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Spatial and Temporal Distribution of Polycyclic Aromatic Hydrocarbons in Sediments from Michigan Inland Lakes

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Concentrations of polycyclic aromatic hydrocarbons (PAHs) were measured in sediment cores collected from 11 inland lakes in Michigan for examination of spatial and temporal trends in accumulation and sources. Concentrations of PAHs varied widely among these lakes; the highest concentrations were found in sediment collected from Cass Lake, located in an urbanized watershed. Concentrations of PAHs were correlated with watershed population density on a spatial scale. PAH concentrations have decreased over time since the 1980s in nine of the 11 lakes studied, most of which are located in suburban and rural areas. The rate of decline in PAH concentration was faster in Gratiot Lake, a remote lake with no known local sources of pollution in recent years. Concentrations of PAHs in surface sediments from Cass and Cadillac Lakes were greater than the threshold for adverse effects. Despite the wide variations in total PAH concentrations, fluoranthene, pyrene, chrysene, benzo[*b*]fluoranthene, and benzo[*k*]fluoranthene were the major PAHs in all of the lakes studied. The proportions of individual PAHs within the total PAH concentrations have changed both temporally and spatially, suggesting a shift in the sources of PAHs in the environment. A general increase in the proportion of high-molecular-weight PAHs suggests an increase in combustion-related sources recently.

Introduction

Polycyclic aromatic hydrocarbons (PAHs) are ubiquitous environmental pollutants, released into the environment primarily by incomplete combustion of fossil fuels and burning of vegetation and other organic materials (*1*). In aquatic ecosystems, PAHs, because of their hydrophobicity, partition preferentially to sediments. As the deposition of sediments continues over time, sediments act as geochronometers of the contaminant deposition in the environment as well as of general environmental change over time. Contaminated sediments can directly affect bottom-dwelling organisms and represent a continuing source for toxic substances in aquatic environments that may affect wildlife and humans via the food chain. Therefore, an understanding of the trends of toxic chemical accumulation in sediments is necessary if we are to assess the current state of surface water quality. The use of sediment cores to evaluate and reconstruct historical records of contaminants, including PAHs, has been well documented in several studies (*1–5*).

Earlier studies of PAHs in sediment cores collected from a number of locations in the United States, Europe, and Japan revealed a gradual decrease in overall concentrations in the 1970s and the 1980s (*1–3, 6–8*). Concentrations of PAHs in sediment cores collected from Grand Traverse Bay, and other Great Lakes locations around Michigan, leveled off after 1980, reflecting relatively constant current inputs over the last two decades (*4*). However, other recent studies have suggested that the emissions of PAHs have actually increased in certain urban areas of the United States (*5, 9*).

Even as point sources for several known environmental contaminants are regulated and emissions from these sources decline, humans continue to alter the environment in significant ways (e.g., urban sprawl) that will have undetermined impacts on the input of contaminants to the environment (*10, 11*). Therefore, it is essential to understand the contaminant loadings, both that we may assess the effects of environmental legislation and that we may identify emerging sources of pollution. This study compares spatiotemporal patterns of PAH accumulation among a number of inland lakes to determine current and historical influences of PAH loadings to the Great Lakes region. Michigan has a surface area of 151 586 km², extends over 7° of longitude and 6° of latitude, and has a large number of lakes, making it an ideal geographical area for such a study.

Materials and Methods

Sediment cores were collected from Cass, Elk, Gratiot, Gull, and Higgins Lakes in the summer of 1999 (Figure 1). Sediment cores were collected from Crystal and Littlefield Lakes in the summer of 2000. Sediment cores from Cadillac, Crystal, Mullett, and Whitmore Lakes were collected in 2001. The Crystal Lakes from Montcalm and Benzie Counties are referred hereafter as Crystal M and Crystal B, respectively (Table 1). Lakes were also chosen to represent a broad range of human disturbance, from areas of high development (e.g., Cass Lake) to relatively remote lakes (e.g., Gratiot Lake).

