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ALIPHATIC HYDROCARBONS IN SEDIMENT CORES FROM THE SOUTHERN BASIN OF LAKE MICHIGAN*

Paul V. Doskey

Environmental Research Division
Argonne National Laboratory
Argonne, IL 60439

Anders W. Andren

Water Chemistry Program
University of Wisconsin
Madison, WI 53706

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ABSTRACT. Aliphatic hydrocarbons in sediments of the southern basin of Lake Michigan have planktonic, terrigenous, and petroleum residue origins. Surficial sediments collected near the eastern shore in 60-80 m of water contained more petroleum residue and planktonic hydrocarbons and exhibited less terrigenous character than sediments collected from the deepest location in the basin. Petroleum residue inputs have increased since 1900 as evidenced by a change in the flux of an unresolved complex mixture (UCM) of hydrocarbons from 6 ng/cm²·yr to a flux of approximately 100 ng/cm²·yr in 1980 . Sediment profiles of the UCM exhibited subsurface concentration maxima that may be due to reduced inputs of combustion products or feeding by oligochaetes. Profiles of n-C₁₇ and pristane indicated that planktonic n-alkanes undergo degradation in the aerobic, mixed zone of the sediments.

ADDITIONAL INDEX WORDS: Petroleum hydrocarbons, n-alkanes, hydrocarbon geochronologies, lake sediments.

INTRODUCTION

Investigations of the distribution of aliphatic hydrocarbons in freshwater lake sediments indicate that these hydrocarbons have both biogenic and anthropogenic origins (Giger *et al.* 1974 and 1980, Wakeham and Carpenter 1976, Meyers and Takeuchi 1979, Wakeham and Farrington 1980). Terrestrial plants and plankton are the most prevalent biogenic sources. Anthropogenic sources include activities associated with the transportation, storage, processing, and combustion of fossil fuels. Hydrocarbons from these sources have unique chemical signatures. For example, the predominant n-alkanes in plankton are C₁₅, C₁₇, and C₁₉ (Clark and Blumer 1967, Blumer *et al.* 1971, Youngblood *et al.* 1971, Youngblood and Blumer 1973), while terrestrial plants contain mainly C₂₁-C₃₅ n-alkanes (Eglinton *et al.* 1962, Eglinton and Hamilton 1963, Douglas and Eglinton 1966, Caldicott and Eglinton 1973) with a carbon preference index (CPI; Bray and Evans 1961) of 4-10 (Brassell *et al.* 1978). Sediments containing petroleum residues exhibit an unresolved complex mixture (UCM) of hydrocarbons (Wakeham and Carpenter 1976, Wakeham and Farrington 1980) with n-alkanes having a CPI of 1 (Blumer and Sass 1972). The UCM is composed of a mixture of branched and cyclic, aliphatic and olefinic hydrocarbons.

Spatial variations of hydrocarbon concentrations in surficial sediments and vertical profiles in sediments are influenced by changes in material inputs and also by physical, chemical, and biological processes. For example, Hites *et al.* (1980) speculated that subsurface maxima in polyaromatic hydrocarbon (PAH) profiles in sediments reflected decreases in inputs caused by a change in home heating fuels from coal to oil and natural gas during the 1950s. Particles with

different sizes and densities have unique hydrocarbon signatures (Thompson and Eglinton 1978, Wade and Quinn 1979, Prah1 and Carpenter 1983). Therefore, hydrodynamics can influence hydrocarbon distributions in surficial sediments via differential particle dispersal (Prah1 1985). Biological processes can also alter hydrocarbon distributions. Several investigations have indicated that n-alkanes in plankton are more susceptible to decomposition than those in terrestrial plant wax (Meyers *et al.* 1980a, Prah1 *et al.* 1980, Wakeham *et al.* 1980, Bates *et al.* 1984). Furthermore, isoprenoid hydrocarbons such as pristane and phytane are not as readily degraded as straight-chain hydrocarbons (Blumer and Sass 1972). The UCM, comprising a complex mixture of branched and cyclic hydrocarbons, tends to persist in sediments. Feeding by oligochaetes can also alter profiles of hydrocarbons in sediments by providing a means of advecting substances from depths of 2-10 cm in sediments to the surface (Krezoski and Robbins 1985, Karickhoff and Morris 1985, Robbins 1986).

