge River (RR; MI, USA) sediments (pg/g dry wt)^a

Isomers ^b	H4IIE-TEFs ^c	DR9805	DR9812	DR9802	RR9805	RR9803	DR9803	DR9814	RR9807	DR9815	RR9804
2,3,7,8-TeCDD	1	0.84	0.8	0.42	2.9	3.5	15.1	5.25	4.91	0.66	3.7
1,2,3,7,8-PeCDD	0.42	0.622	0.752	0.218	2.69	2.7	5.48	3.5	4.15	0.357	3.5
1,2,3,4,7,8-HxCDD	0.083	0.096	0.138	0.035	0.344	0.178	0.544	0.427	0.338	0.055	0.305
1,2,3,6,7,8-HxCDD	0.024	0.064	0.109	0.017	0.763	0.678	1.21	1.24	1.01	0.049	1.04
1,2,3,7,8,9-HxCDD	0.034	0.027	0.084	0.015	0.328	0.192	0.057	0.056	0.089	0.024	0.181
1,2,3,4,6,7,8-HpCDD	0.023	0.361	1.24	0.191	4.03	1.07	3.25	1.62	0.83	0.345	2.23
OCDD	0.00054	0.037	0.006	0.025	0.036	0.014	0.549	0.157	0.062	0.041	0.074
Σ PCDDs		2.05	3.13	0.921	11.1	8.34	26.2	12.3	11.4	1.53	11
2,3,7,8-TeCDF	0.2	0.944	0.832	0.42	1.32	0.374	10.1	2.97	1.01	0.392	2.08
1,2,3,7,8-PeCDF	0.2	0.41	0.446	0.166	0.858	0.188	3.07	1.08	2.32	0.162	1.29
2,3,4,7,8-PeCDF	0.28	0.61	0.795	0.235	1.74	0.56	11.8	3.06	1.24	0.484	2.36
1,2,3,4,7,8-HxCDF	0.02	0.046	0.081	0.025	0.229	0.071	0.65	0.322	0.143	0.031	0.308
1,2,3,6,7,8-HxCDF	0.6	0.714	1.96	0.33	4.84	1.79	7.99	4.8	2.68	0.264	5.77
2,3,4,6,7,8-HxCDF	0.2	0.168	0.736	0.09	1.72	0.586	0.764	0	0.428	0.124	1.54
1,2,3,7,8,9-HxCDF	0.3	0.015	0	0	0	0	0	0	0	0	0.165
1,2,3,4,6,7,8-HpCDF	0.3	2.47	3.02	0.951	3.17	0.375	1.51	3.88	1.88	0.993	1.16
1,2,3,4,7,8,9-HpCDF	0.02	0.007	0.034	0.005	0.115	0.03	0.048	0.039	0.018	0.005	0.139
OCDF	0	0	0	0	0	0	0	0	0	0	0
Σ PCDFs		5.38	7.91	2.22	14	3.98	35.9	16.1	9.72	2.46	14.8
Σ PCDDs PCDFs		7.43	11.0	3.14	25.1	12.3	62.1	28.4	21.1	3.99	25.8

^a See Table 1 for sample ID.

^b OCDD = octachlorodibenzo-*p*-dioxin; OCDF = octachlorodibenzofuran.

^c [13]. TEFs = toxic equivalency factors.

Table 9. Correlation matrix for organic contaminants in sediments from the Detroit and Rouge rivers, Michigan, USA^a

	TOC	PCBs	PCNs	PAHs	NP	PCDDs	PCDFs
TOC	1	0.48	0.02	0.52	0.56	0.39	0.45
PCBs		1	0.06	0.05	0.19	0.92	0.87
PCNs			1	0.42	0.3	0.75	0.16
PAHs				1	0.18	0.22	0.33
NP					1	0.69	0.66
PCDDs						1	0.96
PCDFs							1

^a Values in bold represent statistical significance ($p < 0.05$). TOC = total organic carbon, PCBs = polychlorinated biphenyls, PCNs = polychlorinated naphthalenes, PAHs = polycyclic aromatic hydrocarbons, NP = nonylphenol; PCDDs = polychlorinated dibenzo-*p*-dioxins, PCDFs = polychlorinated dibenzofurans.