Four replicate sediment cores were taken from the deepest portion of each lake by use of a MC-400 Lake/Shelf multicorer (Ocean Instruments, San Diego, CA) deployed from either the U.S. EPA (United States Environmental Protection Agency) research vessel Mudpuppy or the Michigan Department of Environment Quality monitoring vessel Nibi. The multicorer was outfitted with four sampling tubes (10 cm i.d. × 58 cm long). If the cores showed any evidence of disturbance, a new set of cores was immediately taken. A core was considered compromised if there was no surface water present and/or the surface sediments of the core looked

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FIGURE 1. Michigan lakes sampled in the summers of 1999, 2000, and 2001.

combined by taking an equal amount of sediment from several layers. PAHs were analyzed following methods described elsewhere (*13*). Briefly, sediment samples (~10 g dry weight) were Soxhlet-extracted and then treated with activated copper. Extracts were passed through 10 g of activated Florisil column (60−100 mesh; Sigma, St. Louis, MO) and the fraction eluted with 100 mL of 20% dichloromethane in hexane was concentrated and injected into a gas chromatograph interfaced with a mass spectrometer (GC-MS).

PAHs were quantified on a Hewlett-Packard 5890 series II gas chromatograph equipped with a 5972 series mass spectrometric detector. The MS was operated in selected ion monitoring mode by use of the molecular ions selective for individual PAHs (*13*). The PAH standard consisted of 16 priority pollutant PAHs identified by the U.S. EPA (method 8310). Recoveries of PAHs in the analytical procedure were between 80% and 105% (*14*). The detection limits of individual PAHs were between 1 and 5 ng/g dry wt. Procedural blanks were analyzed with every batch of 10 samples, as a check for interference and contamination arising from solvents and glassware.

Results and Discussion

^{210}Pb Profiles. ^{210}Pb profiles for Cass, Crystal M, Elk, Gratiot, Gull, Higgins, Mullet, and Whitmore Lakes showed no significant disturbance in the cores. ^{210}Pb profiles in all of the lakes studied here are discussed in detail elsewhere (*11*). However, deviations from general trends in ^{210}Pb profiles were observed for Littlefield and Cadillac Lakes, which need to be discussed here to understand the PAH trends in these lakes. Littlefield Lake had a disturbed record and could not be dated by use of ^{210}Pb profiles. The ^{210}Pb profile in Littlefield Lake did not decrease with increasing depth, which indicated that the sediment or the process of deposition was disturbed. Anecdotal information indicates that Littlefield Lake may have historically been mined for marl, which would significantly influence the sediment record. Although dating by use of ^{210}Pb profiles was not feasible for this lake, we roughly estimated the dates on the basis of the stable lead profile (*11*). The rationale for this approach is that lakes sampled in 1999 showed similar lead profiles, with peak deposition in the mid to late 1970s. This similarity in lead profiles was used to estimate dates for the Littlefield Lake sediments. The amount of sediment deposited from the sample with the highest lead concentration (assigned as 1972) to the surface (2000) was determined (grams per square meter), and that value was divided by 28 years (1972−2000), to obtain a sedimentation rate of 693 g m^{-2} y^{-1} for Littlefield Lake. Furthermore, the focusing factor was estimated to be 2, which is an average value for most inland lakes in Michigan. In the

disturbed. Cores were immediately extruded and sectioned at 0.5-cm intervals for the top 5−8 cm and at 1-cm intervals for the remainder of the core. Also, care was taken to remove sediment from around the edges of the slice, to minimize smearing effects. All samples were initially stored at 4 °C (for 1−5 days) and then frozen until analysis.

^{210}Pb was measured on one subcore from each lake for determination of porosity, accumulated dry mass, sedimentation rate, sediment age, and focusing factor (Freshwater Institute in Winnipeg, Manitoba, Canada). Results from a few lakes were verified by use of ^{137}Cs. ^{137}Cs is an artificial radionuclide that was produced by atmospheric testing of nuclear weapons in the late 1950s and early 1960s. The peak level of fallout occurred in 1963; therefore, the peak activity in the sediment should occur in the early 1960s (*12*). Stable lead has a historical pattern of deposition that is generally consistent across lakes, with concentrations increasing from the mid-1800s to the mid-1970s and then decreasing to the present (*10, 11*). The peak in lead concentrations in the mid-1970s, due to the removal of lead from gasoline after that time, is sufficiently consistent that it can be used for dating verification. Details regarding the models used for dating the sediments analyzed in this study have been described elsewhere (*10, 11*).

