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Atmospheric Loading of Polycyclic Aromatic Hydrocarbons to Lake Michigan as Recorded in the Sediments

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Five sediment cores from a north–south transect of Lake Michigan were collected using box cores deployed from the RV *Lake Guardian* and from a submersible (*Johnson Sea Link II*, RV *Seward Johnson*). The sediments, analyzed for PAHs ($n = 28$) and ^{210}Pb to obtain accumulation rates and inventories of PAHs, were used to determine the role of the atmosphere in contaminant loading to Lake Michigan. The accumulation of PAHs in the sediments increased dramatically around 1900, reached a plateau around 1930–1975, and decreased slightly in recent time. Surface sediment accumulation rates and inventories for $\sum$PAHs ($n = 17$ parent), corrected for sediment focusing with ^{210}Pb, equaled 50–70 ng cm^{-2} yr^{-1} and 5000–7000 ng cm^{-2}, respectively. The relative abundances of individual PAH compounds from Lake Michigan sediments, PM-10 aerosol of Chicago, and a coke oven signature are statistically similar establishing a linkage between combustion sources in the south, atmospheric deposition, and sediment accumulation. Further support for this linkage is the historical PAH accumulation in lake sediments and historical coal use in Illinois over the same time period. The major source of PAHs to Lake Michigan sediments is coke and steel production found in the urban/industrial complex around Chicago, IL, and Gary, IN. These PAHs are deposited primarily in the southern basin after which they are redistributed throughout the lake as a result of in-lake integration processes (water and sediment transport).

Introduction

The atmosphere is a major pathway for the loading of hydrophobic organic contaminants (HOCs) to many large water bodies (*1–8*) including Lake Michigan (*1, 9*). This study was carried out to explore the role the atmosphere plays in contaminant loading to Lake Michigan using polycyclic aromatic hydrocarbons (PAHs) as environmental markers. PAHs are compounds containing typically two to eight aromatic rings that are produced during the combustion of wood and fossil fuels, such as petroleum products and coal, and are an important component of uncombusted petroleum. PAHs exhibit a wide range of physical–chemical properties (vapor pressure, aqueous solubility) (*10*) that demonstrate their semivolatile and hydrophobic character and influence their environmental fate (*11*). Some PAHs have both natural and anthropogenic origins because they are the product of both wood and fossil fuel combustion. Another natural source of two and three ring PAHs is the early diagenesis of natural organic matter (*12*). However, the anthropogenic contribution frequently outweighs PAH input from nearly all other sources (*13–16*). Despite their large source strength in urban/industrial centers, PAHs occur at relatively high concentrations in rural and remote areas (*2, 8, 17–21*). This behavior is attributed to their ability to be transported long distances as gases or aerosol and their apparent resistance to degradation on atmospheric particles (*22–25*).

The hypothesis of this work is that emissions from the urban/industrial complex around Chicago, IL, and Gary, IN, represent the dominant source of PAHs to the Lake Michigan sediments. High-temperature combustion of fossil fuels has been reported as the most significant source of PAHs to these sediments (*26*). Griffin and Goldberg conclude that 68–80% of the carbon particles in Lake Michigan sediments result from coal combustion from ~1900 to ~1978 (*27*). Our strategy was to collect a series of sediment cores in depositional basins along the south-to-north axis of the lake. Lead-210 geochronologies and inventories in the sediment permit the calculation of sedimentation rates and sediment focusing factors. Historical profiles of PAHs in the sediments were then constructed for an historical record of sedimentary accumulations. Also sedimentary accumulation rates and inventories of PAHs are corrected for sediment focusing in order to determine the aereal accumulation of PAHs on a whole-lake basis. The relative abundances of individual PAH compounds and historical profiles are consistent with the urban/industrial complex of southwest Lake Michigan, especially coal used in the production of coke and steel.

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Site Description and Ancillary Data

	site 18	site 19	site 47s	site 68k	site 70m
lattitude	42°44′44″ N	42°44′00″ N	44°42′31″ N	45°05′59″ N	45°40′00″ N
longitude	87°00′10″ W	86°35′00″ W	86°41′01″ W	86°22′58″ W	86°10′00″ W
date sampled	Sep 1991	Sep 1991	Jul 1992	Jul 1992	Aug 1993
sampling vessel[a]	RV LG	RV LG	JSL II	JSL II	RV LG
water depth (m)	150	90	250	190	110
surficial sediment accumulation rate (g/cm^2 yr)	0.039	0.023	0.016	0.026	0.011
surficial organic carbon content (%)	4.90	5.46	4.20	4.21	6.31
^{210}Pb focusing factor	2.43	1.22	1.5	1.27	1.69

[a] RV LG = overboard depoloyed box core from the RV *Lake Guardian*; JSL II = submersible deployed box core from the *Johnson Sea Link II* (RV *Seward Johnson*).

