

Carbon Particles in Dated Sediments from Lake Michigan, Green Bay, and Tributaries

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Carbon particle analysis is carried out on four sediment cores from Lake Michigan (CLM-I), Green Bay (GB-D), and the Fox (FR-C) and Kinnickinnic Rivers (KK-6) to explore the inputs of pollution from incomplete combustion of fossil fuels. Elemental carbon content is determined by CHN analyzer, and carbon particle type (from burning of coal, wood, and petroleum), abundance, and size are determined through scanning electron microscopy. Carbon contents are between 0 and 1.0% except for core KK-6, where high values (3–33%) appear to be linked to a now defunct coke and coal gasification plant. Maxima are found in the 1950s (CLM-I) or during 1940–1962 (FR-C). The abundance of coal particles is between 40 and 95% in all four cores. The wood fraction is between 0 and 40% with the highest value in the central Lake Michigan core (CLM-I), indicating long-range transport of small diameter (18–22 μm) wood particles with a minimum during 1960–1970 in agreement with the U.S. consumption record. The fraction of oil particles increases in the top layers of KK-6, FR-C, and CLM-I, reflecting increasing emissions from automobile traffic since 1920–1940. Core GB-D shows the opposite trend since 1953, demonstrating reduced significance of Green Bay as a commercial port. PAH data for these areas, obtained by others, generally support our results.

Introduction

The incomplete combustion of fossil fuels produces several byproducts, many of which can be harmful to aquatic life and man. Polycyclic aromatic hydrocarbons (PAHs) are common byproducts of incomplete fossil fuel combustion, and many of them are known carcinogens (1). It is therefore desirable to identify the sources of these harmful byproducts. Fortunately, combustion of different fossil fuels produce different signature emissions, and it is therefore possible to identify the sources from their emission “fingerprints”. These byproducts are discharged directly to a receiving water or may be transported atmospherically and can settle onto lakes or rivers. The pollutants then settle through the water column and become part of the sediment record, where they often remain intact, particularly in anoxic sediments. It may then be possible to study the history of emissions into an area by examining the sediment record (2–11).

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TABLE 1. Coordinates, Water Depths, and Core Lengths

core	coordinates		water depth (m)	core length (cm)
	latitude north	longitude west		
KK-6	43°00.61'	87°54.30'	2.8	255
FR-C	44°28.80'	88°02.70'	1.7	100
GB-D	44°45.00'	87°44.50'	11	20
CLM-I	43°25.00'	87°32.40'	140	16

Some work has been done recently in identification of combustion sources using PAHs (2, 4, 8). Christensen et al. (3) used chemical mass balance (CMB) modeling for PAHs for sediments of the Kinnickinnic River. PAH source apportionment in the Fox River and Green Bay has also been carried out based on CMB modeling (6). The Fox River cores showed generally a decrease in coal and an increase in oil from 1930 to 1990. It was discovered that the combustion sources in Green Bay vary greatly, depending on whether the location is in the Fox River plume. Those in the plume show a decrease in oil from the 1960s to 1995. Those not in the plume show an increase of oil from the 1960s to a peak around 1990 and then a decrease to 1995. Simcik et al. (5) studied PAHs in sediments from the eastern half of Lake Michigan. They concluded that coal was the dominant PAH source. Also, Rachdawong et al. (7) performed source apportionment modeling for PAHs in central Lake Michigan. This work showed coal as a major PAH source in the northern sediment cores and oil as a relatively more important PAH source in the southern cores.

Carbon particles produced during combustion have been studied in Lake Michigan (1, 9–11) for a few cores. However, no detailed dated records of carbon particles by type, abundance, or size were published. Also, there has been no comparison with dated PAH records for the same or nearby cores. Carbon particles may also serve as tracers of fossil fuel combustion.

This study focuses on characterization of carbon particles in dated sediments from combustion sources by comparing carbon particle signals in industrial and remote sites of the same region. We present here detailed records of particles by type (from burning of coal, wood, and petroleum), abundance, and size as well as comparisons with PAH data including source apportionment. In addition, carbon particle profiles from central Lake Michigan are compared with U.S. consumption records of coal, wood, and petroleum.

Materials and Methods

Sampling and Sediment Dating. Four cores were taken from Lake Michigan Basin, Green Bay, Fox River, and Kinnickinnic River. Table 1 gives a summary of their locations, water depths, and core lengths. Core KK-6 was taken in the Kinnickinnic River in an area that is in a heavily industrialized part of Milwaukee. The Milwaukee Solvay Coke Company operated there from 1900 to the late 1970s, and there is also foundry activity in the area. Sampling was done from the R/V *Pelagos* by a vibra corer using a 6.7 cm diameter aluminum irrigation pipe. Core FR-C was taken in the Fox River near its mouth, where it empties into Green Bay. This location is in an industrial part of the city of Green Bay. Sampling was done by a vibra corer using a 10.2 cm diameter aluminum pipe with a polybutyrate liner aboard the U.S. EPA R/V *Mudpuppy*. The liner was removed and sealed at both ends. The core was then frozen for transport to the Center for Great Lakes Studies in Milwaukee.