PCDDs and PCDFs in sediments ranged from 3.99 to 62 pg/g dry weight (Table 8). Depending on the location, TCDD, 1,2,3,4,6,7,8-heptachlorodibenzofuran, or 1,2,3,6,7,8-hexachlorodibenzofuran contributed the greatest proportion of the TEQs. The TEFs of several PCDFs are greater than those of several PCDDs as determined using H4IIE in vitro bioassays [13]. This has resulted in their higher contribution to TEQs compared with that of PCDDs.

Relationship among residues

A significant correlation was found between total organic carbon content and PCBs, PAHs, NP, PCDDs, or PCDF concentrations in sediments (Table 9). However, PCN concentrations were not significantly correlated with total organic carbon content. The PCB concentrations were significantly ($p < 0.05$) correlated with those of PCDDs and PCDFs. Similarly PCDD concentrations were significantly correlated with PCDF concentrations. These results suggest the existence of similar sources for these contaminants. On the other hand, PAH and NP concentrations were not related to the other contaminants analyzed. This suggests that PAHs and NP originate from sources independent of those providing the other chlorinated organic contaminants analyzed.

Dioxin-like activities

The relative contributions of PCBs, PCNs, PCDDs, and PCDFs to the concentrations of TEQs were estimated using H4IIE cell line-specific TEFs for all the above compounds. Because PCNs, PCDDs, and PCDFs were measured only in selected sediments, the concentrations for all the target compounds were available only for sediments from locations DR9802, DR9805, and DR9815. The total TEQs of PCNs, PCBs, PCDDs, and PCDFs in these sediments ranged from 5.7 to 31 pg/g dry weight. The PCNs contributed the greatest TEQs (42–84% of the total), followed by PCDFs (8–39%), PCDDs (5–16%), and then PCBs (2–3%) (Fig. 4). Despite the lower concentrations of PCNs in the upper Detroit River, PCN-TEQs are greater than those for PCDDs, PCDFs, and PCBs.

SUMMARY

The results of this study suggest that sediments from the upper Detroit and lower Rouge Rivers are contaminated with target organic compounds. Considerable spatial heterogeneity in contaminant distribution was found. Several industrial facilities and combined sewer overflows located along the upper Detroit and lower Rouge Rivers have influenced the sediment contamination. The Connors Creek combined sewer overflow

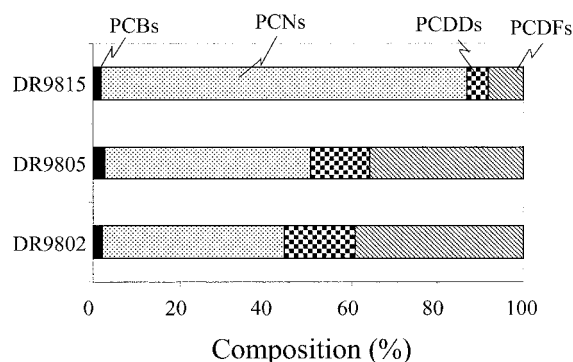


Fig. 4. Proportion (%) of 2,3,7,8-tetrachlorodibenzo-*p*-dioxin equivalents (TEQs) contributed by polychlorinated biphenyls (PCBs), naphthalenes (PCNs), dibenzo-*p*-dioxins (PCDDs), and dibenzofurans (PCDFs) in sediments from selected locations in the upper Detroit River (MI, USA). Locations DR9815, DR9805, and DR9802 are Powerline-Inner, Scott Middle Ground, and South Peche Island, respectively.

is one of the potential sources for organic contaminants in the upper Detroit River, in which the highest concentrations of PCBs, PCDDs, and PCDFs were found. The concentrations of PAHs and NP were consistently high in sediments collected in the Rouge River, which suggests the presence of multiple emission sources for these compounds. A small number of samples analyzed in this study indicated that the contribution of PCNs to dioxin-like activities in sediments is greater than those of PCBs, PCDDs, and PCDFs, which is consistent with earlier observations noted for fish from the Detroit River [29].