Lake Michigan Limnology

Lake Michigan is a large mesotrophic lake in the middle of the North American continent. It has a mean depth of 82 m, a maximum depth of 282 m, a watershed area of 118 104 km^2, a surface area of 57 780 km^2 (*28*), a volume of 4920 km^3, and a hydraulic residence time of 62 yr (*29*). Because the lake takes up approximately 49% of the total watershed surface area, it is greatly influenced by the input of pollutants via the atmosphere. The mean annual rainfall is ~74 cm (*3*). The northern and southern basins are divided by a sill across the lake between Milwaukee, WI, to Muskegon, MI. The water depth at the sill is ~40 m at its shallowest point, which influences both basin intermixing and sedimentary deposition patterns (*30*). Water currents flow generally in counter-clockwise patterns, both in the northern and the southern basins (*31*). Occasionally when there are sustained winds out of the north or northwest, there is intermixing of the water currents of the two basins (*32*). When there are prolonged winds from the southwest, there is significant upwelling along the eastern shore (*31*, *32*) delivering sediment to surface waters where it is carried from south to north. Even during periods of stratification when there is little interaction between the epilimnetic and hypolimnetic waters, 63.5 kg s^{-1} of sediment is transported across the sill from the southern to the northern basin (*33*), almost certainly as a result of previous resuspension (*34*). Studies of ^{137}Cs have clearly documented that the majority of the fine sediment of the southern basin is focused from shallower areas to deep quiescent zones near the center of the basin (*30*). Significant resuspension occurs both during and after the sediments have been transported to these depositional zones (*35*). Epilimnetic primary productivity is about 625 mg of C m^{-2} day^{-1} for the southern basin (*36*), while that in the northern basin is measurably lower (*37*). Also 39% of Lake Michigan's shoreline is classified as urban/industrial, concentrated in the southwestern corner of the southern basin from Milwaukee, WI, to Gary, IN. The steel, coal, and coke industries are concentrated in this area (*28*).

Methodology

Sediment cores were collected in 1991–1993 using box cores deployed from the RV *Lake Guardian* (U.S. EPA) and a submersible, the RS *Johnson Sea Link II* deployed from the RV *Seward Johnson* (Harbor Branch Oceanographic Institution, Ft. Pierce, FL). Site description and ancillary data are summarized in Table 1, and a map showing their locations is given in Figure 1. Subcores were taken from the surface-deployed box cores using 7.5 cm diameter Plexiglas tubes in such a manner as to avoid mixing and cross-contamination. Subcores and whole box cores (15
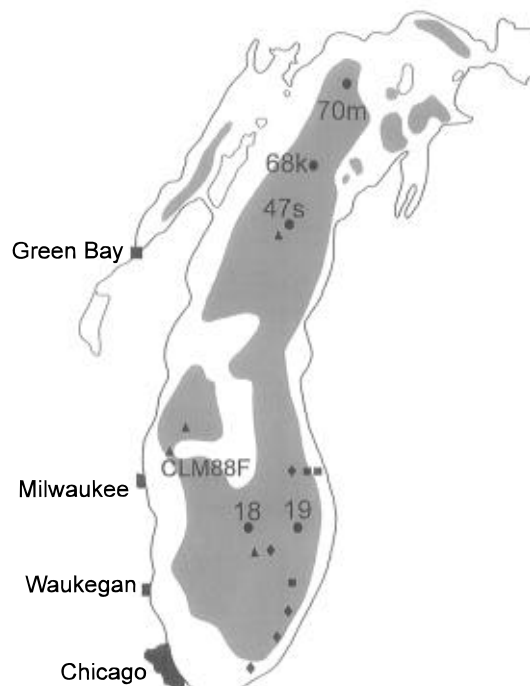

FIGURE 1. Lake Michigan sediment core sites 1991−1993: circles, this study; diamonds, Eadie et al. (*64*); squares, Helfrich and Armstrong (*26*); triangles, Christensen and Zhang (*51*). The shaded region indicates the 100-m depth contour and corresponds generally to the depositional zones of the lake.

× 15 cm^2 surface area by ~50 cm deep) obtained by the submersible were sectioned into either 0.5- or 1.0-cm increments for the first few centimeters and 1.0- or 2.0-cm increments for the rest of the core. The samples were stored in glass jars sealed with aluminum foil and kept at 4 °C until analysis. In the case of cores collected from the RV *Lake Guardian*, separate subcores were obtained for ^{210}Pb and hydrophobic organic compound (HOC) analysis.

Samples were analyzed for ^{210}Pb on 7−20 sections in each core by a modification of the Eakins and Morrison method (*38*). Sediments were spiked with a known amount of ^{208}Po, digested using concentrated HCl, and plated onto silver planchets for analysis of Pb isotopes. Activity of the ^{210}Po daughter species was measured using conventional α-spectroscopy to determine the total ^{210}Pb content. ^{137}Cs was also measured in core 47s using nondestructive γ spectroscopy (*39*) to confirm the dating suggested by ^{210}Pb.