The U.S. EPA's 16 priority PAHs were analyzed in one of the four cores collected per lake. Because there was insufficient material (i.e., 10 g dry weight) for analysis in each section of the core from certain lakes, the sections were

TABLE 1. Characteristics of Michigan Lakes Sampled during 1999−2001

lake	county	focusing factor	sedimentation rate (g m^{-2} y^{-1})	lake area (km^2)	water depth (m)	watershed area (km^2)	population density in 2000 (people/km^2)	approx. mixed depth (cm)
Cadillac	Wexford	1.7	117	4.7	8.2	42.8	121	14
Cass	Oakland	6	3480	5.2	36.5	41.9	745	3
Crystal B	Benzie	2.9	624	39.3	50	66.2	20.5	4
Crystal M	Montcalm	1.7	465	2.9	16.7	9.2	23.7	6
Elk	Antrim	2.1	420	31.3	59	98.1	32.1	1
Gratiot	Keweenaw	2.5	260	5.8	23.7	21.1	2.1	5
Gull	Kalamazoo	1.8	500	8.2	33.4	53.4	41.4	3
Higgins	Roscommon	2.0	240	38.9	41.3	67.2	29.9	3
Littlefield	Isabella	2.0[a]	693[b]	0.7	21.3	16.4	11.9	NA
Mullet	Cheboygan	3.6	801	70.3	35.5	1286	10.8	4
Whitmore	Livingston & Washtenaw	2.8[c]	556	2.7	20.4	9.1	150.4	6

[a] Average for Michigan lakes except Cass. [b] Estimated based on stable lead profile. [c] Estimated focusing factors (extrapolated).

TABLE 2. Concentrations[a] of Selected and Total PAHs in Surficial Sediments (0−2 cm) from Inland Lakes in Michigan

lake	Fl	pyrene	B[a]A	chrysene	B[b]F + B[k]F	B[a]P	total PAHs	focus-corrected PAH accumulation rate (μg m^{-2} y^{-1})
Cadillac	1710	1270	305	732	1230	665	6580	450
Cass	3440	2680	988	2310	1400	2200	16 900	9790
Crystal B	93	32	<5	16	39	<5	200	43.6
Crystal M	197	156	26.2	90.5	150	6.5	767	215
Elk	68	51	20	47	25	24	235	48.1
Gratiot	<5	<5	<5	<5	<5	<5	<50	<5.2
Gull	291	131	53.4	152	89.7	71.3	800	225
Higgins	824	105	87	539	410	312	2390	284
Littlefield	198	152	27.6	87.6	120	<5	665	230
Mullet	<5	<5	<5	<5	<5	<5	<50	<11.3
Whitmore	144	108	<5	99	140	<5	490	97.3

[a] Concentrations are given in nanograms per gram dry weight. Fl, fluoranthene; B[a]A, benzo[*a*]anthracene; B[b]F + B[k]F, benzo[*b*]fluoranthene + benzo[*k*]fluoranthene; B[a]P, benzo[*a*]pyrene.
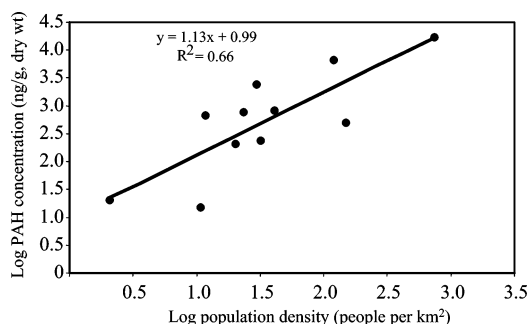

FIGURE 2. Relationship between watershed population density (in 2000) and PAH concentration in surface sediment from several inland lakes in Michigan.

case of Cadillac Lake with a deep mixing zone of ∼14 cm, all three models gave different dates. We chose the CRS model for dating Cadillac Lake (*11*). Focusing factors, calculated for each of the lakes, ranged from 1.7 to 3.6, except for Cass Lake, which had a focusing factor of 6 (Table 1).