Both cores KK-6 and FR-C were cut into 15 sections at the Center for Great Lakes Studies. The aluminum tubes from KK-6 were cut with a hacksaw, and the polybutyrate tubes with frozen sediment from FR-C were cut with a bandsaw. In order to avoid contamination, approximately 0.5 cm of material was carefully removed from each end of the subsections. The KK-6 subsections were 17 cm thick, and the FR-C sections were 6.5 cm thick. One half of the material was stored in plastic containers at 4 °C for radionuclide analysis, and the other half was stored in glass containers at -18 °C for PAH and carbon particle analysis.

Both GB-D, taken from Green Bay, and CLM-I, taken from the Lake Michigan Basin off the coast of Port Washington, were taken using a box corer aboard the R/V *Neeskay*. The box corer brought up a sediment sample 30.5 cm by 30.5 cm in cross section and 30–70 cm deep. Subcores were then taken from the box core using six 7.62 cm diameter polybutyrate liners. These subcores were then sliced into layers on the boat using a hydraulic extrusion device. The GB-D sections were 1 cm thick for layers 1–10 and 2 cm thick for layers 11–15. Core CLM-I sections were 0.5 cm for layers 1–4, 1 cm for layers 5–12, and 2 cm for layers 13–15. As with the other samples, half of the sediment was stored in glass containers for PAH and carbon analysis, and the other half was transferred into plastic containers for radionuclide analysis.

Dating of these cores was done using ^{137}Cs and ^{210}Pb dating techniques (12). KK-6, FR-C, and CLM-I were dated using the constant initial concentration (CIC) model where the sedimentation rate is calculated using log excess ^{210}Pb activity versus cumulative mass. Due in part to a discrepancy between the CIC model prediction and the 1963 ^{137}Cs maximum for GB-D, this core was dated using the constant rate of supply (CRS) model (8, 13). ^{137}Cs and ^{210}Pb methods gave similar results for cores CLM-I, FR-C, and KK-6. For GB-D, ^{137}Cs was used for normalization of the CRS model since supported ^{210}Pb activity had not been reached at the lowest layer.

Carbon Particle Analysis. The first step in carbon particle analysis is to chemically separate the carbon particles from the rest of the sediment. These particles are composed of a graphite form of elemental carbon. This form of carbon is relatively chemically inert, and it is therefore possible to separate it from the sediment. The technique employed is described by Griffin and Goldberg (11). The sediment is first dried at 105 °C to remove the water. Then, the sediment is digested in 6 N hot Hydrochloric Acid (90–98 °C) for 2–4 h. This step removes carbonates, metals, and organics. The sediment is then centrifuged, and the supernatant is discarded. The sediment is rinsed with distilled water between each process. The sample is then digested in a solution of 10 N hydrofluoric acid and 12 N hydrochloric acid for 2 weeks at room temperature. This step removes the silicates and more metals. The sample is then centrifuged, and the supernatant is discarded. Next, the sample is immersed in a 6 N potassium hydroxide solution, and 800 mL of hydrogen peroxide is added to break down the organics, while not affecting the elemental carbon. The sample is again centrifuged and digested in hot 6 N HCl for 4 h to remove any metals and organics that remain. The sample is then centrifuged and triple rinsed with distilled and deionized water to remove any traces of chemicals. Finally, the sample is dried at 105 °C and weighed. The ratio of initial to final sample weight is then calculated.

The carbon remaining from the chemical procedure was subsequently subjected to elemental carbon analysis using a Carlo Erba Model 1106 CHN analyzer. This procedure reveals how efficient the chemical separation was by giving the percent of hydrogen, nitrogen, and carbon in the sample. The hydrogen and nitrogen content reflect the remaining

TABLE 2. Sedimentation Rates

core	segment (cm)	r ($\text{g cm}^{-2} \text{ yr}^{-1}$)
KK-6	0–255	2.4
FR-C	0–26	0.30
	26–80	0.47
GB-D	0–3	0.154
	3–6	0.125
	6–9	0.103
	9–14	0.085
	14–20	0.058
CLM-I	0–16	0.036

hydrocarbons, and the carbon percent gives the purity of the sample. The percent of elemental carbon in the original sample can be calculated by multiplying the purity of elemental carbon given by CHN analysis by the ratio of initial to final sediment sample weight. Replicate samples were run for selected layers to ensure that the chemical separation and CHN analysis gave consistent results.