The purpose of our investigation was to examine the spatial distribution and vertical profiles of aliphatic hydrocarbons in sediment cores collected from the southern basin of Lake Michigan. Our intent was to (1) determine aliphatic hydrocarbon sources by using n-alkane distributions, (2) investigate variations of material inputs with time by examining hydrocarbon profiles in sediments, and (3) investigate hydrocarbon diagenesis by comparing downcore variations of n-alkane homologs and isoprenoid hydrocarbons. Results from four cores taken within areas of fine-particle sedimentation in the southern basin are discussed.

SAMPLING AND ANALYSIS

Sediments were collected in September 1980 at four sites (Table 1) located in the areas of fine-grained deposition in the southern basin of Lake Michigan (Fig. 1). The composition of sediments in these areas has been described by Cahill (1981) as silty clay. Undisturbed sediment cores (250 cm² x 20 cm) were collected with a box coring device. The surfaces of all four cores were light brown and very flocculent, while deeper sections were grayish black and consolidated. Immediately after collection, the box cores were sectioned at 1- or 2-cm intervals, and sections were transferred to solvent-rinsed glass jars and frozen.

Details of the analytical methodology have been described elsewhere (Doskey 1982, Doskey and Andren 1986). Briefly, sediments were freeze dried with a Virtis (model 10-100) freeze drier. The freeze drier was modified to eliminate contamination from vacuum pump oil and pump exhaust by isolating the pump in a vented hood and replacing the rubber vacuum ports on the drier with plastic plugs. Dried samples were pulverized with a mortar and pestle and then Soxhlet extracted with methylene chloride for 36 hours. Concentrated extracts were eluted through silica gel to isolate the aliphatic hydrocarbon fraction by following procedures by Tan (1979) and Macleod *et al.* (1977) as modified by Doskey (1982). Analysis was performed on a Hewlett Packard 5840 gas chromatograph equipped with a 25 m x 0.2 mm SE-30 fused-silica capillary column (Scientific Glass Engineering, Austin, TX) and flame ionization detector. n-Alkanes, pristane, and phytane were quantified using authentic standards (Alltech Associates, Deerfield, IL). The UCM was quantified by measuring the unresolved area with a graphics tablet and by using the average response factor of the n-alkanes eluting above the UCM to convert the unresolved area to a UCM concentration. Total

carbon and inorganic carbon were measured in dried samples by using a Perkin-Elmer model 203B Elemental Analyzer. Organic carbon was calculated by difference.

Precision for the individual n-alkanes was $\pm 8\%$. Procedural recoveries increased with carbon chain length and reached a maximum at n-C₂₀. The mean recovery for n-C₁₈ to n-C₃₂ was 78.8%, while the mean for n-C₁₁ to n-C₁₇ was 62.6%. To check possible evaporative losses of n-alkanes during freeze drying, our technique, which included extraction of freeze dried sediment with methylene chloride, was compared to a method in which wet sediment was extracted with methanol. The results of the two techniques were not significantly different, indicating that evaporative losses of n-alkanes during freeze drying are insignificant. Precision for the organic carbon analysis was $\pm 1.5\%$.

RESULTS

Spatial variations of organic carbon concentrations in surficial sediments and changes in organic carbon levels in vertical profiles in sediments were evident at all four coring locations (Fig. 2a). Organic carbon concentrations in surficial sediments were highest at coring locations 6A and 18A. To compensate for varying proportions of inorganic and organic material in texturally dissimilar samples, the aliphatic hydrocarbon concentrations reported here are normalized to organic carbon (Barrick *et al.* 1980).

Sources and Surficial Sediment Concentrations

Several characteristics of aliphatic hydrocarbon distributions can be used to derive information on their origins. The carbon preference index (CPI), which is simply defined as the ratio of the mole fractions of the odd- to even-numbered homologs in a hydrocarbon distribution (Bray and Evans 1961), is one of these characteristics. The CPI₁₄₋₂₀ in all sediment core sections varied from 1.3-1.7. The prominence of n-C₁₅, n-C₁₇, and n-C₁₉ in Lake Michigan sediments resulted in a CPI₁₄₋₂₀ value greater than 1, which is typical of sediment hydrocarbons having a planktonic origin. These n-alkanes are prevalent in plankton, and the predominant homolog is species dependent (Clark and Blumer 1967, Blumer *et al.* 1971, Youngblood *et al.* 1971, Youngblood and Blumer 1973). Concentrations of n-C₁₇ in surficial sediments were greatest at coring locations 12A and 24A-A and approximately twice the levels at locations 6A and 18A (Fig.4).

