

FATTY ACID AND HYDROCARBON CONTENT OF SETTLING SEDIMENTS IN LAKE MICHIGAN

Philip A. Meyers, Sally Jo Edwards, and Brian Eadie¹
*Department of Atmospheric and Oceanic Science
The University of Michigan
Ann Arbor, Michigan 48109*

ABSTRACT. *Fatty acid and aliphatic hydrocarbon contents have been examined in sediment collected in traps suspended at three depths at a location in Lake Michigan. Fatty acid distributions are similar at all depths and suggest an autochthonous origin of these materials. Concentrations of acids decrease with greater depths of traps and indicate a combination of active microbial reworking and of dilution by resuspended sedimentary materials. Hydrocarbons in the metalimnion trap contain mostly algal and bacterial components, whereas near-bottom hydrocarbons contain a large land plant contribution, presumably from resuspension of bottom sediments. Comparison of trap contents with fatty acid and hydrocarbons obtained from faunal debris and with published diatom compositions indicates that a mixture of such sources is combined in the organic matter settling in Lake Michigan. Estimated fluxes to the bottom of this part of the lake are 6.5 g/m²/yr for organic carbon, 1.8 g/m²/yr for fatty acids, and 27 mg/m²/yr for aliphatic hydrocarbons.*

INTRODUCTION

Settling of particles within the water column is a process important to the accumulation of organic matter in sediments. Interception and collection of settling particles with sediment traps is a means of obtaining information about materials reaching the sediment surface. Soutar *et al.* (1977) showed that the use of sediment traps is an effective way to monitor the chemical and biological inputs to coastal marine sediments. In a related study, Crisp *et al.* (1979) characterized hydrocarbon contents of sediment traps deployed in four coastal California basins. Indications of inputs from fresh and weathered petroleum, marine aquatic, and terrigenous sources were identified, with each basin receiving different proportions from these sources. Sediment traps situated at multiple depths in a sub-Antarctic bay were used by Platt (1979) to estimate the annual flux of organic carbon to underlying sediments and to quantify the amount of sediment resuspension. Up to 80 percent of sediment trapped within 5 meters of the bottom

was resuspended bottom material, and the organic matter associated with this material may be made more available to benthic organisms by this process of physical recycling.

Prahl and Carpenter (1979) determined seasonal and annual fluxes of organic carbon, aliphatic hydrocarbons, and polycyclic aromatic hydrocarbons in sediment trap materials collected in Dabob Bay, Washington. Organic carbon fluxes correlate with rates of primary production, but the hydrocarbon fluxes do not, leading to their conclusion that land runoff and atmospheric deposition are major sources of much of these hydrocarbons. Furthermore, zooplankton fecal pellets evidently have an important role in sedimentation of organic matter in coastal locations.

As part of a broad investigation of sedimentation processes in the Great Lakes, we have determined the amounts and types of fatty acids and saturated hydrocarbons collected by sediment traps suspended at three depths in Lake Michigan. These data provide indicators of sources and fluxes of organic matter into the bottom sediments of this lake and of processes operative in the water column which affect organic materials.

¹National Oceanic and Atmospheric Administration, Great Lakes Environmental Research Laboratory, 2300 Washtenaw Avenue, Ann Arbor, Michigan 48104.

SAMPLING AND ANALYSIS

Sediment traps consisting of 50 cm × 10 cm Plexiglas cylinders connected to 500-mL LPE bottles were deployed from June 6 to September 15 at station 78-3 of Chambers and Eadie (1980) during 1978. This location is in 83 m of water at the base of the coastal slope off the mouth of the Grand River, southeastern Lake Michigan. Samples were obtained from water depths of 35 m, 73 m, and 82 m. The metalimnion/hypolimnion boundary during the sampling period was approximately 35 m. Mercuric chloride was added to each trap at about 100 ppm to prevent decomposition of organic materials during the collection period. Details of the deployment and efficiencies of the traps are given in Chambers and Eadie (1980).

