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POLYCYCLIC AROMATIC HYDROCARBONS IN THE SEDIMENTS OF THE MILWAUKEE HARBOR ESTUARY, WISCONSIN, U.S.A.

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Abstract. From 1990 to 1994, a total of 21 sediment cores and 37 grab sediment samples were collected from the Milwaukee Harbor Estuary. Each sediment core was sectioned and dated using ^{210}Pb and ^{137}Cs radioisotope techniques. A total of 305 samples were analyzed for sixteen polycyclic aromatic compounds (PAHs). Grain size distribution, porosity, and total organic carbon content as measured by loss on ignition were also determined. The results provide a historical overview of the impact of industrialization in the Milwaukee area. Although highly variable, the concentration profile of PAHs show, in general, peaks in the 1950's through 1980's. The PAH concentrations have declined since then for most sediment cores. The current levels of total PAHs in most surface sediment samples range from 25 to 200 ppm. A few cores, some of which were collected in 1994, have an elevated PAH concentration at the surface. Toxicity of the surface sediments was evaluated by comparing with the benchmark values developed by the United States National Oceanic and Atmospheric Administration (NOAA). The most heavily contaminated area was found in the Kinnickinnic River between the Becher Street Bridge and the Wisconsin Wrecking Company Wharf. The highest total PAH concentration determined from seven vibra cores collected in this area ranges from 380 to 1000 ppm. The former Wisconsin Solvay Çoke Company may have been a major point source of PAHs until the 1970's. Highway traffic and various industrial discharges also contribute to the sediment PAHs in this area.

Key words: freshwater estuary, PAHs, sediments, toxicity sources

1. Introduction

Polycyclic aromatic hydrocarbons (PAHs) are highly hydrophobic and have strong affinity for particulates. After entering natural water bodies via various pathways, they rapidly sink to the sediments without substantial removal in the water column (Gschwend and Hites, 1981). High levels of PAHs have been found in sediments in many industrialized areas (NOAA 1988, 1991). Consequently, the horizontal and vertical distribution of PAHs in sediments, plus knowledge of the sedimentation patterns and history, provides information useful for identifying historical and present sources of pollution, for assessing the ecological hazards to humans and biota, and for making environmental management plans.

The Milwaukee Harbor Estuary is the confluence of the Milwaukee, the Kinnickinnic, and the Menomonee Rivers within the urban area, and the Inner and Outer Milwaukee Harbors. Due to the historical growth in industry since the nineteenth century, significant amounts of complex environmental pollutants have been

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deposited into the estuary, and constitute a source of contamination to the Lake Michigan. According to the available data, most surface sediments in Milwaukee Harbor Estuary should be categorized as heavily polluted based on the sediment quality criteria for Great Lakes harbors issued by the U.S. EPA (SEWRPC, 1987, Vol. 1). PAHs are among the toxic substances which were determined to be of primary concern in the estuary by the International Joint Commission's Water Quality Board (SEWRPC, 1987, Vol. 2). However, few data are available on the historical contamination of PAHs in the estuary, due probably to the lack of sediment dating information. In addition, we are not aware of any studies focusing on and pointing out the sources of PAHs found in this area.

This study examines the history and current level of PAHs in the Milwaukee Harbour Estuary. The work includes sediment core and grab sampling, dating of cores by radioactive isotopes, sample characterization, and analyses of the samples for sixteen polycyclic aromatic compounds (PAHs). Sediment toxicity is evaluated by comparing the PAH concentrations with benchmark values developed by National Oceanic and Atmospheric Administration (US-NOAA). The data will also be used as input to develop mathematical models for source analysis (Christensen *et al.*, 1997), to examine the relationship between sediment properties and PAH contamination (Ab Razak, *et al.*, 1996), and to assist in making toxic substances management decisions for the Milwaukee Harbor Estuary.

2. Materials and Methods

2.1. SAMPLING

From September 1990 to June 1994, a total of 37 sediment cores including 12 box cores (BC), 8 gravity cores (GC), 17 vibra cores (VC), and 50 surface grab samples (GR) were collected from the Milwaukee Harbor Estuary. A sampling map is shown in Figure 1. The length of box cores was 19 to 25 cm, and that of gravity cores 25 to 30 cm. The retrieved vibra cores (push cores) collected in 1991 were 1 to 2 m long, and vibra cores collected in 1994 were 2 to 3 m long. Each sediment core was sliced into 5 to 15 sections and stored at –15 °C until PAH analysis was performed and at 4 °C until other analyses were carried out.

2.2. POROSITY, LOI, AND GRAIN SIZE ANALYSIS

The weight fraction of water (w) was determined by drying the sediment sample to a constant weight for about 2 to 3 days at 60 °C. The porosity was calculated by equation (1) assuming that the solid sediment density ρ_s equals 2.45 g cm^{-3}.

$$\text{Porosity} = \rho_s\, w/[1 + (\rho_s - 1)\, w]. \quad (1)$$

The total organic carbon of the sample was estimated by determining the loss on ignition (LOI), which is the percent weight loss of a dried sample after being