Sediment stored in glass jars for HOC analysis was homogenized by mixing with a stainless steel spatula, and ~2 g was analyzed for percent water. About 20 g of wet sediment was dried by adding ~40−50 g of cleaned
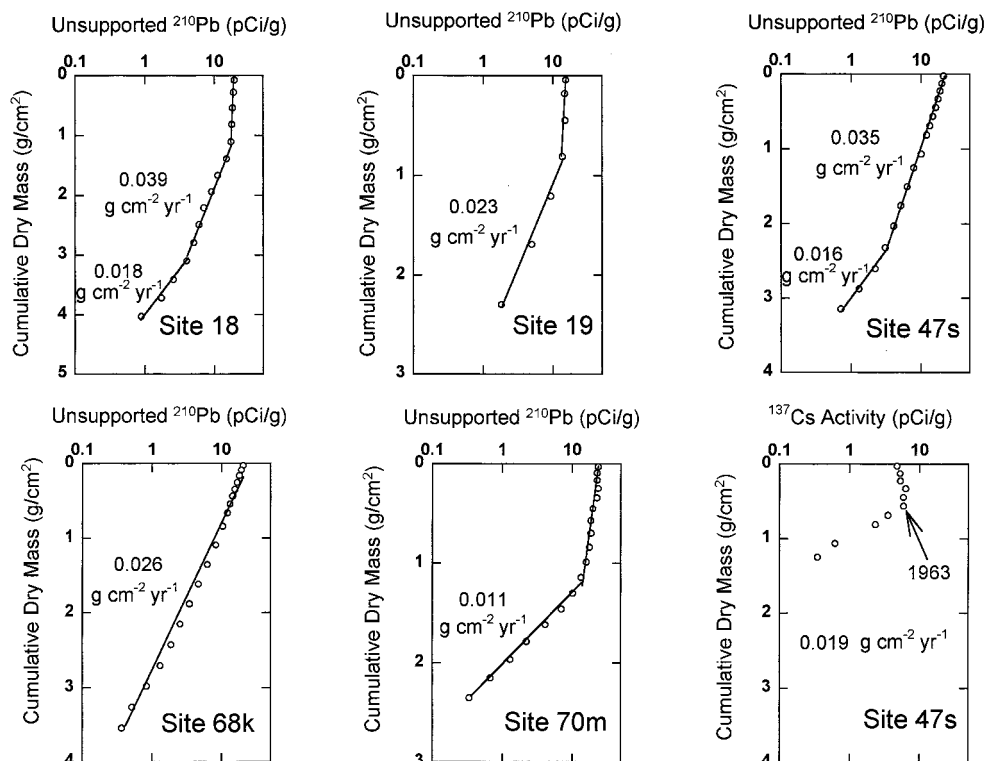
FIGURE 2. Excess ^{210}Pb and ^{137}Cs (47s only) profiles in Lake Michigan sediment cores.

anhydrous sodium sulfate and grinding the mixture with a ceramic mortar and pestle to ensure homogenous mixing. The dried sediment was spiked with a surrogate standard consisting of four deuterated PAHs and extracted in a Soxhlet apparatus with methylene chloride for 24 h; the solvent was changed to hexane and reduced to approximately 1 mL using a rotary evaporator (Buchi Type Re-111). Approximately 75% of the extract volume was set aside for organochlorine analysis (40), and ~25% was used for PAH analysis. The PAH subfraction was reduced to about 100 μL under a gentle stream of nitrogen and charged to an alumina-silica microcolumn (41). The sample was charged to the top of the column and eluted with 2.5 mL of hexane followed by 7 mL of a 4:1 solution of hexane: methylene chloride and 7 mL of a 4:1 solution of methylene chloride:methanol. The first fraction contained the non-aromatic hydrocarbons; the second contained PAHs; and the third contained more polar compounds such as alkanols and alkanoic acids. The PAH fractions were reduced to approximately 1 mL in a rotary evaporator transferred to combusted amber vials, activated copper was added to remove elemental sulfur, and the fractions were reduced in volume to approximately 50 μL under a gentle stream of pre-purified nitrogen.

Known quantities of an internal standard consisting of five perdeuterated PAHs were added to the sample and analyzed on a Hewlett Packard 5890 gas chromatograph equipped with a Hewlett Packard 5970 mass selective detector operated in the selective ion monitoring mode. The m/z peak corresponding to the molecular weights of the individual PAHs were used for quantification except for retene where both the 234 and 219 m/z peaks were summed since retene fractures into almost equal amounts of the two ions. The identity of the selective ion monitoring peaks was confirmed by analyzing a suite of standards, and possible interferences were investigated by analysis of spiked sediments; none were found. The compounds were

quantified using the relative response factors corresponding to the appropriate internal standard that was nearest in elution time and size. PAHs from naphthalene to dibenzofuran were quantified relative to d_{10}-acenaphthylene, fluorene to dimethylphenanthrenes relative to phenanthrene-d_{10}, fluoranthene to chrysene were quantified relative to pyrene-d_{10}, benzo[$b+k$]fluoranthenes to perylene were quantified relative to benzo[e]pyrene-d_{12}, and the highest molecular weight PAHs of indeno[1,2,3-cd]pyrene to coronene were quantified using benzo[g,h,i]perylene-d_{12}. Accuracy of the quantification was ensured by the recovery of the surrogate standards. Surrogate recoveries are as follows: fluorene-d_{10} = 59 ± 16%; fluoranthene-d_{10} = 82 ± 15%; perylene-d_{12} = 86 ± 23% (n = 72 samples). Analysis of sample replicates yielded standard errors from shallow sediments (2−2.5 cm) ranging from 0.01 to 24% for an individual PAH and from 0.4 to 2.6% for the sum of 17 parent PAHs, corresponding to concentrations of 0.01−44 and 15−77 ng/g, respectively. Replicates of deep sediment samples where PAH concentrations are low have higher standard errors (0.34−100% for individual PAHs, corresponding to 0.0−4.1 ng/g, and 27−30% for the sum, corresponding to 14−16 ng/g). The higher standard errors deep in the sediment core had little influence on accumulation rates, inventories, or history. A series of procedural blanks were also performed in which only naphthalene was found in some samples.