Organic carbon content of trap material and surficial sediment was determined by placing a portion in an ampule and using the oxidative procedure of Menzel and Vaccaro (1964) to generate CO₂. The amount so formed was measured with an Oceanography International Carbon Analyzer. TOC content of the three trap samples is very similar to the 30.0 mg organic C/g present in surficial sediment at this location and considerably less than that of Lake Michigan plankton (Meyers, unpublished), indicating that the bulk of sediment trap material is indeed nonliving particles. The respective values at 35 m, 73 m, and 82 m are 35.4, 23.8, and 25.0 mg organic C/g dry sediment.

Sediment trap material was freeze-dried prior to extraction. Faunal debris was separated with tweezers from sediment material and treated as discrete samples. Alkaline hydrolysis of each sample was done in 50-mL heavy-wall centrifuge tubes having Teflon-lined screwcaps. A mixture of 4 mL 0.5 N KOH in 95% methanol and 10 mL benzene was added to each tube, and the sealed tubes were heated at 100° for 30 minutes. After the tubes had cooled, 10 mL methanolic BF₃ (Supelco, Inc.) was added, and freed fatty acids converted to methyl esters by heating the sealed tubes at 100° for 5 minutes. Lipid compounds were extracted with five 10-mL volumes of petroleum ether after adding 15 mL H₂O to the contents of the tube. Hydrocarbon and fatty acid methyl ester fractions were isolated by thin-layer chromatography on silica gel. Blanks were done using the entire extraction and analysis scheme, and the results have been corrected for the small amount of contamination found.

According to studies of Meyers and Quinn (1971, 1973), the single-tube extraction scheme gives recoveries of over 90% for n-alkanoic acids and n-alkane hydrocarbons. In addition, because an aqueous/organic partitioning of fatty acid salts from nonsaponifiable materials is not involved, possible selective losses of long-chain alkanolic acids is avoided.

Gas-liquid chromatography was used to identify and to quantify the components of these fractions. For the sediment trap samples, analyses were done on 3 m × 2.1 mm ID stainless steel columns packed with 3% SP2100 with 100–200 mesh Supelcoport (Supelco, Inc.). These columns were operated dual differentially from 150° to 325° C at 4°/min. The zooplankton debris samples were analyzed using a 10 m SP2100 glass capillary column operated from 150° to 275° at 4°/min. Internal injection standards of n-tetradecane, n-hextriacontane, or n-heptadecanoic acid were added to samples for quantification. A Hewlett-Packard 5831 Recording Gas Chromatograph was used for all analyses.

RESULTS AND DISCUSSIONS

Concentrations of total fatty acids decreased with the depth of the sediment trap. In the 35-m sample, 9.8 mg acids were found per gram sediment. In the 73-m sample, 10 m off the bottom, the concentration was 5.3 mg/g and at 82 m it was 1.7 mg/g. After adjusting for the fraction of organic carbon contained in fatty acids, these concentrations represent 21 percent of the 35-m TOC, 17 percent of the 73-m TOC, and 5% of the near-bottom TOC. These concentrations and percentages are substantially greater than those found in Lake Huron surface sediments (Meyers and Takeuchi 1979).

Normalized distributions of the straight-chain acids in these samples are presented in Figure 1. These are dominated by C₁₆ acids characteristic of algae and bacteria and by large proportions of monounsaturated acids. Palmitoleic acid, the monounsaturated C₁₆ acid dominating the compositions in Figure 1, has been found to be the major fatty acid in a number of marine diatoms (Lewis 1969, DeMort *et al.* 1972, Boutry and Barbier 1974). The unsaturated fatty acid content of the three sediment trap samples indicates substantial proportions of recently biosynthesized acids. Sample 3-10 at 73-m depth contains proportionally more unsaturated acids than does sample 3-1

close to the sediment/water interface and suggests that more biological material is present in this trap.