The CPI₂₀₋₃₂ of n-alkanes in all sediment core sections was 2.0-3.6. The slight predominance of odd carbon numbers over the range C₂₀-C₃₂ indicates that a fraction of the hydrocarbons have a terrestrial origin. The waxy coatings of terrestrial plants contain n-alkanes in the range C₂₅-C₃₃ (Eglinton *et al.* 1962, Eglinton and Hamilton 1963, Douglas and Eglinton 1966, Caldicott and Eglinton 1973) with a CPI of 4-10 (Brassell *et al.* 1978). Our samples exhibit CPIs lower than those of purely terrestrial plant waxes, suggesting that some contributions are from other sources. Concentrations of n-C₂₉ in surficial sediments were fairly uniform at all coring locations (Fig. 4).

The most prominent feature of the aliphatic hydrocarbon distribution in surficial sediments at all coring locations was a UCM. Concentrations of the

UCM were greatest at locations 12A and 24A-A (Fig. 2b). UCM concentrations were similar to the total n-alkane concentrations at 6A, 18A, and 24A-A and exceeded the level at 12A (Fig. 2c). The UCM has been observed in sediments from diverse environments and has been used as an indicator of petroleum pollution (Wakeham and Carpenter 1976, Wakeham and Farrington 1980). The CPI of n-alkanes in petroleum is approximately one (Blumer and Sass 1972). Consequently, the CPI of a hydrocarbon assemblage having a planktonic and terrestrial plant wax origin should be decreased by additions of petroleum residues. Because the CPIs of the n-alkanes in Lake Michigan sediments are >1 , petroleum residues cannot be the sole source of aliphatic hydrocarbons in southern basin sediments.

The n-C₂₉/n-C₁₇ ratio has been used to indicate relative strengths of allochthonous and autochthonous inputs of n-alkanes to aquatic systems (Meyers *et al.* 1980b). Because n-C₁₇ is prevalent in plankton, it can be used as an indicator of autochthonous inputs of organic matter, while n-C₂₉ is abundant in terrestrial plant waxes and therefore can be used to represent allochthonous inputs. Spatial variations of the ratio are apparent (Fig. 2d). Coring locations 6A and 18A exhibit a greater predominance of allochthonous material.

A more quantitative way of apportioning sources of aliphatic hydrocarbons in sediments is to separate the n-alkanes into CPI=1 and CPI=10 members via a mass balance (Schneider *et al.* 1983, Doskey and Andren 1986). We define the total aliphatic hydrocarbon concentration as the sum of the concentrations of CPI=1 n-alkanes, CPI=10 n-alkanes, and the UCM. These groups represent contributions from plankton and petroleum, terrestrial plants, and petroleum, respectively. Aliphatic hydrocarbons in surficial sediments from coring locations

12A and 24A-A exhibit the highest contribution by the UCM and the lowest contribution by the CPI=10 n-alkanes (Fig. 3). Contributions by the CPI=10 and CPI=1 n-alkanes at these locations are nearly equal. Terrestrial n-alkanes represent a greater proportion of the aliphatic hydrocarbons in sediments at stations 6A and 18A. This result agrees nicely with trends indicated by the n-C₂₉/n-C₁₇ ratios.