Results and Discussion

^{210}**Pb.** The profiles of unsupported ^{210}Pb versus cumulative dry mass are plotted for each core in Figure 2 and provide specific information on sediment accumulation rates, radionuclide inventories, and extent of mixing. The plots for sites 18 and 19 in the southern basin show a steep slope of unsupported ^{210}Pb near the surface, indicating sediment mixing to depths of 4 and 3.5 cm, respectively. In contrast, sites 47s and 68k have a constant and shallow ^{210}Pb slope

TABLE 2
Surface Concentrations and Inventories for Individual PAHs[a]

compd	site 18 concn (ng/g dry wt)	site 18 inventory (ng/cm²)	site 19 concn (ng/g dry wt)	site 19 inventory (ng/cm²)	site 47s concn (ng/g dry wt)	site 47s inventory (ng/cm²)	site 68k concn (ng/g dry wt)	site 68k inventory (ng/cm²)	site 70 m concn (ng/g dry wt)	site 70 m inventory (ng/cm²)
Naph	10.20	359	18.54	80	71.74	491	44.02	659	9.08	119
Me-Naphs	13.15	394	46.20	308	74.25	542	76.39	926	27.02	263
Biphen	0.00	51	6.57	31	10.01	96	14.07	159	0.00	22
Acy	29.10	87	17.69	79	16.10	221	28.30	419	5.21	37
Ace	21.27	82	16.18	63	7.79	137	15.50	181	0.00	27
DBF	13.80	210	29.70	127	23.07	308	41.25	460	9.59	82
Fl	7.10	109	23.00	107	20.09	293	30.32	400	5.90	52
1Me-Fl	11.71	123	23.65	121	17.95	316	4.26	507	0.00	53
DBThio	6.91	74	23.52	107	12.17	248	33.99	444	4.58	46
Phen	209.60	1340	312.56	1520	154.12	3440	366.07	4660	125.60	703
Anthr	36.79	206	55.39	274	40.19	535	53.63	743	12.33	98
Me-Phens	201.51	1240	340.23	1580	272.84	3490	264.02	4780	119.56	659
4,5Me-Phe	31.29	209	43.88	204	39.74	532	51.79	438	8.82	76
DiMePhen	69.02	468	119.42	520	77.35	957	157.18	1860	37.57	190
Fluo	495.90	2350	307.93	1440	375.47	5030	404.30	5520	129.12	778
Pyr	399.87	1970	296.93	1300	346.72	4110	343.98	5190	103.40	631
Ret	13.57	117	15.59	78	12.85	204	18.32	269	9.18	66
BaA	161.99	1040	144.90	658	130.40	1770	153.46	2240	17.57	184
Chry	347.86	1590	253.72	1120	325.11	3580	294.68	4380	129.32	674
B[b+k]Fl	614.52	3240	534.14	2440	525.77	7340	583.26	8580	275.30	1620
BaP	268.11	1270	217.29	886	211.67	2530	232.84	3140	80.10	476
BeP	268.11	1440	226.07	997	222.57	2940	254.44	3700	127.24	711
Per	83.43	312	64.18	265	61.06	1020	64.01	1430	41.16	199
IDP	497.99	2310	220.37	1280	302.01	4810	316.38	4910	138.46	879
DBA	370.78	510	51.02	265	57.74	820	63.59	1250	22.40	159
BPer	302.39	1700	185.76	964	255.41	3470	248.30	3980	143.47	855
AntA	49.39	264	28.19	127	43.90	627	33.45	575	11.30	82
Cor	124.60	1120	74.36	457	88.29	1710	110.73	2230	32.46	377

[a] Concentrations of individual PAHs in the top 0.5-1.0 cm of each core where Naph = naphthalene, Me-Naphs = methyl naphthalenes, BiPhen = biphenyl, Acy = acenaphthylene, Ace = acenaphthene, DBF = dibenzofuran, Fl = fluorene, 1Me-Fl = 1-methylfluorene, DBThio = dibenzothiophene, Phen = phenanthrene, Anthr = anthracene, Me-Phen = methyl phenanthrenes, 4,5Me-Phen = 4,5-methylenephenanthrene, DiMe-Phen = dimethyl phenanthrenes, Fluo = fluoranthene, Pyr = pyrene, Ret = retene, BaA = benz[a]anthracene, Chry = chrysene, B[b+k]Fl = benzo[b+k]fluoranthenes, BaP = benzo[a]pyrene, BeP = benzo[e]pyrene, Per = perylene, IDP = indeno[1,2,3-cd]pyrene, DBA = dibenz[a]anthracene, BPer = benzo[g,h,i]perylene, AntA = antanthracene, and Cor = coronene.