None of the fatty acid distributions in Figure 1

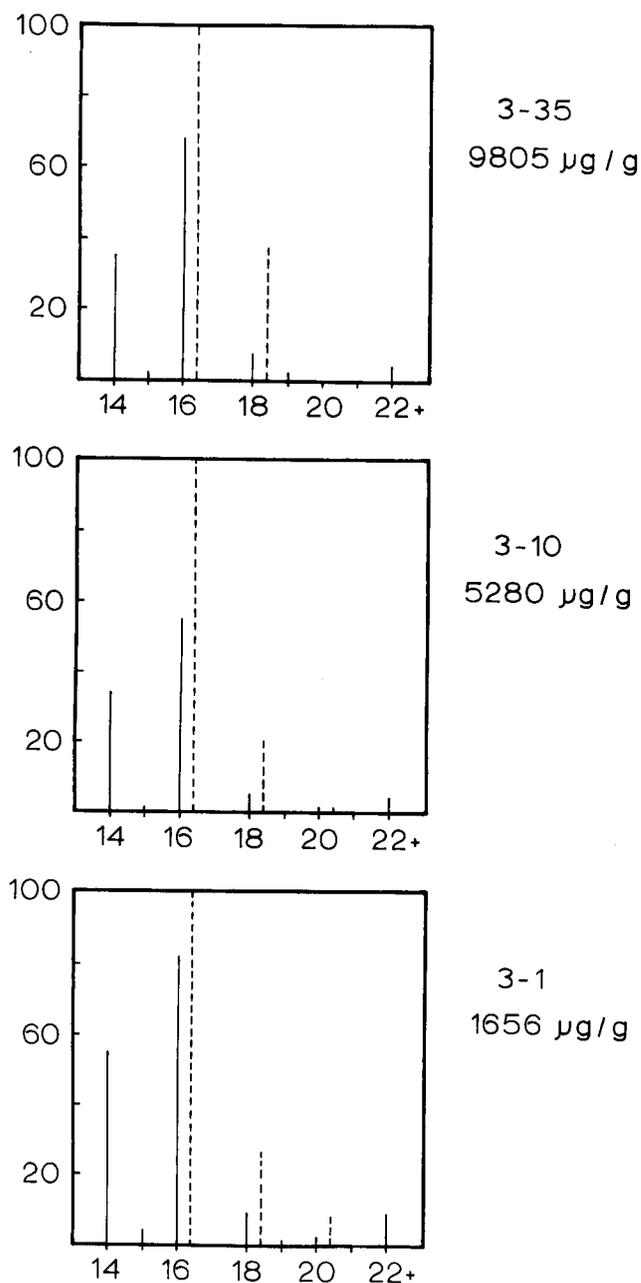


FIG. 1. Fatty acid compositions of settling sediment collected in Lake Michigan waters. Acids identified by carbon chain length and normalized to major component (100). Solid lines = alkanolic acids; dashed lines = alkenolic acids. All acids having 22 carbon atoms and more summed as 22+. Trap depths are 35 m (sample 3-35), 73 m (sample 3-10), and 82 m (sample 3-1).

contains a large percentage of longer chain acids, grouped as C_{22} and longer in the histograms. Acid distributions having maxima at C_{24} or C_{26} and strong even-to-odd predominance are typical of terrigenous higher plants (*cf.* Simoneit 1977). Instead, the distributions are dominated by C_{14} , C_{16} , and C_{18} straight-chain acids characteristic of aquatic plant origin (Cranwell 1974). As concluded by Meyers, Bourbonniere, and Takeuchi (1980a) for fatty acids in Lake Huron sediments, these sediment trap acids appear to originate from within the lake environment. Land-derived acids associated with sedimenting particles are evidently degraded by biological and biochemical processes before they can become incorporated in Great Lakes sediments.

Unlike the fatty acid distributions in the sediment trap samples which change little with depth, aliphatic hydrocarbon distributions are markedly different. In Figure 2, the 35-m distribution contains large contributions of shorter chain C_{17} to C_{19} n-alkanes considered typical of freshwater algal hydrocarbons (Giger and Schaffner 1977; Cranwell 1973; Giger, Schaffner, and Wakeham 1980) and lower amounts of C_{27} to C_{31} n-alkanes characteristic of terrigenous plant waxes (Douglas and Eglinton 1966, Cranwell 1973, Giger and Schaffner 1977). In contrast, the two deep samples are dominated instead by C_{27} , C_{29} , and C_{31} n-alkanes and contain little of the short chain, algal hydrocarbons. These hydrocarbon patterns indicate the origins of the materials from the three depths.

In all three distributions, n- C_{25} is an important constituent. This n-alkane has been found at high levels in lake sediments (Giger and Schaffner 1977, Meyers *et al.* 1980a) and in some dust particles (Simoneit 1977). In their comparison of hydrocarbons from a limited number of biota sources, Giger and Schaffner (1977) found the C_{25} n-alkane to be an important component of a sample of mixed freshwater zooplankton and of the leaves of an unidentified lakeshore reed, but to be virtually absent in the blue-green alga *Microcystis sp.* Hence, this hydrocarbon may indicate an aquatic yet non-algal input to the sediment trap compositions.