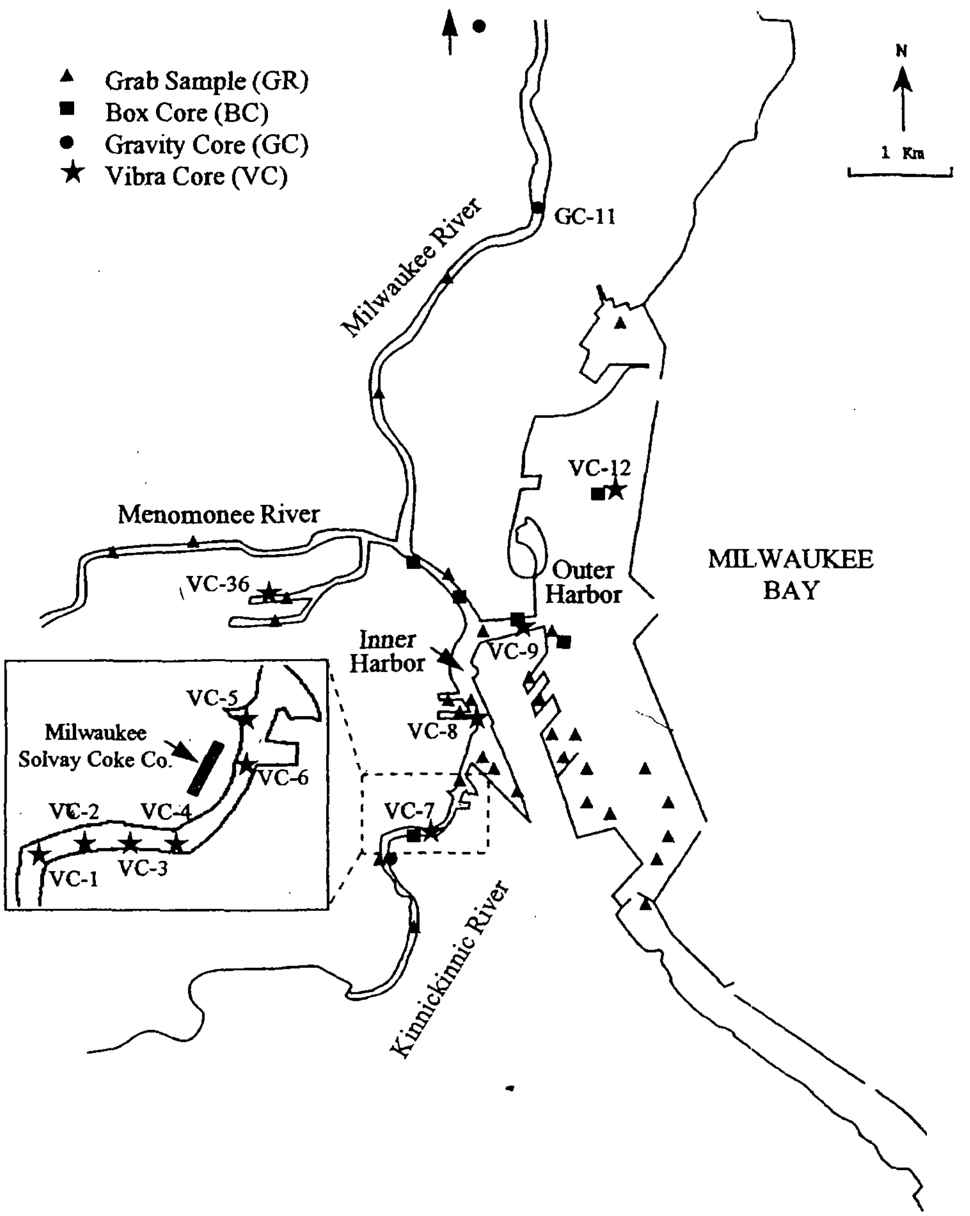

Figure 1. Map of the Milwaukee Harbor Estuary with sampling sites. The section enclosed in the enlarged inside map is the stretch of the Kinnickinnic River between the Becher Street Bridge and the Wisconsin Wrecking Company Wharf. Sampling locations marked in the map insert were sampled in 1994, all other samples were collected in 1990 or 1991.

heated in a 550 °C oven for 10 to 15 min. The grain size analysis consists of separating the coarse portion of a dried sample by sieves, and hydrometric analysis of the portion finer than 0.075 mm in diameter. Detailed procedures are outlined in Roderick (1991) and AASHTO (1982).

2.3. SEDIMENT DATING

Both ^{137}Cs and ^{210}Pb measurements were used as dating tools in order to determine sedimentation rates and patterns. Determination of ^{137}Cs was accomplished by placing a plastic bag containing a sediment pellet on top of a high resolution, lithium-drifted germanium, Ge(Li), detector (EG&G Ortec Model 576) overnight. Data from the detector were collected and analyzed using EG&G Maestro™ Adcam® multichannel analyzer software. ^{137}Cs emits gamma energy at 661 keV, and this was quantified using the software as net area count per second. ^{210}Pb activity was determined by detecting alpha emmissions from ^{210}Po decay, using ^{208}Po as a yield tracer. The procedures involved in chemical separation are described in detail in Li *et al.* (1995).

The excess ^{210}Pb activity is calculated by subtracting supported ^{210}Pb from the total activity detected. The supported ^{210}Pb was approximated to be 1.4 dpm g^{-1} based on the ^{210}Pb value of the bottom layers of deep cores. The sedimentation rate and velocity were calculated according to a linear regression of log excess ^{210}Pb activity against cumulative mass of the sediment core. Generally, sediment layers registering the highest level of ^{137}Cs activity reflect sediment deposited in 1963 when nuclear weapons testing peaked. The date of sedimentation from ^{137}Cs data was determined by assuming a constant sedimentation rate (cm yr^{-1}).

2.4. POLYCYCLIC AROMATIC HYDROCARBONS

Sediment samples stored under −15 °C were freeze-dried and then homogenized by grinding. An aliquot of 5.00 g of the dried sediment was added with known amount of surrogate 2-fluorobiphenyl. It was then Soxhlet-extracted with either a mixture of methanol and isopropanol (1:2) for 24 hr followed by methylene chloride for another 24 hr, or a mixture of hexane and acetone (1:1) for 24 hr. When two-step extraction methods were used, the two extracts were combined. The volume of the extract was reduced in a Kuderna-Danish (K-D) concentrator (500 mL flask, 3-ball Snyder column, 10 ml concentrator tube) to about 5 mL and solvent-exchanged into about 40 mL hexane. The volume was reduced again to about 5 mL in the same K-D apparatus. Then a gentle stream of nitrogen was used to bring down the volume of the extract to about 2 mL.

Interfering substances were largely removed by passing the sample through a chromatographic column (11 × 300 mm). The column was packed with HCl-rinsed copper at the bottom to absorb elemental sulfur, 10 g of 1% deactivated solica-gel, and about 10 g of dried sodium sulfate on the top to absorb residual water. Samples were charged onto the column in about 2 mL hexane. The column was eluted sequentially with 35 mL hexane, 45 mL 10% methylene chloride in hexane, and

45 mL of methylene chloride. It was found that all PAHs are eluted in the second and third fractions. Thus these fractions were combined, the volume was reduced by K-D concentrator to about 5 mL anf then further reduced by nitrogen to 2 mL.

PAHs were analyzed by a Hewlett-Packard GC(5890-II)/MS(5971A) system equipped with a DB–5 column (30 m × 0.25 mm id). Helium was used as carrier gas with a flow rate of about 1 mL min^{-1}. Peak areas obtained were corrected based on the internal standard (triphenylmethane), which was added before injection. PAHs were identified by searching the mass spectra in a computer spectra library and by matching retention times. Concentrations of individual compounds in the sample were calculated from response factors determined by analyzing external calibration standards.

The recovery of the surrogate ranged from 30 to 138%, with an average at 72%. Recoveries of the sixteen PAHs from matrix spike duplicate samples averaged at 87%. A certified marine sediment sample, Standard Reference Material 1941a, was purchased from the National Institute of Standards and Technology (NIST). The PAH recovery of this material ranged from 36% for naphthalene to 123% for chrysene with an average of 70%. At least one sample in each core was analyzed in duplicate to assess the analytical reproducibility. The relative standard deviation (RSD) of the duplicates had an average of 24% at the early stage of the study and was reduced to 11% for all samples collected in 1994. No significant differences in RSD were found between high and low contaminant concentration samples.