Vertical Profiles

The UCM concentrations in southern basin sediments approached background levels (10 µg/g OC) at different depths in each core (Fig. 2b). Because the UCM has been attributed to anthropogenic inputs, this feature of the UCM profiles may indicate that sedimentation rates at coring locations 12A and 24A-A are greater than those at 6A and 18A. The UCM profiles for cores 12A and 24A-A both contained subsurface maxima (Fig. 2b). Maxima in cores 6A and 18A could be obscured by wide sectioning intervals because sedimentation rates at these locations are lower than the other coring sites. Swackhamer (1985) determined a linear sedimentation rate and a mass sedimentation rate of 0.066 cm/yr and 0.016 g/cm²·yr, respectively, for a duplicate core of 18A. This result is in good agreement with the value of 0.012 g/cm²·yr reported by Robbins and Edgington (1975) for this location. Applying Swackhamer's data to UCM concentrations reported here indicates that the UCM first appeared about 100 years before 1980 at coring location 18A. For a mass sedimentation rate of 0.016 g/cm²·yr, the pre-1900 flux of the UCM was approximately 6 ng/cm²·yr, and the 1980 flux is about 96 ng/cm²·yr. The input of petroleum residues to the southern basin of Lake

Michigan has apparently increased by more than an order of magnitude since 1900.

All four cores exhibited a decrease of n-C₁₇ relative to pristane within the top few centimeters (Figs. 4a-4d). Profiles of n-C₂₉, an n-alkane attributed to terrestrial plant wax, are similar to that of n-C₁₇ in the the upper 3 cm of each core except 18A (Figs. 4a-4d). Subsurface maxima are present in three of the four cores. The n-C₂₉ maximum in core 24A-A coincides with the subsurface maximum exhibited by the UCM.

DISCUSSION

Several processes may be responsible for spatial variations in the aliphatic hydrocarbon composition of southern basin sediments. Thompson and Eglinton (1978) fractionated sediments by size and found that planktonic n-alkanes and the UCM were concentrated in the silt/clay fraction (<66 μm), while plant wax n-alkanes were concentrated in a coarse-particle fraction (>125 μm) containing terrestrial plant detritus. Organic carbon concentrations were highest and were similar in the coarse-particle and silt/clay fractions. It is unlikely that hydrodynamics is responsible for dissimilarities in hydrocarbon distributions at the four coring locations because they are all within active zones of sedimentation. However, the UCM data (Fig. 2b) indicate that mass sedimentation rates at locations 12A and 24A-A are more rapid than they are at locations 6A and 18A. Sediments in high-sedimentation zones receive greater inputs of inorganic material than those in low-sedimentation zones. This may explain why organic

carbon concentrations in surficial sediments at 6A and 18A were greater than those observed at 12A and 24A-A.

Microbial decomposition has probably altered the planktonic n-alkane distribution of surficial sediment. Several investigations have indicated that n-alkanes associated with plankton are more susceptible to decomposition than those associated with terrestrial plant wax (Meyers *et al.* 1980a, Prahl *et al.* 1980, Wakeham *et al.* 1980, Bates *et al.* 1984). Biodegradation of hydrocarbons in aerobic sediments is also more rapid than microbial decomposition of hydrocarbons in anaerobic sediments (Jobson *et al.* 1979). n-Alkane distributions in sediments having slow sedimentation rates or deep mixing zones would exhibit a lower planktonic n-alkane contribution because sediments within this layer spend a longer time in the aerated zone. This may explain why surficial sediments at 6A and 18A have lower concentrations of n-C₁₇ than at locations 12A and 24A-A. Planktonic n-alkane fluxes at 12A and 24A-A may be greater also because of the higher primary productivity of nearshore areas.

Terrestrial hydrocarbon concentrations in surficial sediments were fairly uniform (Figs. 4a-4d). However, contributions of terrestrial hydrocarbons were greatest in the low-sedimentation areas (Fig. 3). Biodegradation of the planktonic fraction apparently has enriched the aliphatic hydrocarbon distribution in plant wax n-alkanes at locations 6A and 18A.

Both the UCM concentrations and contributions were greatest at locations 12A and 24A-A and appear to be correlated with planktonic n-alkane concentrations. This correlation agrees with the data of Thompson and Eglinton (1978), who found that planktonic n-alkane and UCM concentrations were highest

in the silt/clay fraction. The UCM may enter Lake Michigan as an oily residue that partitions to organic-carbon-rich particles. Wade and Quinn (1979) speculated that the UCM associates with fine particles because of their large surface area.