Carbon particle analysis by type and size was carried out using a Topcon ABT-32 scanning electron microscope. One hundred particles per layer were analyzed. Carbon particles from oil, wood, and coal combustion have distinct individual morphologies (10). Carbon particles derived from oil burning are round and have a convoluted surface. Carbon particles derived from wood burning are long and narrow and have an obvious cellular structure. Carbon particles derived from coal burning are of different shapes and have a smooth surface. Examples of these particles can be seen in Figure 1.

Particle size was reported as the geometric average of the longest and shortest dimension for the carbon particle. Typical sizes range from 10 to 100 μm , with some particles as small as 3 μm and some as large as 400 μm . Particles of different types (coal, oil, or wood) were averaged separately.

Results and Discussion

Sediment Dating and Carbon Profiles. Mass sedimentation rates for the four cores are listed in Table 2. The highest rates are for the river cores KK-6 and FR-C, followed by the Green Bay core (GB-D) and the core from central Lake Michigan (CLM-I). Figure 2 shows the percent elemental carbon vs depth and year for the four cores. KK-6 has very high carbon values. From 1950 to the present, the percent carbon ranges between 2 and 6%. Before 1950, the percent carbon was between 4 and 33%. There is a falloff of carbon values around 1900, but they are still above 10%. The carbon percentages, coupled with the fast sedimentation rate (Table 2), suggest a very strong local source or sources. It is likely that the Solvay Coke Company, which operated from 1900 until the late 1970s, was a major contributor to the carbon and PAH input (14).

GB-C, FR-C, and CLM-I all have sediment carbon percentages less than about 1%. These cores have comparable carbon contents, but if one considers the sedimentation rate, it becomes apparent that FR-C has the greatest carbon input, followed by GB-D and then CLM-I. This is what would be expected, since FR-C is in an urban area, GB-D has both local and remote sources, and CLM-I is at a remote site.

For CLM-I, we see that the amount of elemental carbon has a peak in the mid 1950s. This result is similar to that of Goldberg et al. (9). In core FR-C, there is a poorly defined peak between 1960 and 1940. Griffin and Goldberg found a similar result in a Lake Michigan Core (11). GB-D has no distinct peaks. In core KK-6, the carbon peak was in the late 1930s. This peak represents strong local sources and thus does not follow regional trends.