PAH Concentrations. Concentrations of total PAHs (sum of 16 priority PAHs) and selected individual PAHs in surficial (0−2 cm) sediments from all of the lakes studied are shown in Table 2. PAH concentrations varied considerably among the lakes. High concentrations were found in sediments from Cass, Cadillac, and Higgins Lakes (>1000 ng/g dry wt). The lowest concentrations were found in Crystal B, Elk, Gratiot, and Mullet Lakes (<250 ng/g dry wt). These four lakes are located in northern Michigan, which is a less industrialized and less urbanized region than is southern Michigan. A maximum PAH concentration of 16 800 ng/g dry wt, found in the surface sediment from Cass Lake, was the highest concentration measured in this study. High concentrations of PAHs in Cass and Cadillac Lakes can be related to the high population densities of these two lakes' watersheds (Table 1). Watershed population densities of all of the lakes in 2000 were plotted against total PAH concentrations measured in surface sediments (Figure 2). In general, in spatial terms, the concentration of total PAHs correlated significantly with watershed population density for each lake (r^2 = 0.66; P < 0.05). However, concentrations of PAHs in Whitmore Lake (490 ng/g dry wt) were relatively low compared to concentrations in other lakes that had similar or lower watershed population densities. This suggests that watershed population density is an important factor in determining PAH contamination, although other factors cannot be ignored. Lake and watershed surface areas, impervious cover, sedimentation rate, mixing depth, and hydraulic retention time can also play a role in determining the magnitude of contamination

within a lake. Watershed population densities of most lakes have increased over time, with accelerated increases after the 1940s (*11*). The highest rates of watershed population growth are for lakes located in southern Michigan (Cass, Crystal M, Gull, and Whitmore).

To place the current concentrations of PAHs into an ecological perspective, we compared threshold effect concentrations (*15*) with the surface sediment concentrations determined for the lakes. Concentrations of total PAHs in surface sediments of Cass and Cadillac Lakes were greater than the lowest effect level of 4000 ng/g dry wt (*15*), whereas those in other lakes were below the threshold concentrations.

Temporal Trends. Several layers of the sediment core were pooled for the analysis of PAHs in samples from Cass, Elk, Gratiot, Gull, and Higgins Lakes. This compromised the fine temporal resolution of PAH data, although a general trend was still evident (Figure 3). In general, PAH concentrations declined gradually in Elk, Gratiot, and Gull Lakes over the past 20 years. In contrast, concentrations of total PAHs in surficial sediment (top 1 cm corresponding to the year 1999) from Cass Lake were greater than the concentration determined from subsurface layers, suggesting a recent increase in PAH inputs. Because of the high sedimentation rate, the oldest sediment collected in the core from Cass Lake was from 1971. PAH concentrations in Higgins Lake declined after 1983, but as at Cass Lake, a recent increase in concentration in 1999 was found (Figure 3).