and exhibit no apparent evidence of mixing. The ^{137}Cs profile for site 47s (Figure 2) shows a broad peak indicating either mixing or focusing of fine sediment containing ^{137}Cs. The sediment accumulation rate based on ^{137}Cs peak at 1963 is 0.019 g cm^{-2} yr^{-1}, approximately half of the ^{210}Pb derived rate of 0.035 g cm^{-2} yr^{-1}. Site 70m shows a fairly constant value of ^{210}Pb in the upper sediments extending deep into the core, showing evidence of intense sediment mixing to a depth of at least 4.5 cm consistent with observations of burrowing worms. The sediment accumulation rates for each core were calculated using the constant flux/constant sedimentation rate model (CF:CS) run on several depth increments of each core. The sedimentation rate at site 18 was calculated as 0.039 g cm^{-2} yr^{-1}, which is more than three times higher than the value of 0.0121 g cm^{-2} yr^{-1} reported by Robbins and Edgington (42) for a site just south (42°40.0′ N, 87°0.0′ W) of site 18, and more than twice the value of 0.016 g cm^{-2} yr^{-1} reported by Swackhamer and Armstrong (43) for site 18 in 1980. Our value agrees with the value of 0.033 g cm^{-2} yr^{-1} reported by Hermanson and Christensen (44) for a site to the southeast (42°38′20″ N, 86°57′00″ W) of site 18. The wide range of sediment accumulation rates reported likely results from spatial heterogeneity in sedimentation in this area. The PAH profiles presented here and organochlorine profiles (40) support our dating sequence. From the sedimentation rates, dates were assigned to each depth increment using cumulative mass to eliminate the influence of sediment compaction.

Sediment focusing describes the transport of fine sediment from shallow areas to deeper, quiescent areas through episodic resuspension and settling. The depositional zones of the lake roughly correspond to the 100-m bathymetric contour as shown in Figure 1. The ratio of the unsupported ^{210}Pb inventory in the sediments compared to that deposited from the atmosphere yields a sediment focusing factor (FF):

$$FF = \frac{^{210}Pb \text{ inventory}}{15.5 \text{ pCi/cm}^2}$$

The ^{210}Pb inventory expected from atmospheric deposition is 15.5 pCi/cm^2 (45, 46). Sediment cores exhibiting focusing factors greater than 1 define a depositional environment. If the focusing factor is less than 1, the site is erosional but may accumulate fine sediment on a transient basis. Focusing factors observed here ranged from 1.2 to 2.4 (Table 1). The focusing factors for strongly particle-reactive elements and compounds are assumed to be the same (47). PAH accumulation rates and inventories in the bottom sediments are then corrected for sediment focusing by dividing each by the ^{210}Pb focusing factor.

PAH Accumulation and Concentration. PAH concentrations in surface sediments and whole core inventories for each compound are given in Table 2 with the focus-corrected accumulation profiles for four representative PAHs given in Figure 3: phenanthrene, benzo[b+k]-fluoranthene, benz[a]pyrene, and perylene, which can have
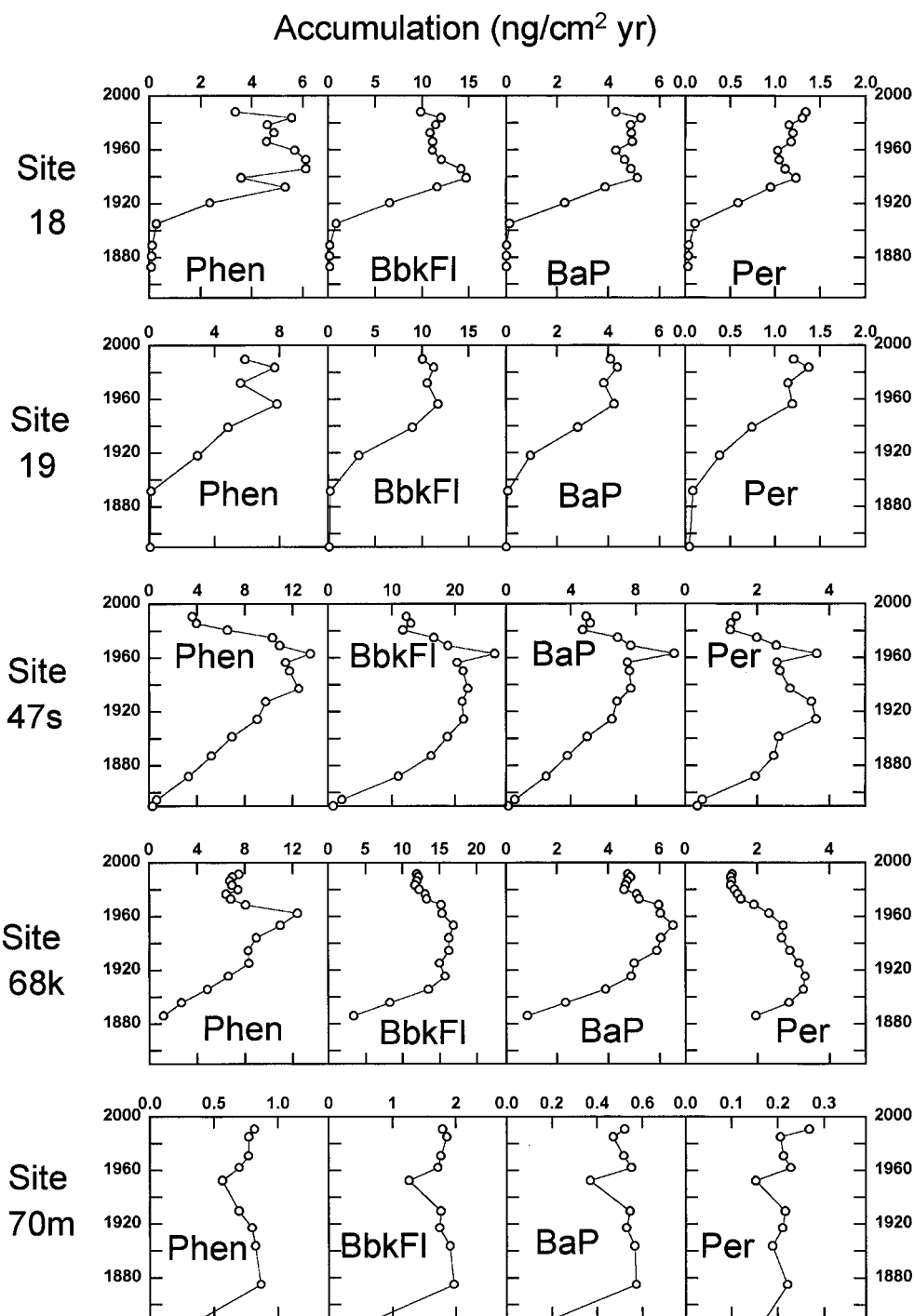
Accumulation (ng/cm² yr)