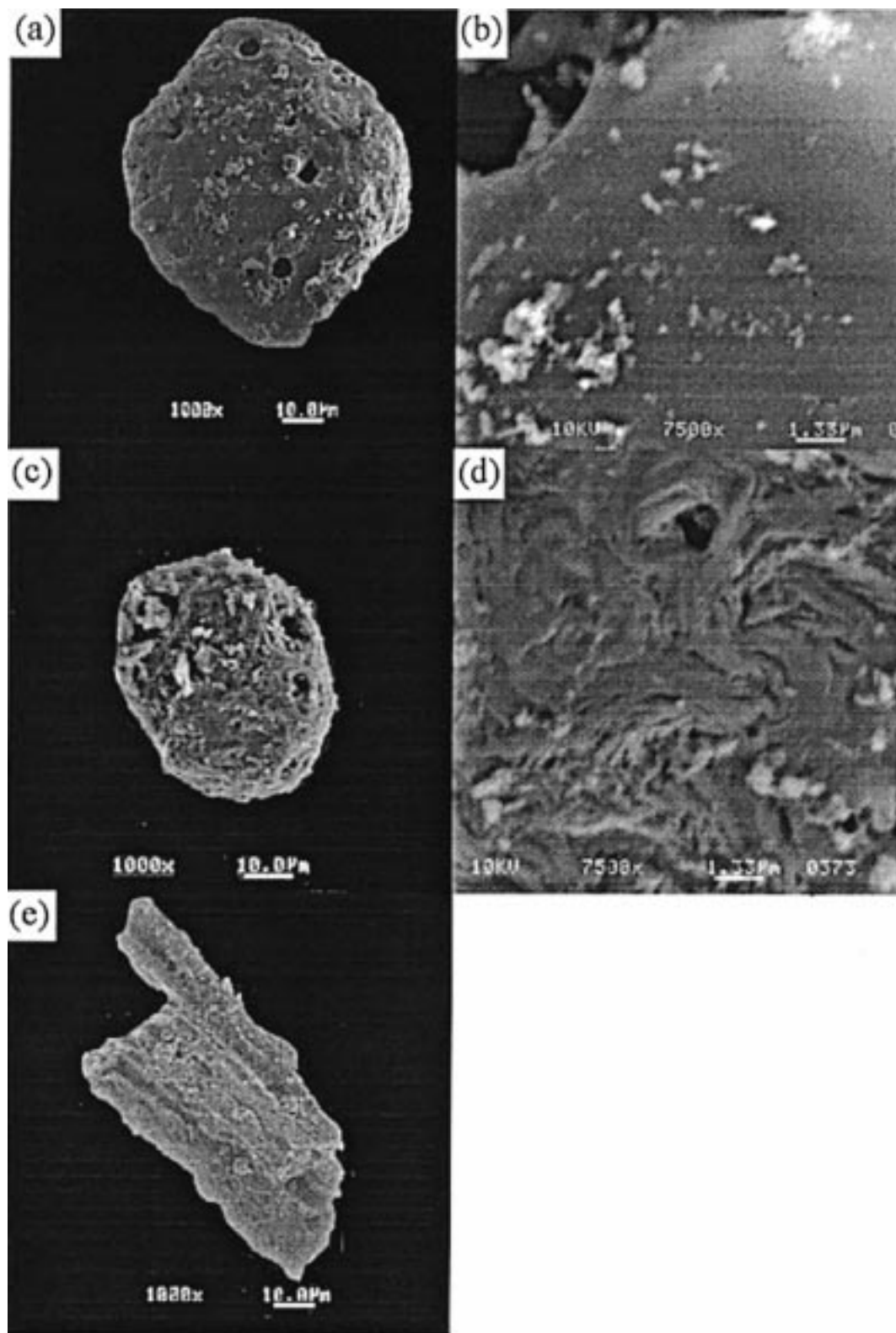


FIGURE 1. Electron micrographs of carbon particles from burning of (a and b) coal, (c and d) oil, and (e) wood. For panels a, c, and e, the magnification is 1000 \times . For panels b and d, the magnification is 7500 \times .

Carbon Particle Abundance Profiles. Figure 3 shows the percentage of particle type vs depth and year. The abundance patterns are discussed in detail below for the four cores.

Core Kinnickinnic River 6. We see very little wood in KK-6, with abundances below 5%. There is an oil input on the order of 15–20% until the late 1950s, when the oil input

drops to between 1 and 6% until before 1902, where it grows to nearly 10%. The coal input dominates this core, especially before the late 1950s. There is over 90% coal particles from 1900 to the late 1950s. Before 1902, coal is between 85 and 90%, and after the late 1950s, it is on the order of 80%. This result also points to the Solvay Coke Company as a main polluter. The foundries in this area use coke in their