Temporal trends in total PAH concentrations in sediments from Crystal M, Crystal B, Cadillac, Littlefield, Mullet, and Whitmore Lakes are shown in Figure 4. Concentrations of total PAHs in Crystal B, Crystal M, and Mullet Lakes were highest in the 1970s or 1980s and then declined. PAH concentrations in Cadillac Lake sediments increased steadily from the 1890s to the 1970s−1990s, when the highest concentrations were found; then they declined slowly. Such a slow decline in PAH concentrations could be due to the high sediment mixing depth of 14 cm in this lake (Table 1). Concentrations of PAHs in Whitmore Lake declined slowly from the 1970s. However, Whitmore Lake had a sediment mixing depth of 6 cm, which was greater than in many other lakes. In general, lakes with a high mixing depth tend to exhibit slower rates of decline in PAH concentrations than do the lakes with low mixing depths. PAH concentrations in Littlefield Lake sediment showed some disturbance in profiles between 1950 and 1980. Moreover, concentrations of PAHs were rather uniformly low (<200 ng/g) in this lake from 1850 to 1950. As mentioned earlier, the ^{210}Pb profile was found to be disturbed in sediment from this lake, due to probable marl mining. Nevertheless, total PAH concentrations in Littlefield Lake declined gradually after 1981.
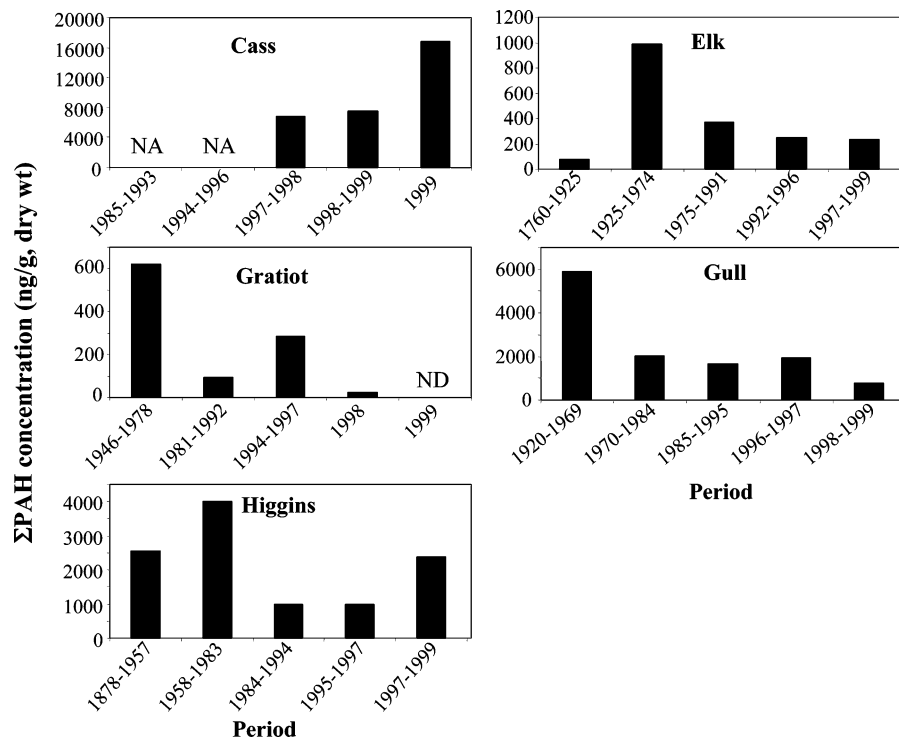
FIGURE 3. Temporal changes in concentrations of PAHs in sediment cores from Cass, Elk, Gratiot, Gull, and Higgins Lakes in Michigan. Core sections have been pooled; therefore, each bar represents the average concentration over a period. NA, not analyzed; ND, not detected.
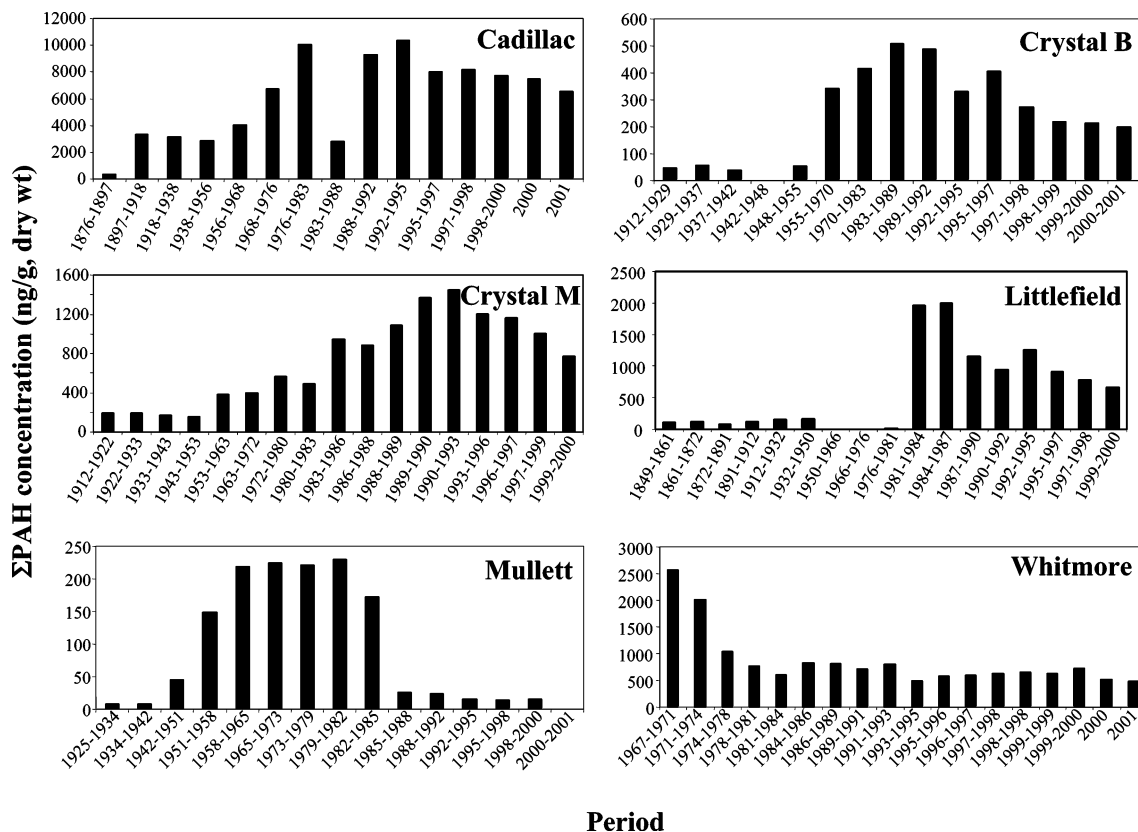