REFERENCES

- Furlong ET, Carter DS, Hites RA. 1988. Organic contaminants in the sediments from the Trenton Channel of the Detroit River, Michigan. *J Gt Lakes Res* 14:489–501.
- Leadly TA, Arcand-Hoy LD, Haffner GD, Metcalfe CD. 1999. Fluorescent aromatic hydrocarbons in bile as a biomarker of exposure of brown bullheads (*Ameiurus nebulosus*) to contaminated sediments. *Environ Toxicol Chem* 18:750–755.
- Leadly TA, Balch G, Metcalfe CD, Lazar R, Mazak E, Habowsky J, Haffner GD. 1998. Chemical accumulation and toxicological stress in three brown bullhead (*Ameiurus nebulosus*) populations of the Detroit River, Michigan, USA. *Environ Toxicol Chem* 17:1756–1766.
- Ali FN, Lazar R, Haffner GD, Adeli K. 1993. Development of a rapid and simple genotoxicity assay using a brown bullhead fish cell-line: Application to toxicological surveys of sediments in the Huron-Erie corridor. *J Gt Lakes Res* 19:342–351.
- Froese KL, Verbrugge DA, Snyder SA, Tilton F, Tuchman M, Ostaszewski A, Giesy JP. 1997. PCBs in the Detroit River water column. *J Gt Lakes Res* 23:440–449.
- Lau YL, Oliver BG, Krishnappan BG. 1989. Transport of some chlorinated contaminants by the water, suspended sediments, and bed sediments in the St. Clair and Detroit Rivers. *Environ Toxicol Chem* 8:293–301.
- Fallon ME, Horvath FJ. 1985. Preliminary assessment of contaminants in the soft sediments of the Detroit River. *J Gt Lakes Res* 11:373–378.
- Kaiser KLE, Comba ME, Hunter H, Maguire RJ, Tkacz RJ, Platford RF. 1985. Trace organic contaminants in the Detroit River. *J Gt Lakes Res* 11:386–399.
- Khim JS, Kannan K, Villeneuve DL, Koh CH, Giesy JP. 1999. Characterization and distribution of trace organic contaminants in sediment from Masan Bay, Korea. 2. Instrumental analysis. *Environ Sci Technol* 33:4199–4205.
- Khim JS, Villeneuve DL, Kannan K, Hu WY, Giesy JP, Kang SG, Song KJ, Koh CH. 2000. Instrumental and bioanalytical measures of persistent organochlorines in blue mussel (*Mytilus edulis*) from Korean coastal waters. *Arch Environ Contam Toxicol* 39:360–368.