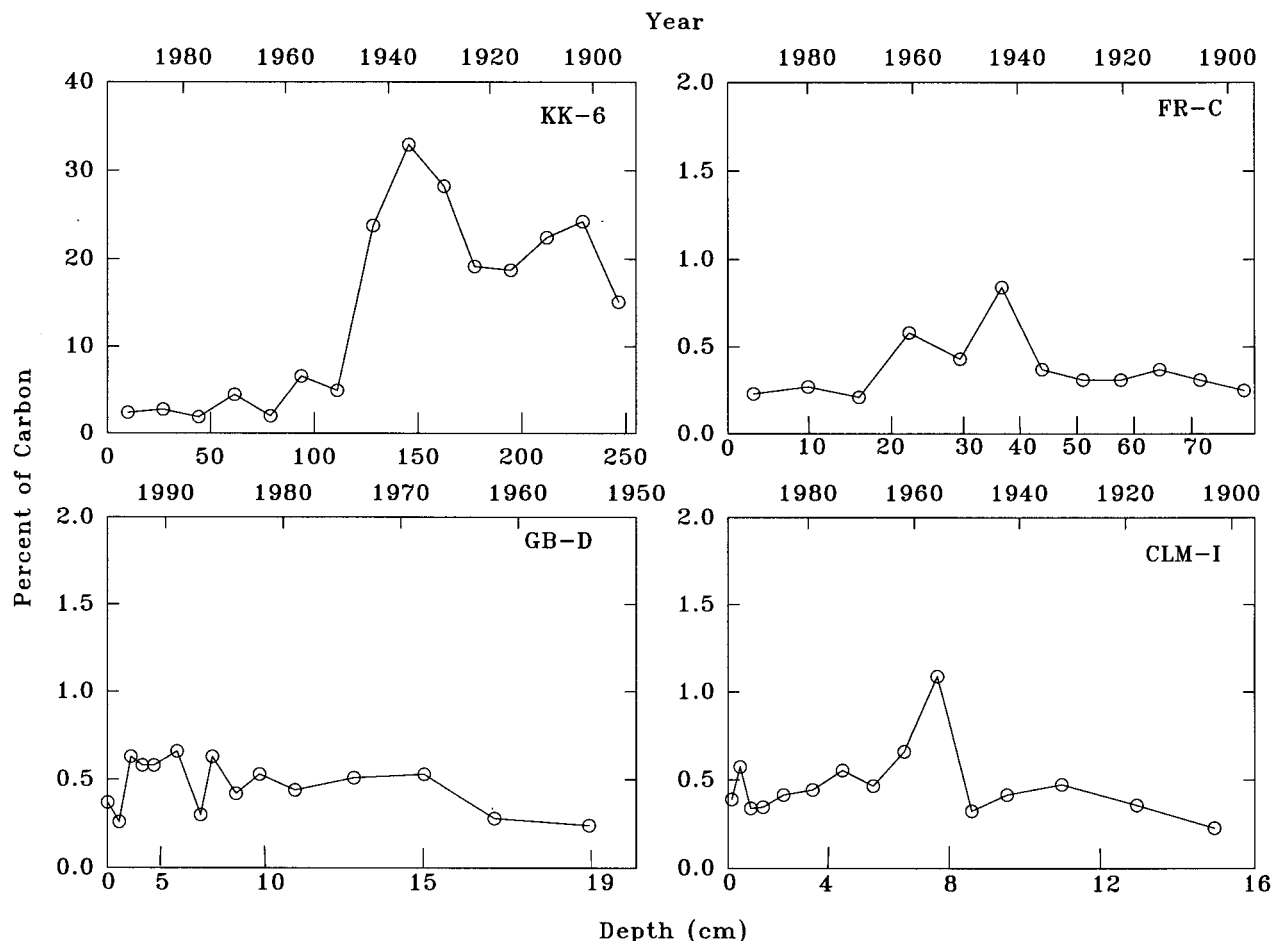


FIGURE 2. Percent carbon vs depth and year for cores KK-6, FR-C, GB-D, and CLM-I.

processes, adding to the coal input. The oil signal is due to automobile traffic and industries switching to oil in the later part of this century.

The general trends follow the trends discovered modeling PAH sediment inputs using the CMB model by Christensen et al. (3) for the same core. They found that the oil concentration from the CMB model is of the order of 40% from 1995 until 1943, where it falls to around 10%. There is a recovery of oil before 1902 to around 20–25%. The PAHs from coal–wood gasification are under 10% after the late 1950s, but increase to between 30 and 40% before this period (3). In the CMB modeling, it is next to impossible to see the difference between wood burning and coal–wood gasification, because of the similarity of the source signals. Therefore, without carbon particle analysis, one would not know the origin of the jump in the percentage of PAHs from coal–wood gasification. On the basis of the low and near constant wood particle count, it is clear that the increase in coal–wood gasification is not due to wood burning, but is in fact caused by coal gasification processes.

Core Fox River C. In core FR-C, the wood signal starts in 1995 at around 14%, decreases to a minimum (a few percent) during 1945–1960, and then increases again to around 10% in 1900. The oil signal starts at about 15% and then falls to a weak minimum at 1920–1950 of a few percent until 1900–1920, where it recovers to 6–8%. Coal dominates this core as well. The oil and wood increase in recent years may be due to the increase in recreational activities in the area.

These results are supported by the PAH work carried out by Su (6) for the same core. The oil percentage is 40% in 1980, falls to under 20% during 1920–1940, and then recovers to 36% in 1900. Coal–wood gasification starts around a few

percent in 1995, then increases to 7–8% during 1940–1970, and decreases again to 2% during 1900–1940. From the profile of wood particles (no maximum 1940–1970), it seems clear that the high PAH levels from coal–wood gasification during 1940–1970 are in fact caused by coal gasification processes.

Core Green Bay D. For core GB-D, the coal signal starts out in 1995 at around 85% and then decreases to around 60% in the early 1950s. The wood signal stays relatively constant throughout this time frame at between 4 and 10%, with no trends seen. The oil signal starts at around 10% and then rises to over 30% in 1953. It is thought that the decrease of the oil signal in recent years is due to the diminishing importance of the Green Bay harbor as a commercial port (6).

The results of PAH analysis for cores GB-B and GB-E near GB-D support these trends (6). For GB-B and GB-E, oil starts (1995) around 10% and increases to around 60% in 1965. Wood remains relatively constant. Coal starts (1995) at around 80%, but falls to 20% in 1965. These cores (GB-B and GB-E) are similar to GB-D in that they are close in location and are also both in the Fox River Plume, as is GB-D.

Core Central Lake Michigan I. CLM-I is from the most remote site of the cores studied. One would, therefore, expect the results to most closely mimic the regional historical signal. This is indeed the case. The percentage of wood is high, and there is a minimum in the mid 1960s. Oil is increasing from 1905 to 1995. These results follow the U.S. energy consumption data (4).