Period

FIGURE 4. Temporal changes in concentrations of PAHs in sediment cores from Cadillac, Crystal B, Crystal M, Littlefield, Mullet, and Whitmore Lakes in Michigan. Core sections have been pooled; therefore, each bar represents the average concentration over a period. NA, not analyzed; ND, not detected.

An increase in watershed population density, with a concomitant increase in sediment PAH concentrations, was also evident for several lakes. For example, in Cadillac Lake, increase in the population density from 1900 to 1930 was followed by an increase in the concentrations of PAHs until 1980 (Figure 5). However, for suburban and rural lakes, the increase in watershed population density was not positively correlated with PAH concentrations, after the 1980s. For
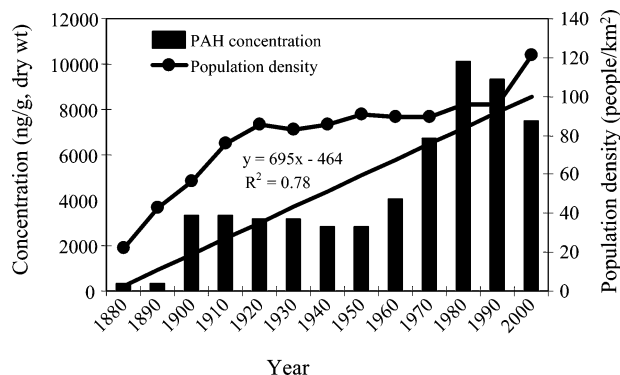
FIGURE 5. Temporal changes in watershed population density and PAH concentration in sediment core from Cadillac Lake, Michigan (solid line represents the line of correlation).

example, while the watershed population density in Mullet Lake increased steadily from 1870 (0.4 people/km^2) to 2000 (10.8 people/km^2), PAH concentrations increased until 1982 but decreased thereafter. A similar trend was also observed for Crystal M and Crystal B Lakes. However, Cass Lake, located in an urban watershed, showed an increase in PAH concentration concurrent with the increase in watershed population density until recently. Population density can be related to sewage and stormwater discharge, burning and disposal of yard waste, and other local inputs as well as sources related to automobiles and highways (e.g., tire wear, auto emissions, road maintenance). Nevertheless, PAH concentrations in some suburban and rural/remote lakes have declined since the 1980s.

Overall, concentrations of PAHs in inland lakes increased from the early to mid 1900s onward and then declined after the 1980s. For instance, the overall rate of decline in PAH concentrations from 1985 to 2000 ranged from 19% to 85% (for 15 years) for all of the lakes, except Cass and Higgins Lakes, which recorded an increase in PAH concentrations recently. The rate of decline in PAH concentration from the peak to the present differed among lakes. The rate of decline was pronounced in Gratiot and Mullet Lakes, which recorded 73−85% decline in PAH concentrations in 15 years. Lakes in suburban areas showed a gradual decrease in PAH concentrations (36−61% in 15 years). The rate of decline was very low, from 19% to 29% since 1985, in Cadillac and Crystal M

Lakes. In contrast, an increase in the concentrations of PAHs was observed in Cass and Higgins Lakes, which are located in urban areas. There has been little documentation of this phenomenon for multiple lakes at this spatial scale. There are several possibilities for the differing rates of decline in PAH concentrations. In addition to changes in local sources, mixing of the sediment and focusing can cause broadening of contaminant peaks and differences in the rates of decline of PAHs among lakes. Several processes within the lakes, such as dilution and degradation, can also affect the rates of reduction in PAH concentrations.