Verticle profiles of hydrocarbons in sediments may also be affected by several processes. Subsurface maxima have been observed in profiles of energy-related substances. Goldberg *et al.* (1981) found a subsurface maximum in the profile for charcoal particles $> 38 \mu\text{m}$ in diameter in a core taken from a depositional region in the southern basin of Lake Michigan. Charcoals in this size range are products of coal combustion. The maximum occurred in sediments deposited in about 1955, the same period in which Hites *et al.* (1980) hypothesized that subsurface maxima in PAH profiles reflect decreases in inputs caused by a change in home heating fuels from coal to oil and natural gas. Helfrich and Armstrong (1986) observed subsurface maxima in PAH profiles in sediments from the southern basin of Lake Michigan. Like the PAHs, the UCM has been detected in unburned coal and vehicle exhaust (Tripp *et al.* 1981, Simoneit 1984). The UCM has also been found in aerosols and precipitation collected in the Midwest region (Doskey and Andren 1986, Meyers and Hites 1982). Consequently, subsurface maxima in UCM profiles may reflect decreases in material inputs.

Biological activity may also produce subsurface maxima in profiles. Oligochaetes in sediments selectively feed on fine particles containing high concentrations of organic matter (McCall and Fisher 1980). These organisms feed at depths of 2-10 cm in sediments and eject material at the sediment surface. Subsurface maxima in profiles of various substances have been shown to be

produced by this mechanism (Karickhoff and Morris 1985, Krezoski and Robbins 1985, Robbins 1986). Thompson and Eglinton (1978) found that the UCM was associated with organic-carbon-rich, fine particles. Consequently, UCM profiles in Lake Michigan sediments may have been altered by this mechanism. Thompson and Eglinton (1978) also found that planktonic n-alkanes were concentrated in the same size fraction. The dissimilarity between profiles of the planktonic n-alkanes and the UCM is probably caused by recalcitrance of the UCM to biodegradation.

Microbial decomposition of the planktonic n-alkanes is illustrated by the decrease of n-C₁₇ relative to pristane within the top few centimeters of each core. Isoprenoid hydrocarbons such as pristane and phytane are not as readily degraded as straight-chain hydrocarbons (Blumer and Sass 1972). Differences in n-C₁₇ and pristane concentrations in deeper sections of the cores become constant, indicating that n-C₁₇ is being preserved within the anoxic layers of the sediment. Anaerobic decomposition of hydrocarbons is much slower than aerobic decomposition (Jobson *et al.* 1979).

CONCLUSIONS

The prominence of n-C₁₅, n-C₁₇, and n-C₁₉; a slight odd-carbon-number predominance within the range C₂₀-C₃₂; and an unresolved complex mixture (UCM) all suggest that aliphatic hydrocarbons in southern basin sediments originate from planktonic, terrigenous, and petroleum residue sources. Sediments from coring locations 24A-A and 12A contained more petroleum residues and planktonic hydrocarbons and exhibited less terrigenous character

than sediments collected at locations 6A and 18A. Greater biodegradation of planktonic n-alkanes within the aerobic, mixed zone in locations having slow sedimentation rates is believed to be responsible for the low planktonic and high plant wax contributions at 6A and 18A. Large contributions of the UCM at locations 12A and 24A-A probably result from the association of the UCM and planktonic n-alkanes with particles of the same size or density.

Analysis of the UCM profile in a dated sediment core from the deepest area of the southern basin indicated that petroleum residue inputs have increased since 1900. The UCM flux has increased by an order of magnitude, from approximately 6 ng/cm²·yr before 1900 to about 96 ng/cm²·yr in 1980. The UCM profiles at two of the coring locations exhibited subsurface maxima that may be the result of reduced inputs of combustion products or feeding by oligochaetes. Unlike UCM profiles, profiles of terrestrial and planktonic n-alkanes exhibited surface maxima. Downcore decreases of n-C₁₇ relative to pristane suggest that n-C₁₇ is degraded within the aerobic, mixed zone of the sediments.

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Table 1. Lake Michigan sampling stations.

Station	Coordinates		Water Depth (m)
	Longitude	Latitude	
6 A	86° 39'00' W	42° 00'00" N	27
12 A	86° 35'00" W	42° 23'00" N	62
18 A	87° 00'00" W	42° 44'00" N	161
24 A-A	86° 24'40" W	43° 03'00" N	80

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Fig. 1.

Fig. 2.

Fig. 3.

Fig. 4.

a.

b.

c.

d.

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