The results are in qualitative agreement with the PAH work of Rachdawong et al. (7), who considered a group of seven cores in the same area of the Lake Michigan Basin

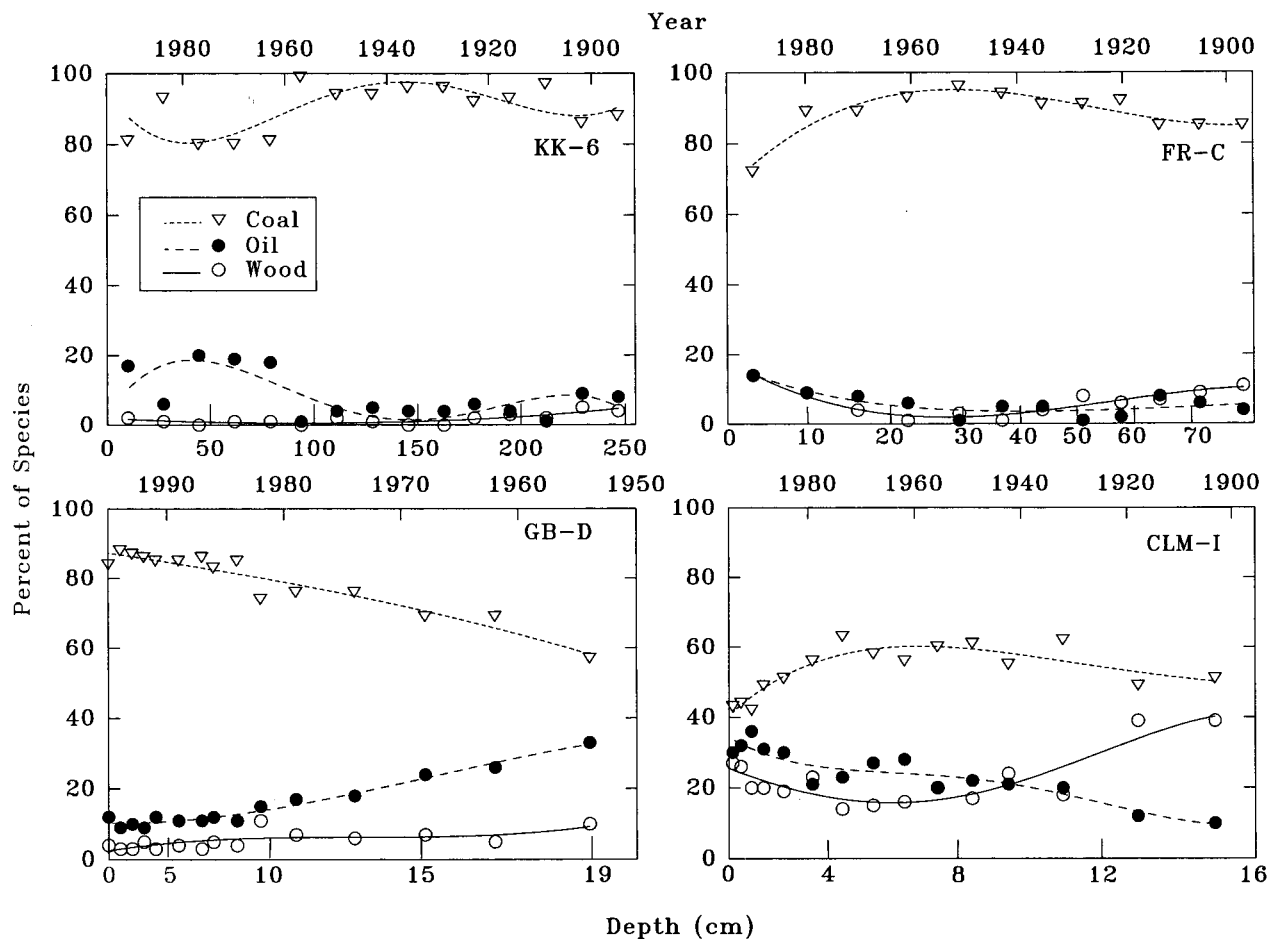


FIGURE 3. Percent species vs depth and year for cores KK-6, FR-C, GB-D, and CLM-I.