Urban sprawl, with concomitant increase in automobile use, was suggested as an explanation for the recent increase in PAH concentrations in urban lakes (9, 16). A recent increase in the contribution of automobile traffic to PAH pollution in sediments in the Great Lakes region has been documented (7, 17). The gradual decrease in PAH concentrations in suburban and rural lakes is consistent with decreases reported for the Laurentian Great Lakes (4, 6). The shift to alternative energy sources in industrial processes and implementation of particulate emission controls have reduced regional-scale emissions of PAHs.

PAH Profiles and Sources. The proportions of individual PAHs (expressed as percentages of the total) comprising the total PAH concentration were calculated for sediment cores for each lake (averaged over the entire section) for evaluation of spatial variations in PAH profiles (Figure 6). Four- and five-ring PAHs were the most abundant compounds in sediments, whereas two- and three-ring PAHs were less abundant. On average, fluoranthene, pyrene, chrysene, and benzo[b+k]fluoranthene together accounted for 75% of the total PAHs in sediment cores from all of the lakes analyzed. Despite the predominance of these five PAHs, there existed differences in the composition of PAHs among lakes. Fluoranthene was the predominant compound in all of the lakes, accounting for 19−37% of the total PAH concentrations. Pyrene was the next most abundant PAH in Cass, Cadillac, Elk, and Gratiot Lakes, whereas benzo[b+k]fluoranthene was the second most abundant PAH in Crystal M, Crystal B, Littlefield, Mullet, and Whitmore Lakes. Chrysene was the second most abundant compound in Gull and Higgins Lakes. Benzo[ghi]perylene was found in Cass, Elk, and Gull Lakes, but it was not found in other lakes. Naphthalene was found only in Cadillac, Crystal M, and Littlefield Lakes. Contributions of phenanthrene and anthracene to total PAH con-
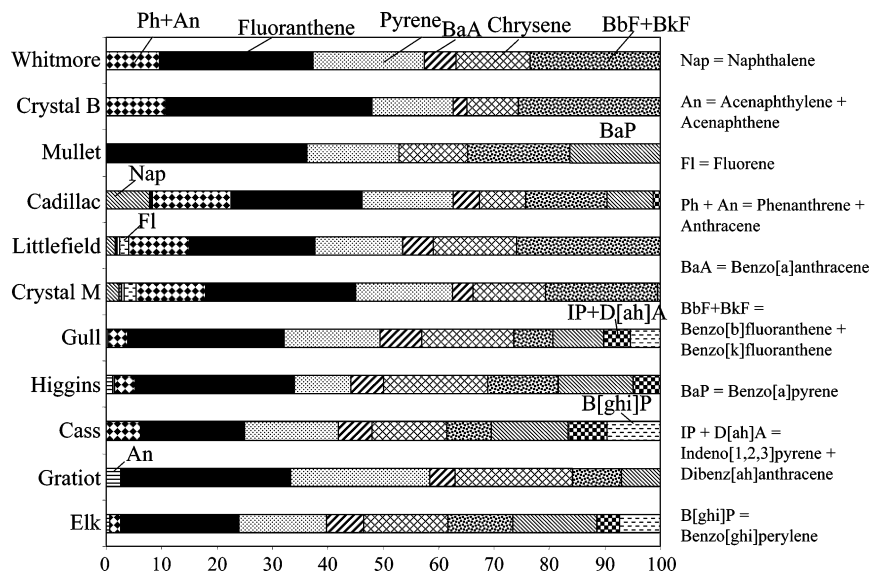

FIGURE 6. Individual PAHs comprising the total PAH concentrations, expressed as percentages, in sediment cores from inland lakes in Michigan. Values have been averaged over the entire depth of the core.
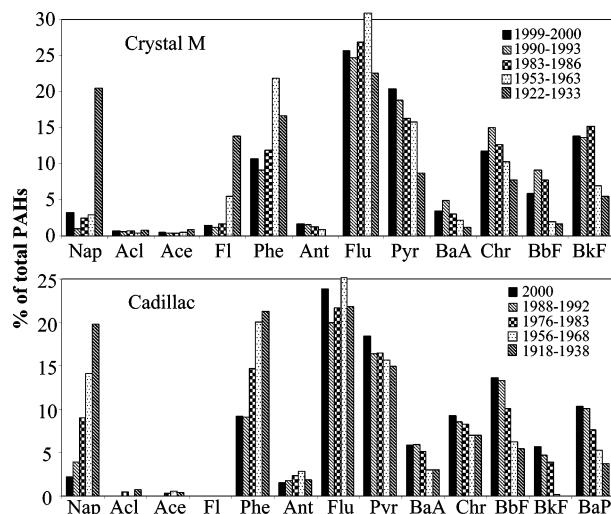
FIGURE 7. Temporal variations in PAH composition (percent) in sediment cores from Crystal M and Cadillac Lakes in Michigan. Names of PAHs are abbreviated as in Figure 6.