3. Results and Discussion

3.1. SEDIMENT CHARACTERIZATION

All samples were analyzed for porosity and LOI. Grain size distribution patterns were determined for samples collected in 1994. Sediment material was classified as clay (< 0.002 mm in diameter), silt (0.002 – 0.074 mm), fine sand (0.074 – 0.42 mm), coarse sand (0.42 – 2,0 mm), and particles > 2.0 mm. Results of the grain size distribution, LOI, and porosity analyses are summarized in Figure 2 for the six vibra cores collected in 1994. For the Kinnickinnic River samples, the percent composition of VC–1 indicates a relatively large amount of sandy materials at depth 30 – 100 cm, where little clay and silt exist. By contrast, other sections in VC–1 and other cores have 20–50% clay and silt. For sediment cores VC–2 through VC–5, the average relative percentages of clay, silt, fine sand, coarse sand, and particles are 7.5, 31.8, 50.0, 10.0, and 0.7, respectively. A weak correlation between porosity and clay-silt materials was observed. Generally, a high porosity is also related to a high LOI value.

The ^{210}Pb activity was determined for all sediment core sections, and that of ^{137}Cs was measured for most of the cores. Figure 3 shows ^{210}Pb and ^{137}Cs profiles versus depth of selected cores. Cores VC–12, VC–9, VC–7, and VC–6

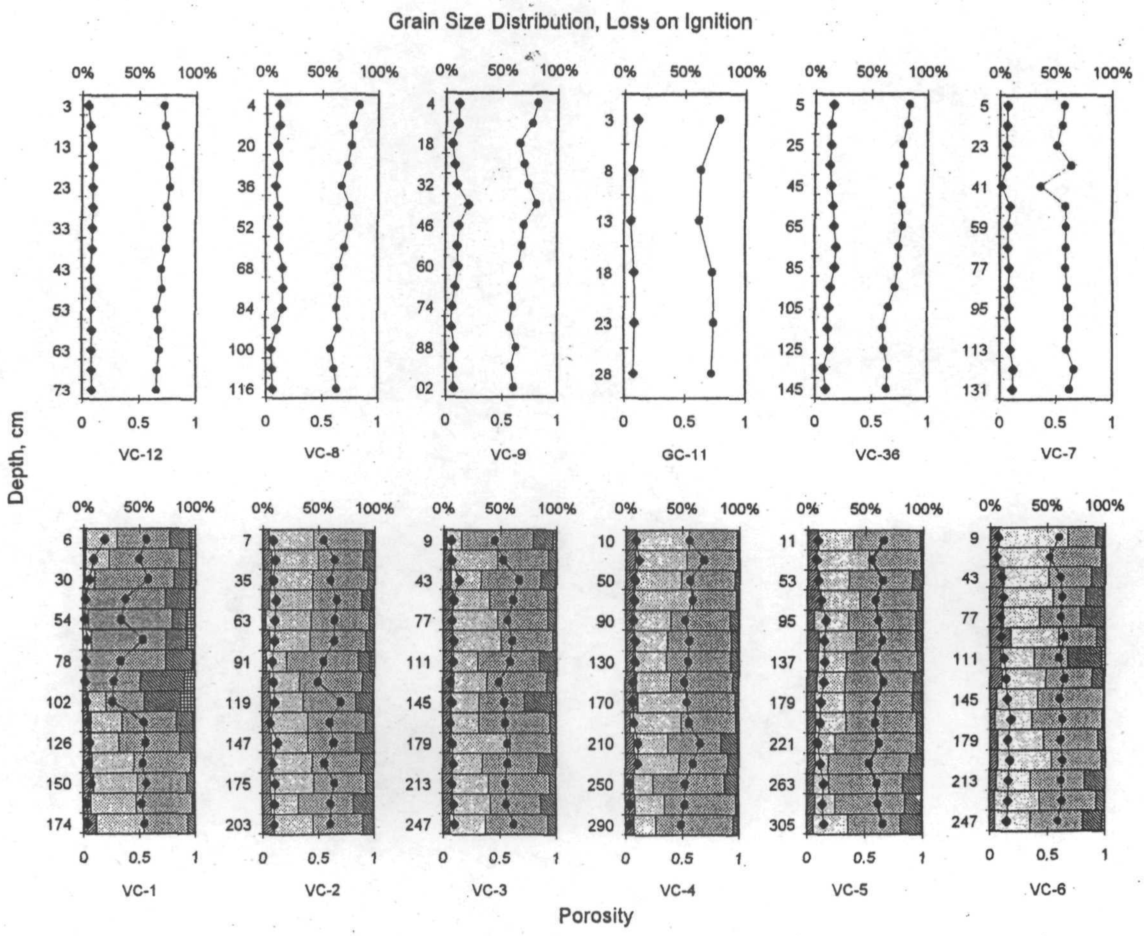

Figure 2. Sediment composition (▨ clay, ☐ silt, ▩ fine sand, ▧ coarse sand, ▦ particles > 2.0 mm in diameter), porosity (●), and loss on ignition ♦) of selected sediment cores.