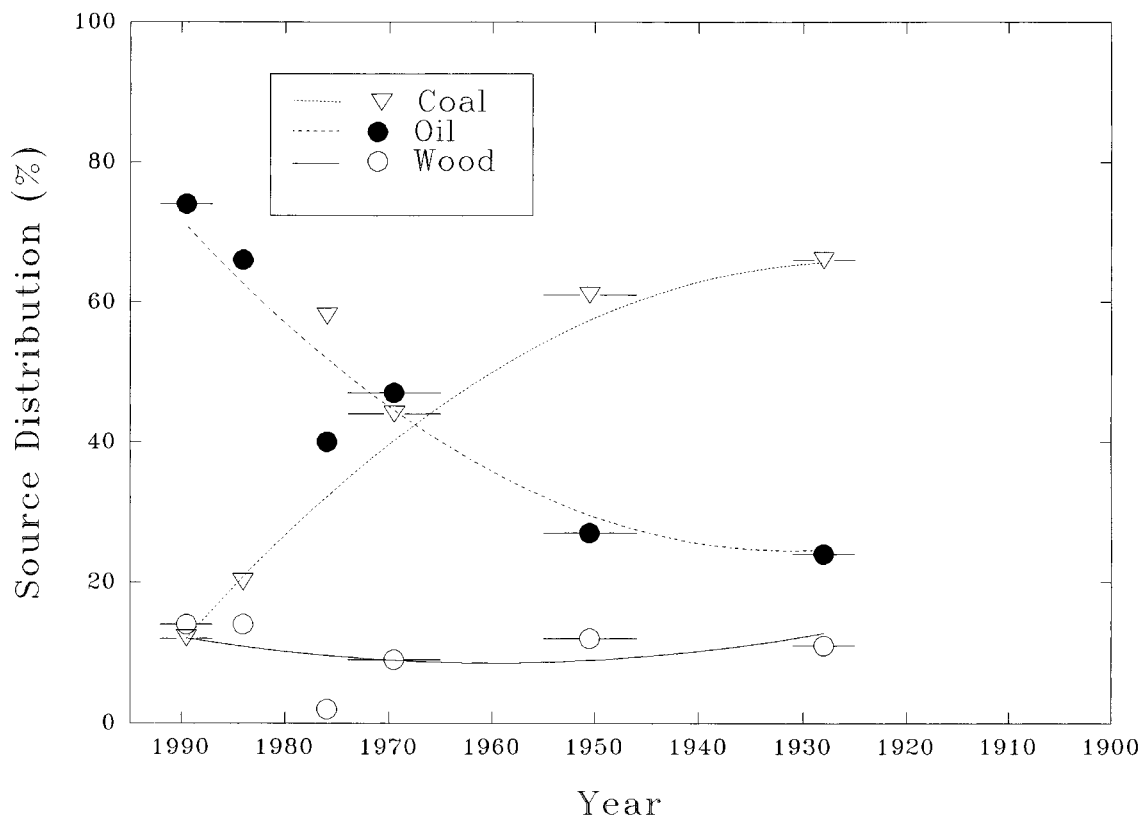


FIGURE 4. Source distribution of PAHs from burning of coal, oil, and wood obtained by CMB modeling. The values represent averages from seven cores in the Lake Michigan Basin (7).