11. Kannan K, Imagawa T, Blankenship A, Giesy JP. 1998. Isomer-specific analysis and toxic evaluation of polychlorinated naphthalenes in soil, sediment and biota collected near the site of a former chlor-alkali plant. *Environ Sci Technol* 32:2507–2514.
12. Yamashita N, Kannan K, Imagawa T, Villeneuve DL, Hashimoto S, Miyazaki A, Giesy JP. 2000. Vertical profile of polychlorinated naphthalenes, dibenzo-*p*-dioxin, dibenzofurans, biphenyls, polycyclic aromatic hydrocarbons and alkylphenols in a sediment core from Tokyo Bay, Japan. *Environ Sci Technol* 34:3560–3567.
13. Giesy JP, et al. 1997. Polychlorinated dibenzo-*p*-dioxins, dibenzofurans, biphenyls and 2,3,7,8-tetrachlorodibenzo-*p*-dioxin equivalents in fishes from Saginaw Bay, Michigan. *Environ Toxicol Chem* 16:713–724.
14. Blankenship A, Kannan K, Villalobos S, Villeneuve DL, Falandysz J, Imagawa T, Jakobsson E, Giesy JP. 2000. Relative potencies of individual polychlorinated naphthalenes and Halowax mixtures to induce Ah receptor-mediated responses. *Environ Sci Technol* 34:3153–3158.
15. Villeneuve DL, Kannan K, Khim JS, Falandysz J, Blankenship AL, Giesy JP. 2000. Relative potencies of individual polychlorinated naphthalenes to induce dioxin-like responses in fish and mammalian in vitro bioassays. *Arch Environ Contam Toxicol* 39:273–281.
16. Michigan Department of Environmental Quality. 1997. Results of the Trenton Channel Project sediment surveys 1993–1996. Michigan Department of Environmental Quality, Surface Water Quality Division, Lansing, MI, USA.
17. Long ER, Field LJ, MacDonald DD. 1998. Predicting toxicity in marine sediments with numerical sediment quality guidelines. *Environ Toxicol Chem* 17:714–727.
18. Swartz R. 1999. Consensus sediment quality guidelines for polycyclic aromatic hydrocarbon mixtures. *Environ Toxicol Chem* 18:780–787.
19. Carr RS, Montagna PA, Biedenbach JM, Klake R, Kennicutt MC, Hooten R, Cripe G. 2000. Impact of storm-water outfalls on sediment quality in Corpus Christi Bay, Texas, USA. *Environ Toxicol Chem* 19:561–574.
20. MacDonald DD, Ingersoll CG, Berger TA. 2000. Development and evaluation of consensus-based sediment quality guidelines for freshwater ecosystems. *Arch Environ Contam Toxicol* 39:20–31.
21. Behymer TD, Hites RA. 1985. Photolysis of polycyclic aromatic hydrocarbons and simulated atmospheric particles. *Environ Sci Technol* 19:1004–1006.
22. Baumard P, Budzinski H, Garrigues P. 1998. Polycyclic aromatic hydrocarbons in sediments and mussels of the western Mediterranean Sea. *Environ Toxicol Chem* 17:765–776.
23. Bennett ER, Metcalfe CD. 1998. Distribution of alkylphenol compounds in Great Lakes sediments, United States and Canada. *Environ Toxicol Chem* 17:1230–1235.
24. Bennie DT. 1999. Review of the environmental occurrence of alkylphenols and alkylphenol ethoxylates. *Water Qual Res J Canada* 34:79–122.
25. Falandysz J, Strandberg L, Bergqvist P-A, Kulp SE, Strandberg B, Rappe C. 1996. Polychlorinated naphthalenes in sediment and biota from the Gdańsk basin, Baltic Sea. *Environ Sci Technol* 30:3266–3274.
26. Imagawa T, Yamashita N. 1996. Estimation of emission sources of polychlorinated naphthalenes using finger-print method for isomer composition. *J Environ Chem* 6:495–501.
27. Falandysz J, Kawano M, Ueda M, Matsuda M, Kannan K, Giesy JP, Wakimoto T. 2000. Composition of chloronaphthalene congeners in technical chloronaphthalene formulations of the Halowax series. *J Environ Sci Health A* 35:281–298.
28. Hanberg A, Ståhlberg M, Georgellis A, de Wit C, Ahlberg UG. 1991. Swedish dioxin survey: Evaluation of the H4IIE bioassay for screening and environmental samples for dioxin-like enzyme induction. *Pharmacol Toxicol* 69:442–449.
29. Kannan K, Yamashita N, Imagawa T, Decoen W, Khim JS, Day RM, Summer CL, Giesy JP. 2000. Polychlorinated naphthalenes and polychlorinated biphenyls in fishes from Michigan waters including the Great Lakes. *Environ Sci Technol* 34:566–572.