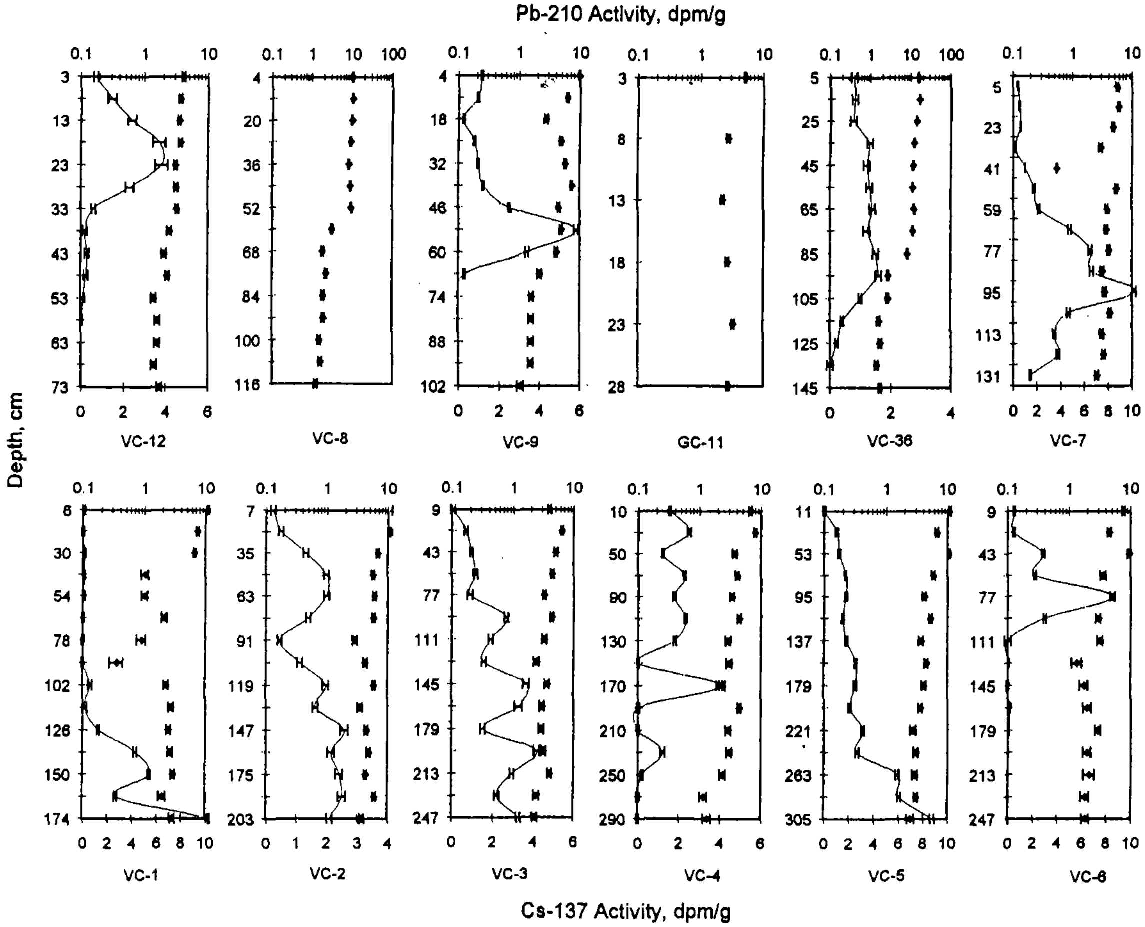

Figure 3. Total ^{210}Pb (♦) and ^{137}Cs (—) activities with error bars versus depth for selected sediment cores.

Table I

Summary of sedimentation rates for selected cores

Location	Year of Sampling	Mass Sedimentation Rate ($g\ cm^{-2}\ yr^{-1}$)	Velocity ($cm\ yr^{-1}$)		
			from ^{210}Pb[a]	from ^{210}Pb	from ^{137}Cs[a]
VC–12	1991	0.56 – 0.81	0.9 – 1.3		0.71
VC–8	1991	4.13 – 13.73	6.7 – 22.4		
VC–9	1991	0.96 – 4.92	1.4 – 7.3		1.8 – 1.9
GC–11	1990		0.42		
VC–36	1991	1.94 – 2.87	4.1 – 6.1		
VC–7	1991	1.42 – 2.28	2.0 – 3.2		3.4
VC–1	1994	2.59 – 3.65	2.19 – 3.08	3.28 – 4.62	≥ 5.6
VC–2	1994	3.67 – 6.12	3.82 – 6.37	4.72 – 7.89	~6.1
VC–3	1994	4.88 – 8.24	4.55 – 7.68	4.72 – 7.98	~6.3
VC–4	1994	4.41 – 7.15	4.12 – 6.67	4.12 – 6.67	5.5
VC–5	1994	3.73 – 4.69	3.89 – 4.90	4.10 – 5.15	≥ 9.8
VC–6	1994	2.06 – 2.82	2.17 – 2.97	2.82 – 3.86	2.4

[a] Compaction during sampling is not taken into account.

give evidence of a distinct peak of ^{137}Cs activity, which clearly indicates the year 1963. For VC–1 and VC–5, the maximum ^{137}Cs activity was detected in the last layers suggesting that the maximum activity might be at a level equal to or deeper than the length of the cores. Multiple ^{137}Cs peaks were found for VC–2, VC–3, VC–4. This could be due to disturbances caused by hydraulic dredging, river traffic, and storm events. The maximum activity was assumed to be around the depths of 189, 195, and 170 cm, for VC–2, VC–3, and VC–4, respectively. For core VC–36, the maximum is around 95 cm depth. However, this may not well correspond to 1963 since ^{210}Pb data indicate a discontinuity beyond this depth. A linear decrease of log ^{210}Pb activity with cumulative mass was usually observed, although a deviation was not uncommon due most probably to variations in sedimentation rate and disturbance at the site. Discontinuity of ^{210}Pb activity was obvious for cores VC–8 at 60 cm, VC–9 at 67 cm, and VC–36 at 95 cm. Dredging has been performed in these area to maintain navigation, and is probably responsible for the discontinuity of ^{210}Pb activity.

Sedimentation rates and velocities determined from ^{210}Pb and ^{137}Cs data are summarized in Table I for selected cores. These values are based on the upper portions of the cores which show no sign of dredging. VC–8 has an extremely high sedimentation rate (average 10.4 cm yr^{-1}) due probably to the slowdown of the river flow in the Inner Harbor. The velocities determined from ^{210}Pb show that sedimentation rates at stations VC–2, VC–3, VC–4, and VC–36 are also high, being around 4 – 8 cm yr^{-1}. By comparison, the sedimentation velocity for core VC–6 is much slower meaning that the deeper core layers are made up from older

Table II

PAH Concentrations in sediment cores of the Milwaukee Harbor Estuary

Location	N_B[a]	N_G[a]	N_V[a]	N_T[b]	Ave. (ppm)	Highest (ppm)	Core[c]	Depth[c] (cm)
Outer Harbor	3	0	2	74	46.6	193.0	VC-9	53
Inner harbor	1	0	1	21	82.9	278.3	VC-8	68
Milw. River	2	2	0	39	44.9	130.9	GC-11	8
Men. River	0	0	1	15	68.7	116.7	VC-36	85
K. K. River	1	1	7	122	287.1	1022.4	VC-2	91

[a] Numbers of box (B), gravity (G), vibra (V) cores.
[b] Numbers of total samples (sections) from sediment cores.
[c] Core and its depth at which the highest PAH concentration was observed.

Table III

PAH Concentrations (ppm) in surface sediment samples from the Milwaukee Harbor estuary

Location	N_G[a]	N_C[b]	Min.	Q1[c]	Median	Q3[c]	Max.
Outer Harbor	16	5	0.2	6.6	17.2	31.6	91.3
Inner Harbor	7	2	27.4	37.8	40.7	51.3	93.9
Milw. River	3	4	7.4	25.9	50.1	60.0	108.1
Men. River	4	1	9.6	27.0	40.5	68.5	117.7
K.K. River	3	9	10.7	104.6	138.3	192.8	390.8

[a] Number of surface grab samples.
[b] Number of cores whose top section is included.
[c] Q1 and Q3 are 25% and 75% quantiles, respectively.

materials. In fact, from the average velocity of 2.5 cm yr^{-1}, the lower layers of core VC–6 should originate from the turn of the century. The Outer Harbor station VC–12 has the lowest sedimentation rate (1 cm yr^{-1}).

3.2. DISTRIBUTION, HISTORY, AND SOURCES OF PAH CONTAMINATION

The results of the PAH measurements for the core samples are summarized in Table II. The most recent levels of PAHs at the sediment surface are compared in Table III, using data obtained from analyzing grab samples and top layers of sediment cores. The overall results indicate that the Outer Harbor is the least contaminated area in the estuary, that the Inner Harbor and the Menomonee River sediments contain significant amounts of PAHs, and that the Kinnickinnic River sediments are the most contaminated ones in the area.