FIGURE 3. Accumulation profiles in Lake Michigan sediment cores for phenanthrene (Phen), benzo[b+k]fluoranthene (BbkFl), benzo[a]-pyrene (BaP), and perylene (Per).

both natural and anthropogenic origins of significant magnitude (48). The individual profiles for the four compounds shown (as well as other compounds measured but not shown) are similar within each core. This suggests that all of the PAHs are from the same source and/or are processed similarly within the lake. The only exception is perylene at site 68k where the accumulation increases with depth. This same behavior has been observed for perylene in sediments from other systems and has been attributed to diagenisis of biogenic precursors (18, 19, 49, 50).

Since the individual PAHs behave similarly within individual cores, differences among cores were investigated by summing the parent (nonalkylated) PAHs (∑PAHs) for each core (acenaphthylene, acenaphthene, fluorene,

phenanthrene, anthracene, fluoranthene, pyrene, benzo-[a]anthracene, chrysene, the benzo[b+k]fluoranthenes, benzo[e]pyrene, benzo[a]pyrene, perylene, indeno[1,2,3-cd]pyrene, benzo[g,h,i]perylene, antanthrene, and coronene).

The focus-corrected profiles of ∑PAHs are given in Figure 4 along with a profile from Christensen and Zhang (51) for a core taken in 1988 near Milwaukee, WI. For each site, the onset of PAH accumulation occurs ~1880−1900, except 70 m, which experiences significant mixing. This increase is consistent with the findings of Christensen and Zhang for Lake Michigan (51) and other aquatic systems (18−20, 49, 52) and is attributed to increased emissions from coal
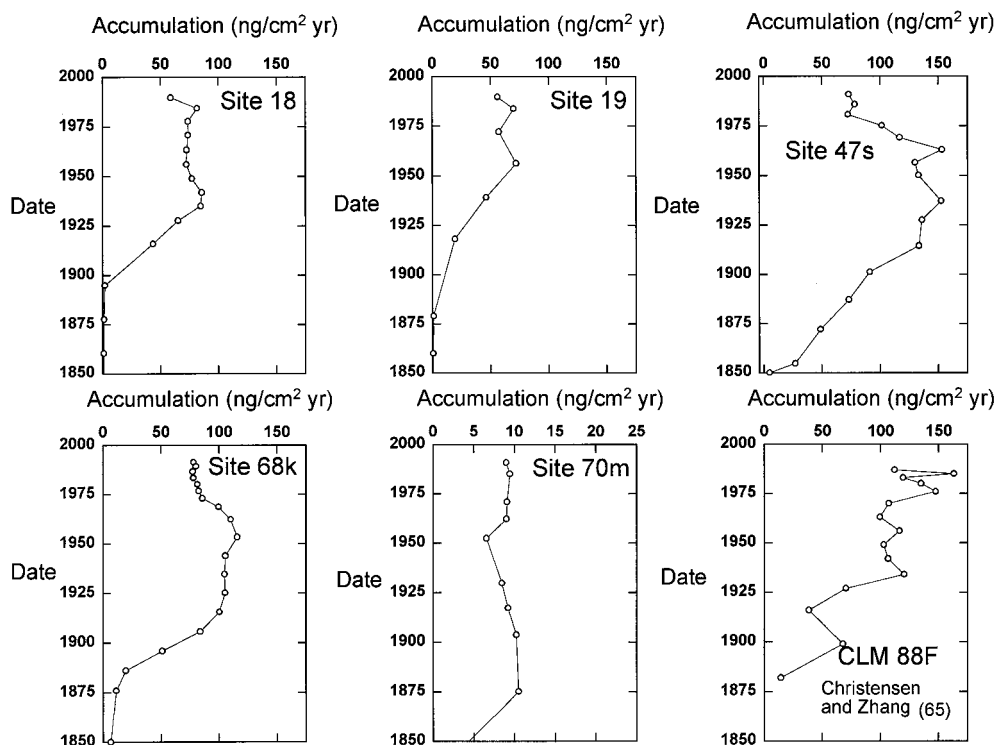
FIGURE 4. Profiles of focus-corrected $\sum$PAH (n = 17 parent) accumulation rates (ng cm^{-2} yr^{-1}) for Lake Michigan sediment cores. The maximum accumulation rate (excluding site 70m) is 70–150 ng cm^{-2} yr^{-1}.