Phytane and pristane are found in the sediment trap hydrocarbons. These isoprenoid compounds are derived from the phytol side chain of chlorophyll *a* by biochemical and geochemical transformations. Blumer, Mullin, and Thomas (1963) proposed that pristane is formed in the digestive

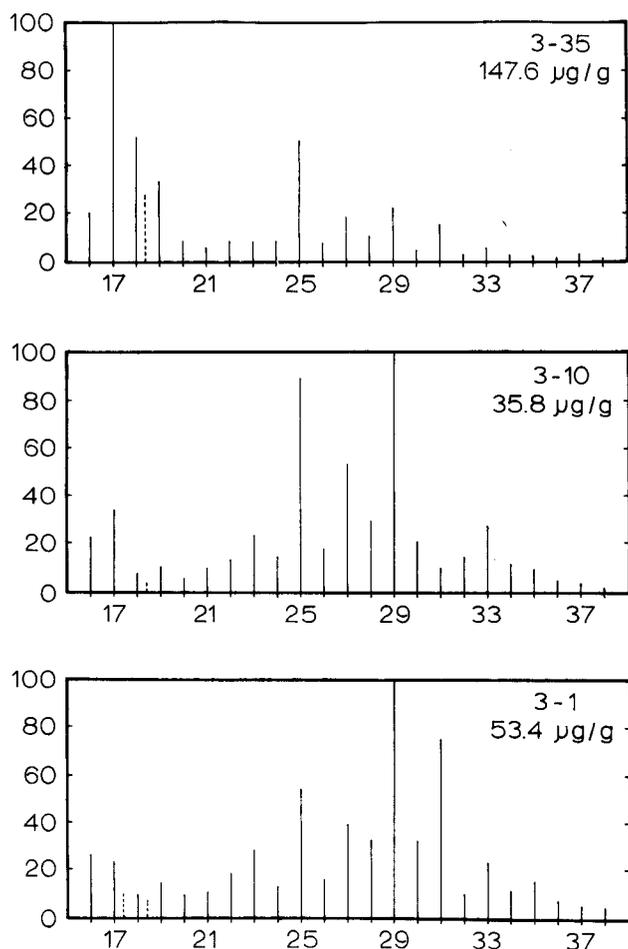


FIG. 2. Aliphatic hydrocarbon compositions of settling sediment collected in Lake Michigan waters. *n*-Alkanes identified by carbon chain length and normalized to major component (100). Pristane appears as dashed line after *n*-C₁₇; phytane as dashed line after *n*-C₁₈. Trap depths as in Figure 1.

tracts of zooplankton. Hence, its presence in the 82-m trap may indicate zooplankton fecal pellet contribution. Phytane is found in all three sediment traps and is most abundant in the 35-m sample. Because important biological sources of phytane are not known, Crisp *et al.* (1979) interpreted its presence in modern sediments to indicate petroleum hydrocarbon input.

The hydrocarbon contents of the three sediment trap samples suggest different sources of input. The 35-m sample contains mostly algal hydrocarbons with a small contribution of long-chain terrigenous components. This pattern agrees with the fatty acid content which is also characteristic of an algal source. The two deeper samples

are dominated by higher plant hydrocarbons in the C₂₅ to C₃₃ range and only 20% of shorter-chain algal hydrocarbons. These differ from the fatty acid source indicators to show that in Lake Michigan land-derived acids are destroyed and replaced by autochthonous components during transport to the lake and settling to the bottom, but that hydrocarbons resist similar degradation.

Similarities between the two deeper fatty acid and hydrocarbon compositions and those found in surficial Lake Huron sediments by Meyers and Takeuchi (1979) suggest these traps contain a large fraction of resuspended lake bottom material. Concentrations of total fatty acids and total aliphatic hydrocarbons are highest in the 35-m sample, reflecting a relatively large biological input. As this material settles deeper into the water column and nears the bottom, it becomes diluted by resuspended sediments which are low in organic content and high in mineral matter. However, even in the near-bottom sample 3-1, levels of acids and hydrocarbons are an order of magnitude higher than those in Lake Huron surficial sediments (Meyers and Takeuchi 1979). The combination of fine grain size and more recent biological input may be responsible for the higher geolipid content of the sediment trap materials.