Historical profiles of PAH concentrations are illustrated in Figure 4 for selected sediment cores collected in the Milwaukee Harbor Estuary. The dates shown in Figure 4 were calculated based on the ^{137}Cs dating results. The histograms for VC-8 and VC-9 are rough approximations of the time records, due to dredging

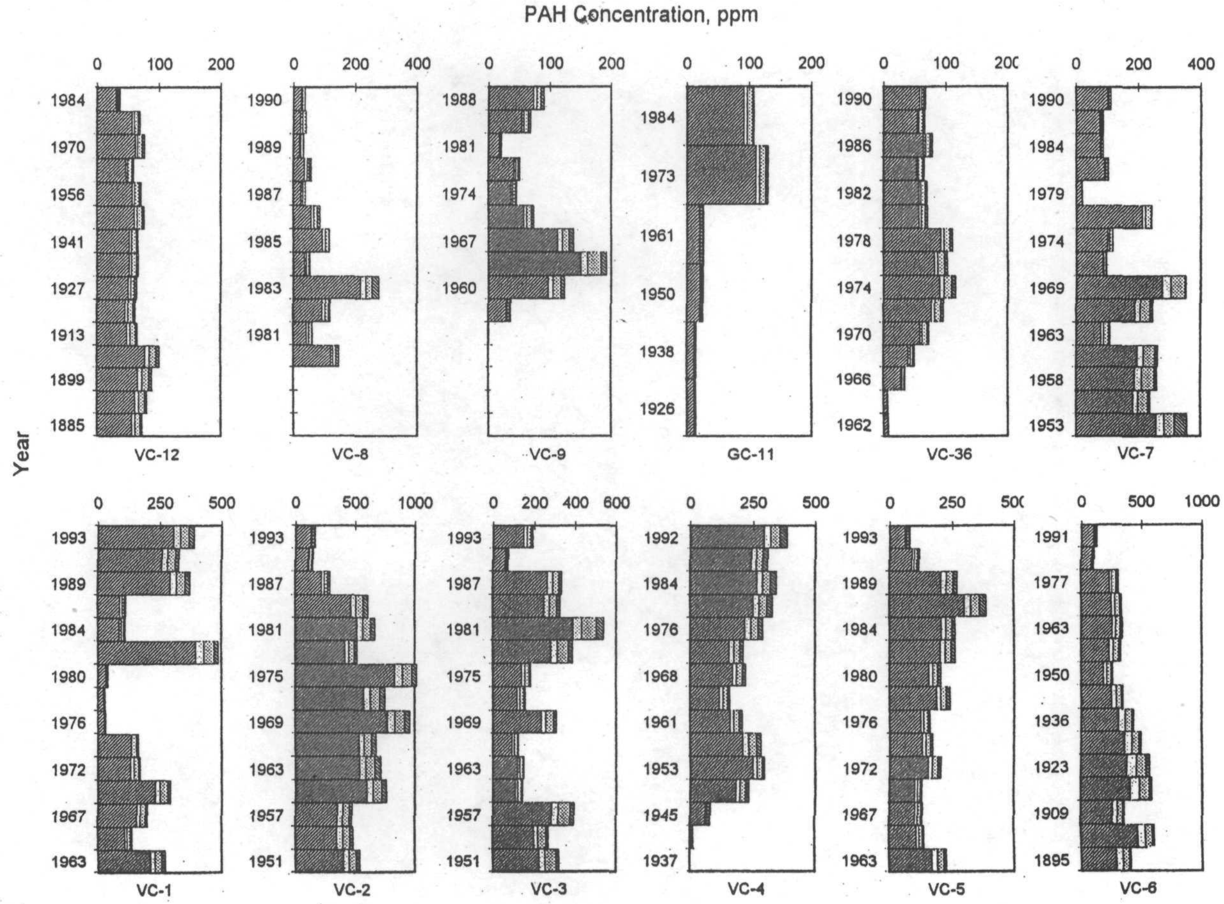

Figure 4. Concentrations of PAHs for selected sediment cores. (▧ benzo[a]pyrene, ▩ chrysene, ☐ benz[a]anthracene, ▨ other.

activities at these sites as mentioned previously. The low concentrations of PAHs in some middle sections of VC–1 is most likely due to the high sand percentage (Figure 2), instead of reduced PAH input.

Sampling location VC–12 in the Outer Harbor exhibits fairly constant levels of PAHs (60–90) ppm) over the past 80 yr, and a significant decrease in the top layer. Such decreases at the sediment surfaces have been observed in the Lake Michigan and in many estuaries and lakes over the world (Gschwend and Hites, 1981; Helfrich and Armstrong, 1986; Ohta *et al.*, 1983; Goldberg *et al.*, 1981). Gschwend and Hites proposed that such a reduction around the 1950's to the 1960's reflects the transition of energy sources from coal to oil and gas. Ohta *et al.* (1983) contributed about 50% of the reduction found in the Tokyo Bay sediments to the legal curbs on industrial and vehicular emissions of particulates and hydrocarbons. Helfrich and Armstrong (1986) argued, however, that resuspension of the fine sediment particles may also be responsible for the lower PAH concentrations observed in surface sediments. They found that cores taken from depositional zones had a subsurface concentration maximum whereas those from transition and non-depositional zones exhibit a surface maximum.

Although highly variable, the concentration profiles of most cores in the Inner Harbor and the rivers show, in general, peaks in the period of 1950's to 1980's. The concentrations have declined since then for most sediment cores. The PAH concentrations of the surface sediments in the most heavily contaminated Kinnickinnic River is generally below 200 ppm, compared with the maxima of 400 to 1000 ppm in subsurface sections. This is in agreement with the reduction in the Outer Harbor and in Lake Michigan as discussed above. Exceptions, however, are observed for cores VC–1 and VC–4. PAH concentrations in these two cores do not show apparent decreases towards the surface. Instead, they seem constant, about 400 ppm, for sediment down to 40 cm (since 1989) for VC–1 and 90 cm (since 1980) for VC–4. Two features are shared by these two cores: both are located near heavy road traffic (VC–1 is close to the I-94 interstate freeway, and VC–4 is between the railroad bridges and close to Highway #32), and both are at the turning points of the Kinnickinnic River. While it is likely that PAH-laden road dust particles are delivered to the river by runoff, and provide a constant PAH input to the sediments at these sites, whether and to what extent the constantly high PAH concentrations in recently deposited sediments are related to the depositional patterns warrant further investigation.