combustion during industrialization. PAH accumulation rates reach a maximum in the period 1950–1975 and may in some instances decrease slightly in the upper few centimeters. This decline has been reported for other systems (18, 19, 53) and has been attributed to a switch from coal to oil and natural gas (19) and controls on industrial emissions. The maximum focus-corrected PAH accumulation rates at sites 18 and 19 are ~70 ng cm^{-2} yr^{-1}. Sites 47s and 68k (northern basin) exhibit maximum rates of focus-corrected PAH accumulation of 100–150 ng cm^{-2} yr^{-1}, ca. twice the accumulation rate found in the southern basin. The increased accumulation of PAHs in northern basin sediments is attributed to south to north transport of sediment bound PAHs adding to the regional atmospheric signal and increasing the load to the sediments. This is consistent with Golden (40) who concluded that 25–50% of the PCBs found in the northern basin sediments were due to particle transport from the southern basin.

PAH Inventories. PAH inventories were calculated by multiplying anthropogenic PAH concentrations (ng/g) for each section by the bulk density of that increment and summing these over the entire depth. Since there are natural sources of PAHs to the environment, a background concentration from deep in the core was subtracted from the concentration in recent sediments to obtain only the anthropogenic contribution:

$$\text{inventory} = \sum (C_i - C_B)\rho_B d$$

where C_i is the concentration of $\sum$PAHs in ng/g dry wt in each depth increment, C_B is the background PAH concentration, ρ_B is the bulk density for each increment (ng/cm^3), and d is the depth of the increment (cm). The background concentration was estimated as the average concentration of $\sum$PAHs in sediment sections where the profiles exhibited rather constant concentrations (pre-1900). The bulk density
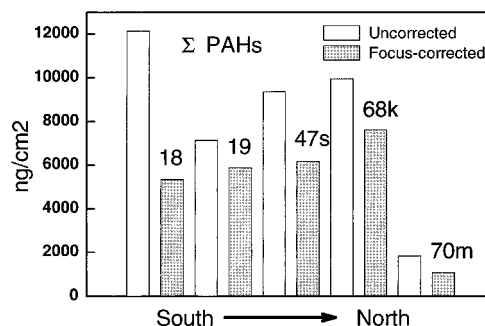

FIGURE 5. Focus-corrected and uncorrected $\sum$PAH inventories (ng/cm^2) from Lake Michigan sediment cores. The focus-corrected inventory (excluding site 70m) is ~5000–7000 ng/cm^2.

is calculated from the porosity of the sediment, the percent of water, and assuming a dry sediment density of 2.45 g/cm^3 (41).

Focus-corrected inventories of PAHs will collapse to a common lake-wide value provided there is one dominant or uniform source of the contaminant to the lake, and sediment focusing is the dominant process responsible for site-to-site variations in concentration/accumulation rates. Wong et al. (54) found that the spatial variability in core inventories of PCBs, DDT, HCB, and Mirex in Lake Ontario was removed when corrected for sediment focusing. Jeremiason et al. (6) also removed spatial variability from PCB inventories from the open water sediments of Lake Superior by correcting for sediment focusing where the authors conclude that the source of PCBs to the lake is uniform atmospheric deposition. Figure 5 shows both the focus-corrected and uncorrected PAH inventories for the five coring sites in this study. Correcting the inventories for sediment focusing reduces the relative standard deviation of their values from 21% to 16% for sites 18, 19, 47s, and 68k. We conclude that there is one major source of PAHs to the sediments of Lake Michigan and that sediment
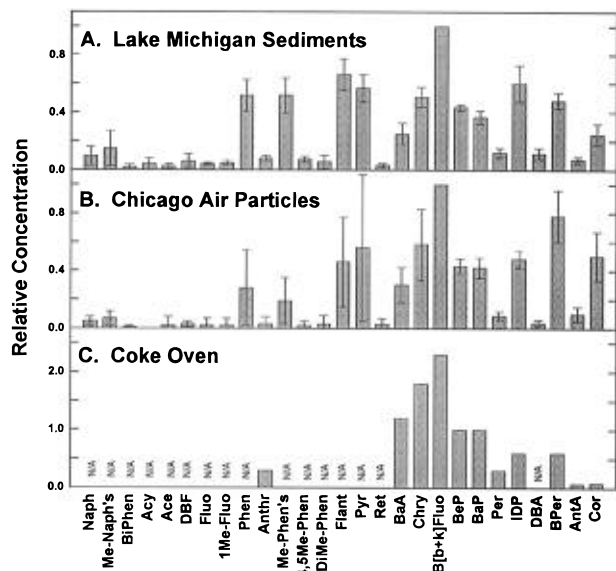
FIGURE 6. Relative concentrations of individual PAHs from (A) Lake Michigan sediment cores (this study); (B) Chicago air particles (*63*), and (C) a coke oven (*58*). All PAH concentrations are normalized to benzo[*b*+*k*]fluoranthene. N/A = data not available.