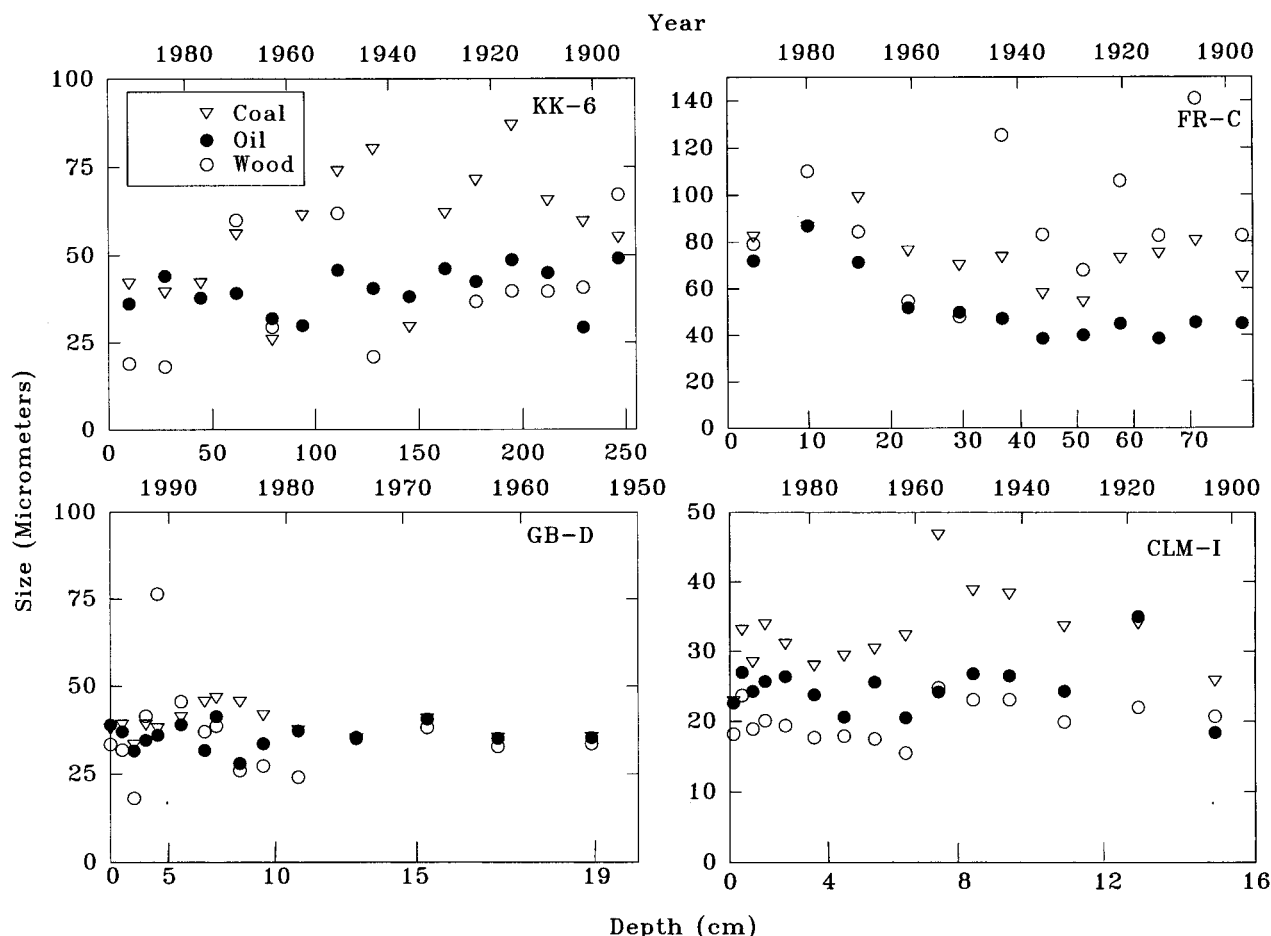


FIGURE 5. Size of particles vs depth and year for cores KK-6, FR-C, GB-D, and CLM-I.

(Figure 4). There is a dominance of oil, with contributions of 66–74% from 1983 to 1992. The oil signal decreases for all cores to an average of 24% for 1925–1931. In addition, carbon particles from oil, PAHs from petroleum combustion, and the U.S. petroleum consumption record (4) all show a decrease from 1975 to 1983, followed by an increase from 1983 to 1988. There is also between a 2 and 14% PAH contribution from wood burning for all seven cores with a minimum during 1968–1976. This minimum is also seen in the U.S. consumption record.

The above results differ from those of Simcik et al. (5), who however considered the eastern half of Lake Michigan. They suggested that the steel industries of Chicago, IL, and Gary, IN, are the major polluters of Lake Michigan. While there is a definite coal component in the central Lake Michigan area considered here, the wood and oil constituents are also strong. In fact, PAH data show dominance of oil for much of this area since 1983.

It is evident that the percentages of particles produced by oil do not coincide with the fractions of PAHs produced by oil combustion. It appears that carbon particles from oil are associated with about 2.5 times and wood with 0.5 times as much PAHs as coal particles. Thus for a given PAH output, wood and coal produce 5 and 2.5 times as many particles, respectively, as oil.

Carbon Particle Size Profiles. Figure 5 shows the size distributions vs depth and year for the four cores. The size of coal particles was large before the 1950s in core KK-6, which is the same time where coal dominated this core. The larger coal size suggests a close source for the coal inputs. Wood fluctuates greatly, but there are so few wood particles in this region that the results may not be conclusive. Carbon particles from oil are between 30 and 50 μm .

Core FR-C has very large coal particles, again demonstrating a close source. Wood is also large here, indicating that its source is local as well. Oil particles start out (1995) quite large (around 70 μm), but decrease to about 40 μm in 1940–1950. This points to a different or additional source of oil input in recent years. The particles in GB-D have a fairly uniform size, between 30 and 40 μm . In CLM-I, the wood particles are the smallest (18–22 μm), followed by oil (20–30 μm) and then coal (25–40 μm) particles. Small wood particles are transported the farthest, meaning that they are relatively abundant in this core (Figure 3). Many of the coal and oil particles have settled out before they could reach CLM-I.

The shapes of the species abundance curves (Figure 3, CLM-I), corrected with the above PAH yield factors, are similar but not identical to the PAH distribution based on a CMB model (Figure 4). This reflects the fact that PAHs are associated not only with charcoal particles (Figure 1) but also with silt ranging between 2 and 74 μm in size, including digestible organic carbon (15).

It is clear that there is a great deal of fluctuations in the amount, type, and size of carbon particles in this region. Cores KK-6, FR-C, and GB-D are clearly influenced by local phenomena, while CLM-I seems to be less influenced by point sources and gives a more regional picture. The coal signal is very strong in KK-6 and FR-C, indicating significant coal-based industrial activity in these areas.

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