The highest PAH levels over the entire study area were found in the sediments collected from the stretch between the West Becher Street Bridge and the Wisconsin Wrecking Company Wharf of the Kinnickinnic River, which is the exploded area in Figure 1. The highest total concentrations of the sixteen PAHs range from 360 to 1100 ppm for the seven cores collected in this area. This is comparable to the PAH levels found at some hot spots in the lower Passaic River, New Jersey (Wenning *et al.*, 1994), and in Hamilton Harbor, Canada (Murphy *et al.*, 1991) where pilot remediation programs are underway. Numerous industrial activities are located in

Table IV

Toxicity of surface sediment samples from the Milwaukee Harbor Estuary[a]

Location	N[b]	Ratio[c]		%[d]		
		Average	Highest	≤ ER-L	< ER–M & > ER–L	≥ ER–M
Outer Harbor	189	0.8	5.3	16	51	33
Inner Harbor	91	2.1	7.3	1	19	80
Milw. River	63	2.5	16.6	6	29	65
Men. River	45	2.1	9.0	6	24	69
K.K. River	108	6.0	39.5	2	16	82

[a] Based on nine PAHs. AcNP, IP, B(ghi)P, BbFlA are not included since their ER-L and ER-M values are not available. NaP and dBahA are not included due to high experimental uncertainties.

[b] Number of measured PAH concentrations.

[c] Measured concentration to ER–M ratio.

[d] Percent of individual PAH concentrations compared with ER-L and ER-M benchmark sediment toxicity values.

that part of Milwaukee, including foundries, coal storage sites, petroleum depots, and other businesses. According to Milwaukee's Department of City Development (Morgan, 1994), the former Milwaukee Solvay Coke Company used to handle coal gas, coal tar, metallurgical coke, and numerous PAH compounds during its operation. In fact, a portion of the site is still being used for coal storage.

It is thus of interest to look more closely at the sources of PAHs in this area. VC–6, one of two cores with the highest PAH concentrations, was taken at the site near the previous Milwaukee Solvay Coke Company, which operated its coke ovens from 1902 until 1970's. It is likely that the high PAH concentration in the sediment deposited during that period at that location originated from the products of this company, which include metallurgical coke, coal tar, coal gas, and some aromatic chemicals. This assumption is supported by analyzing the phenanthrene to anthracene ratio (PhA/An). Gschwend and Hites (1981) found that this ratio was higher at remote areas compared to urban sites, presumably because of selective photooxidation of anthracene during long-range transport. This ratio, along with others, has been used by several investigators for source identification (Zhang *et al.*, 1993; Furlong et al., 1988; Lake *et al.*, 1979). The ratio is approximately 3 for the emissions from combustion of various fuels (Gschwend and Hites, 1981), 5 for highway dust collected in the Milwaukee area (Singh *et al.*, 1993), typically below 10 for sediment samples collected in urban or near urban areas (Gschwend and Hites, 1981; Zhang *et al.*, 1993), while 14 for Lake Superior sediment (Gschwend and Hites, 1981). Figure 5 illustrates the PhA/An versus depth for VC–2, VC–3, and VC–6. These three cores, as well as others sampled in the Kinnickinnic River, have a very similar PhA/An ratio (6–8) at the surface. As the core depth increases, the PhA/An value for most cores, such as VC–2 and VC–3 shown in

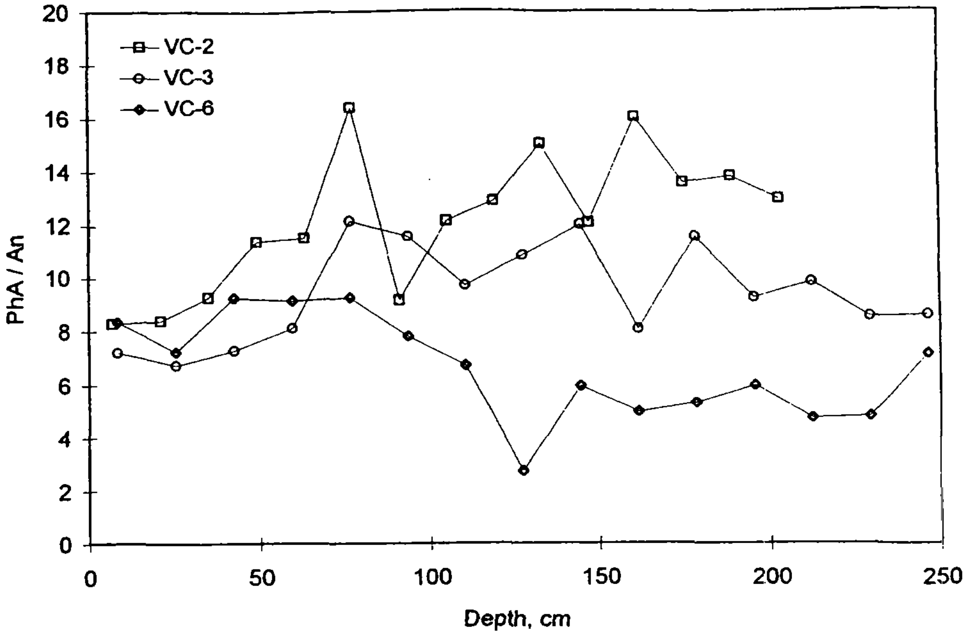

Figure 5. The PhA/An ratio versus depth for selected sediment cores.

Figures 5, tends to increase. However, there is an apparent decrease of PhA/An at about 100 cm for core VC–6, indicating a shift of major PAH source in the 1960's through the early 1970's. The low PhA/An values of the lower core sections indicate that PAHs received by the sediment during 1900 to the early 1960's very likely came from a nearby source. The existence of some specific compounds may also aid the search of a pollution source. It is of interest to note that a very large peak appeared in the GC/MS total ion chromatogram for VC–6 core sections with depths of 128 – 250 cm, corresponding to the period of 1895 to 1943, at a retention time of about 30.6 min. The compound was identified as 1,2,3-trimethyl-4-propenyl-naphthalene (CAS# 26137-53-1) by searching the built-in CHEMPC library and matching the MS spectra. However, whether this compound existed in the discharges of the previous Milwaukee Solvay Coke Company is not known. Recent sources of PAHs to this location may include upstream input, highway dust, industrial wastes. atmospheric deposit, as well as leakage from the coal storage pile which is still at the site.

3.3. INDIVIDUAL PAH COMPOUNDS

The relative abundance of individual PAHs investigated in this work is illustrated in Figure 6. They are average values of all core samples (Figure 6a) or surface samples (grab and top layer of cores, Figure 6b) from the five natural water bodies in the Milwaukee Harbor Estuary. The sixteen PAH compounds are naphthalene (Nap),