centrations were relatively high in sediments from Cadillac, Crystal M, Crystal B, Littlefield, and Whitmore Lakes. Benzo-[a]pyrene was found in several lakes, but it was not found in Crystal B, Littlefield, and Whitmore Lakes. In general, Cass, Cadillac, Elk, and Gull Lakes contained relatively higher proportions of higher molecular weight PAHs.

The differences in profiles of PAHs in sediments of several inland lakes suggest the differing extents of influence of various sources. Whereas the predominance of fluoranthene, pyrene, chrysene, and benzo[b+k]fluoranthene in all of the lakes suggests contribution from a major regional source, the differences in proportions of individual PAHs indicate the influence of local sources or processes in each of the lakes. Although PAHs may be contributed from many sources, coke ovens, automobile traffic, and wood burning have been considered as major sources in recent years (7). Each PAH source may provide an individual profile or signature (18–20), which can be used in the identification of sources. Temporal trends in profiles and composition of PAHs in Gratiot and Mullet Lakes suggest that regional sources have contributed to the occurrence of fluoranthene, pyrene, chrysene, benzo[k]fluoranthene, and benzo[a]pyrene, which are the only PAHs found in these remote lakes' sediments during the 1940s to 1980s. None of these compounds, except chrysene and benzo[a]pyrene, was found in sediments in these lakes after the 1980s. This suggests that the regional sources contributing to fluoranthene, pyrene, and benzo-[k]fluoranthene have decreased after the 1980s. Fluoranthene, pyrene, and benzo[k]fluoranthene are predominant in coal/coke combustion processes (18–20). The decline in their concentrations in Gratiot and Mullet Lakes suggests a general reduction in coal/coke combustion-related sources of PAHs in Michigan. Benzo[a]pyrene can originate from both coal combustion and road traffic (19). A recent increase in benzo-[a]pyrene concentrations in Mullet and Gratiot Lakes suggests contributions from vehicular emissions. It is worth noting that the types of sources of PAHs in these lakes have shifted. Studies have shown that coal/coke-related sources of PAHs have declined recently in areas distant from steel production, while PAHs emitted from motor vehicles have increased (7, 17, 21). Occurrence of benzo[ghi]perylene in urban lakes such as Cass, Elk, and Gull Lakes suggests emissions from automobile traffic.

In addition to such spatial variation, the composition of PAH compounds in sediment cores varied temporally, again indicating a shift in sources of PAHs. In Mullet and Gratiot Lakes, chrysene was the only PAH found in sediments prior

to the 1930s. Fluoranthene, pyrene, benzo[k]fluoranthene, and benzo[a]pyrene were found during the 1950s to the 1980s. Only benzo[a]pyrene and chrysene were found in surface sediments (1998–2000) in these lakes.

A shift in the profiles of PAHs over time has been illustrated for Crystal M and Cadillac Lakes, which represent moderately and heavily contaminated lakes, respectively (Figure 7). Naphthalene and phenanthrene, which are the major PAHs found in sediment deposited prior to the 1930s, declined after that period. Fluorene concentrations declined gradually with time in Crystal M Lake. Concentrations of fluoranthene, a major PAH found throughout the sediment core, remained relatively uniform in both Crystal M and Cadillac Lakes. On the other hand, higher molecular weight PAHs—pyrene, benzo[a]anthracene, chrysene, benzo[b]fluoranthene, and benzo[k]fluoranthene—increased with time. The relative increase in the proportion of high-molecular-weight PAHs suggests a general shift in PAH sources. Uncombusted sources (e.g., oil seeps, petroleum spills) contain predominantly two- and three-ring PAHs, whereas combustion sources (e.g., vehicle exhaust, domestic heating with coal, forest fires) contain predominantly four- and five-ring PAH species (19). A general increase in the proportion of high-molecular-weight PAHs suggests an increase in combustion-related sources in recent years.

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