FIGURE 7. Historical records of coal use in Illinois (*51*) and $\sum$PAH accumulation in Lake Michigan sediments at site 68k of the northern basin (this study).

resuspension and focusing distributes them throughout the northern and southern basins, but bathymetric barriers prevent contamination of the area north of Green Bay (i.e., site 70m).

Sources of PAHs to Lake Michigan. The relative distributions of 27 PAHs were calculated to assess the source(s) of PAHs to Lake Michigan. Sources contributing to PAH accumulations in sediments are assessed using the relative concentrations of individual compounds and comparing them to the relative amounts from specific sources either in the form of compound ratios or on the distribution of an entire suite of PAHs (*8, 18, 19, 21, 55−62*). Despite the great variability in the distributions in and between sources of PAHs to the atmosphere (*58*), the PAH distribution found in the sediments of Lake Michigan are remarkably similar. Figure 6 shows the average individual PAH concentration normalized to benzo[*b*+*k*]fluoranthene, the most abundant of the PAHs, for these sections. A χ^2 test was performed on the PAH distributions from different sediment samples. The PAH distribution of the last 70 years is statistically identical ($P > 0.95$) not only within each core but also between cores over the whole lake. This suggests that the major source(s) of PAHs to Lake Michigan as reflected in the bottom sediments has not changed significantly since ~1900.

A comparison of PAH distributions in sediments to distributions in atmospheric aerosol from the industrialized urban area around Chicago offers potential information on the strength of the atmospheric pathway. Liu (*63*) reports atmospheric particulate PAH concentrations from both the summer of 1993 and the winter of 1994 from urban Chicago using a micro-orifice uniform deposit impactor (MOUDI) for particles <10 mm in diameter (PM-10). The distribution of PAHs on Chicago air particles (Figure 6) is statistically similar to that found in Lake Michigan sediments ($r^2 = 0.89$). The higher molecular weight PAHs are well preserved on the atmospheric particles, are deposited onto the lake and settle, and are incorporated into the bottom sediments. The enrichment of the lower molecular weight PAHs in the sediments are a result of gas-phase PAHs entering the
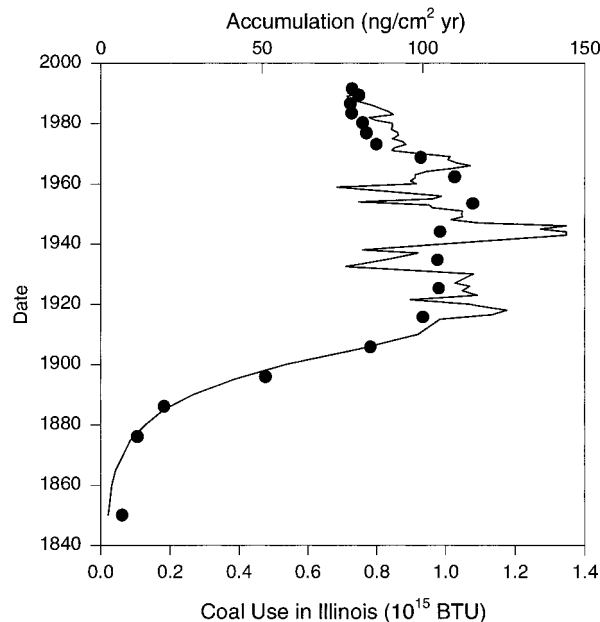
dissolved phase through air−water exchange and then partitioning to natural organic matter. The high correlation of PAH patterns between sediments and urban air particles points strongly to combustion sources in the southern basin as dominant contributors.

Sources of PAHs to the atmospheric aerosol in urban settings are coal used for coke and steel production, vehicular emissions from both gasoline and diesel engines; oil, natural gas, and wood for home heating; and many industrial and municipal combustion processes including coal-fired power plants (*58*). One of the major combustion sources in southern Lake Michigan is coal, especially coal used for coke and steel production. The PAH distribution of the emissions from coke ovens is compared to the distribution in Lake Michigan sediments and Chicago air particles in Figure 6. Correlations of the coke signature to the air particles and sediments yield r^2 values of 0.68 and 0.79, respectively, establishing the linkage between them. Surprisingly the PAH pattern in Chicago PM-10 is dominated by the coke signature even though vehicular emissions must contribute large amounts of PAHs to the regional atmosphere. Further supporting this is the comparison of the historical accumulation of PAHs at site 68k and coal use in Illinois, the source for the coke and steel industry, over the same time period in Figure 7. We conclude that particulate PAHs in the southern Lake Michigan atmosphere are derived primarily from coke and steel production and that these account for the vast majority of PAHs in the sediments all throughout Lake Michigan as a result of localized atmospheric deposition and lake redistribution processes. The atmospheric input rate to Lake Michigan from this source as reflected in the sediments is about 600 to 800 mg m^{-2} yr^{-1}.

Acknowledgments

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