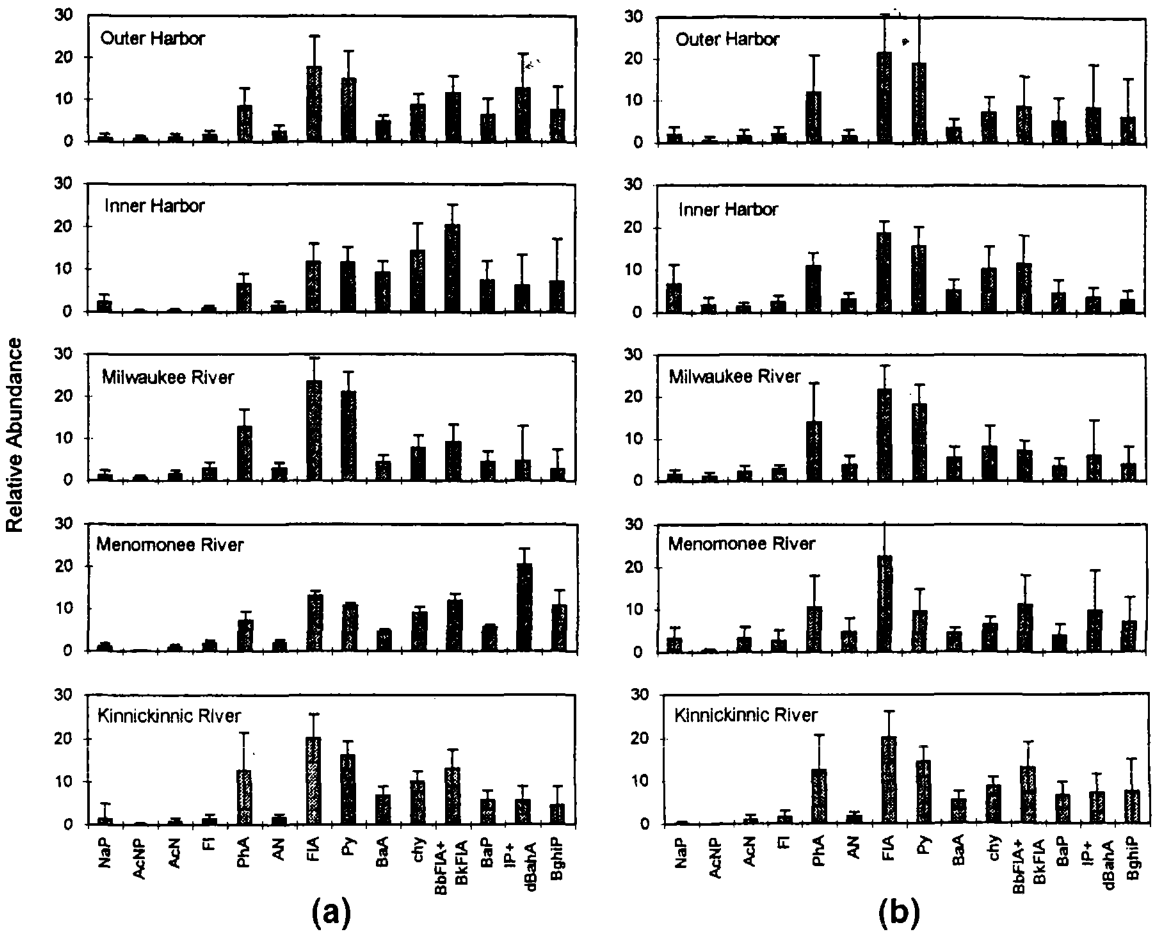

Figure 6. Relative abundance of individual PAH compounds. (a) Core samples. (b) Surface samples (grab sample and top layer of cores). Average (column) ± standard deviation (error bar).

acenaphthylene (AcNP), acenaphthene (AcN), fluorene (Fl), phenanthrene (PhA), anthracene (An), fluoranthene (FlA), pyrene (Py), benz[a]anthracene (BaA), chrysene (chy), benzo[b]fluoranthene (BbFlA), benzo[k]fluoranthene (BkFlA), benzo[a]pyrene (BaP), indeno[123-cd]pyrene (IP), dibenz[a,h]anthracene (dBahA), and benzo[ghi]perylene (BghiP). Due to the relatively high experimental uncertainties caused by poor GC separations, results of BbFlA and BkFlA, and those of IP and dBahA, are combined in Figure 6. The concentrations of these four compounds are less accurate than others due to experimental difficulties in GC separations and peak area integration.

Overall, the most abundant PAH compounds are FlA, Py, PhA. This is especially true for surface sediment samples. On the other hand, Nap, AcN, Fl have relatively low abundance. Such a relative abundance pattern is distinctive of high temperature combustion sources (Lee *et al.*, 1977), Comparing Figure 6 with the relative PAH abundance profiles, presented in Singh *et al.* (1993), of coal tar, coal tar air emission, and highway dust gives a fair match. As another highly possible source, statistical analysis (Christensen *et al.*, 1997) shows that PAH data obtained from analyzing air filters of coke oven emissions (Neff, 1979) also match, in genral, the relative abundance profiles of the samples collected in Milwaukee Harbor Estuary. An in-depth source analysis for PAHs in the Milwaukee Harbor Estuary using a Chemical Mass Balance model is presented elsewhere (Christensen *et al.*, 1997). It is certain, however, that the contributions from various natural sources of PAHs as described by Laflamme and Hites (1978) are negligible compared with anthropogenic combustion sources at the sites investigated in this study. In addition, the delivery of PAHs via runoff and horizontal transport in the water stream greatly outweigh the atmosperic deposition. This should be true for almost all the samples including the Outer Harbor, because the PAH concentrations reported here are in general significantly higher than those reported for the sediments collected from sites more distant from urban areas in the southern and central Lake Michigan (typically under 10 ppm, Zhang *et al.*, 1993; Christensen and Zhang, 1993; Helfrich and Armstrong, 1986).

3.4. SEDIMENT TOXICITY

Bioaccumulation and toxicity of PAH contaminated sediments have been well documented (Ingersoll *et al.*, 1995; Landrum *et al.*, 1994). Benchmark sediment toxicity values have been developed by National Oceanic and Atmospheric Administration (NOAA) in order to predict the potential for adverse effects of persistent chemicals. The effects-range low (ER–L) and effects-range median (ER–M) stand for the 10th and 50th percentiles of the distribution of concentrations in sediment associated with any degree of toxicity to organisms. The values of ER–L and ER–M are available for 18 PAHs (Long and Morgan, 1991; Huntley *et al.*, 1995).

Concentrations of individual PAHs in the surface samples, which include all the surface grab samples and the top layers of the cores, are compared with ER–L and ER–M in Tavle IV. About 80% of the PAH concentrations are higher than their ER–M for the Inner Harbor and the Kinnickinnic River, while more than 60% for the Milwaukee River and Menomonee River. These results suggest the presence of high potential hazards to aquatic organisms in these areas. The PAHs with highest hazard potential seem to be PhA, Py, and FlA, although all PAHs except NaP have mean concentrations exceeding the ER–M over the entire area under study.

Although the hazard potentials of buried sediment were not quantitatively evaluated, it could be expected to be higher, in general, than the surface sediment at most locations in the Estuary. This is because of the fact that the PAH concentrations tend to decline towards the surface for most cores. Therefore, it is possible that the toxicity of the sediment will be enhanced by disturbances such as dredging, if the disturbances results in the exposure of higher concentrations of PAHs to aquatic biota.

4. Summary

The results of this study provide a chronological and spatial overview of PAH contamination in the Milwaukee Harbor Estuary. Significant amounts of PAHs were detected in sediments deposited as early as the end of the last century, indicating synchronism of industrialization and environmental pollution in the Milwaukee area.

Results of this study indicate that the Milwaukee Harbor Estuary may be a source of PAH contamination to the Lake Michigan. Among the five natural water bodies in the Estuary, sediments of the Outer Harbor are the least contaminated, while all others should be categorized as PAH-contaminated. The median total PAH concentrations are 58, 33, and 68 ppm for samples taken in the Inner Harbor, the Milwaukee River, and the Monomonee River, respectively. Recently deposited sediments contain 7 – 70 ppm of total PAHs over these three water bodies. Over the entire investigated area, the concentration of PAHs show, in general, peaks in the 1950's through the 1980's. Results suggest that recent PAH inputs have declined relative to values from two decades ago in most parts of the Estuary. Concentrations of almost all PAHs exceed the toxicity effects-range median values of NOAA by factors of, typically, 2–6. This indicates a high hazard to aquatic life in the area.

A 'hot spot' was found at the Kinnickinnic River between the Becher St. Bridge and the Wisconsin Wrecking Company Wharf. The maximum total PAH levels range between 300 and 1100 ppm for cores taken in this area. It is likely that the former Milwaukee Solvay Coke Company was one of the major contributors to the PAH pollution in this area. The river sediment near the campany (VC–6) received unusually high amount of PAHs during the years of its operation. The low values of phenanthrene to anthracene ratio found in the sediment deposited in that period at this location indicate local PAH sources. Another potential source of pollution appears to be the highway traffic, because the stations (i.e. VC–1 and VC–4) closer to heavy traffic were found to have higher concentrations of PAHs, especially at the surface layers, than other locations.

Remediation of the PAH contaminated areas may be warranted. Because of the rapid sedimentation and dredging activities to maintain navigation, capping may not be a suitable remediation technology for most parts of the estuary. Capping and injection of oxidizers has been, or is being, tested in the Hamilton Harbor which has a similar degree of PAH contamination (Murphy *et al.*, 1991). Oxidizer injection is most effective on low-molecular compounds (Miller, 1995). Thus, dredging plus disposal or treatment would seem to be an attractive alternative.

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References

Ab Razak, I. A., Li, A. and Christensen, E. R.: 1996, 'Association of PAHs, PCBs, ^{137}Cs, and ^{210}Pb with Clay, Silt, and Organic Carbon in Sediments', *Water Sci. Technol.* **34**(7–8), 29.

American Association of State Highway and Transportation Officials Standard Specifications for Transportation Materials and Methods of Sampling and Testing (AASHTO): 1982, 13th Ed. Particle Size Analysis of Soils. AASHTO Designation: T 88-81, pp. 276–287.

Christensen, E. R., Li, A. A., Ab Razak, I. A., Rachdawong. P. and Karls, J. F.: 1997, *J. Great Lakes Res.* (in press).

Christensen, E. R. and Zhang, X.: 1993, *Environ. Sci. Technol.* **27**, 139.

Furlong, E. T., Carter, D. S. and Hites, R. A.: 1988, *J. Great Lakes Res.* **14**, 489.

Goldberg, E. D., Hodge, V. F., Griffin, J. J., Koide, M. and Edgington, D. N.: 1981, *Environ. Sci. Technol.* **15**, 466.

Gschwend, P. M. and Hites, R. A.: 1981, *Geochimica et Cosmochimica Acta* **45**, 2359.

Harvey, R. G.: 1991, *Polycyclic Hydrocarbons: Chemistry and Carcinogenicity*, Cambridge University Press. Cambridge, Great Britain.

Helfrich, J. and Armstrong, D. E.: 1986, *J. Great Lakes Res.* **12**, 192.

Huntley, S. L., Bonnevie, N. L. and Wenning, R. J.: 1995, *Arch. Environ. Cantam. Toxicol.* **28**, 93.

Ingersoll, C. G., Ankley, G. T., Benoit, D. A., Brunson, E. L., Burton, G. A., Dwyer, F. J., Hoke, R. A., Landrum, P. F., Norberg-King, T. J. and Winger, P. V.: 1995, *Environ. Toxicol. Chem.* **14**, 1885.

Lake, J. L., Norwood, C., Dimock, C. and Bowen, R.: 1979, *Geochimica at Cosmochimica Acta* **43**, 1847.

Landrum, P. F., Dupuis, W. S. and Kukkonen, J.: 1994, *Environ. Toxicol. Chem.* **13**, 1769.

Lee, M. L., Prado, G. P., Howard, J. B. and Hites, R. A.: 1977, *Biomed. Mass Spectrometry* **4**, 182.

Li, A., Ab Razak, I. A. and Christensen, E. R.: 1995, *Toxic organic Contaminants in the Sediments of the Milwaukee Harbor Estuary. Phase III – Kinnickinnic River Sediments*, Final report to U. S. Army Corps of Engineers. Detroit. University of Wisconsin-Milwaukee.

Long, E. R. and Morgan, L. G.: 1991, NOAA Tech Memo NOS OMA 52. National Oceanic and Atmospheric Administration, Coastal and Estuarine Asessment Branch, Seattle, WA.

Miller, J.: 1995, Personal Communication.

Morgan, M. L.: 1994, Personal Communication.
Murphy, T. P., Brouwer, H., Fox, M. E. and Nagy, E.: 1991, *Water Poll. Res. J. Canada* **26**(1), 1.
Neff, J. M.: 1979, *Polycyclic Aromatic Hydrocarbons in the Aquatic Environment: Sources, Fates, and Biological Effects*, Applied Science Publishers, London.
National Oceanic and Atmospheric Administration (NOAA): 1991, NOAA Tech Memo NOS ORCA 62, Seattle, WA.
National Oceanic and Atmospheric Administration (NOAA): 1988, NOS OMA-44. Rockville, MD.
Ohta, K., Handa, N. and Matsumoto, E.: 1983, *Geochimica et Cosmochimica Acta* **47**, 1651.
Roderick, G. L.: 1991, *Soil Mechanics Laboratory Manual*, Department of Civil Engineering and Mechanics, University of Wisconsin – Milwaukee, WI.
Singh, A. K., Gin, M. F., Ni, F. and Christensen, E. R.: 1993, *Water Sci. Technol.* **28**, 91.
Southeastern Wisconsin Regional Planning Commission (SEWRPC): 1987, *A Water Resources Management Plan for the Milwaukee Harbor Estuary, Vols. 1 and 2*, Planning Report No. 37.
Wenning, R. J., Bonnevie, N. L. and Huntley, S. L.: 1994, *Arch. Environ. Contam. Toxicol.* **27**, 64.
Zhang, X. C.: 1991, 'Polycyclic Aromatic Hydrocarbons in Dated Sediment Cores from Green Bay and Lake Michigan', Ph. D. Thesis, University of Wisconsin – Milwaukee. Milwaukee, WI.
Zhang, X. C., Christensen, E. R. and Yan, L.-Y.: 1993, *J. Great Lakes Res.* **19**(2), 429.