In an effort to learn more about the contribution of biological materials to the trap contents, intact fauna and faunal fragments that had been removed from the freeze-dried sediment samples were analyzed separately. Dried weights of these faunal remains were 7.7 gm, 57.6 gm, and 52.7 mg from the traps at 35 m, 73 m, and 82 m, respectively. These represent less than 5% of the total trapped material.

The concentration of total fatty acids is highest in the 35-m trap debris and decreases progressively with depth. This pattern is similar to that found in the sediment samples, but the concentrations are an order of magnitude higher than those of the sediment and show that biogenic debris can be an important contribution to sediment organic matter.

Distributions of component acids are given in Figure 3. In all three, palmitic acid is the dominant component, and acids of chain lengths having 14, 16, and 18 carbon atoms comprise the total distribution. Marine zooplankton fatty acids are dominated by palmitic acid and, like the distributions in Figure 3, contain large amounts of 14, 16, and 18 carbon acids (Jeffries 1970, Ackman and Hooper 1970). However, compositions of

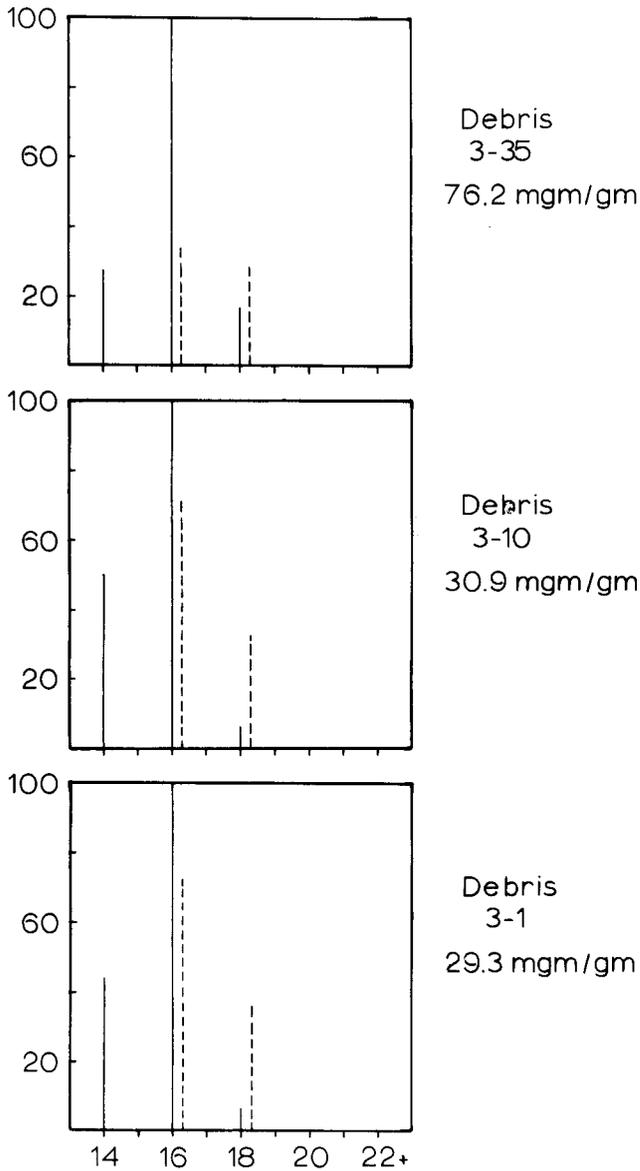


FIG. 3. Fatty acid compositions of faunal debris removed from sediment trap samples. See legend of Figure 1.

these marine species also are characterized by large percentages of polyunsaturated C_{20} and C_{22} acids. The absence of these acids in the sediment trap zooplankton debris is probably due to degradation of these labile acids quickly after the death of the animal, rather than biochemical differences between the related marine and freshwater organisms.

The concentrations and distributions of aliphatic hydrocarbons are given in Figure 4 and differ for the three samples. It is possible that different

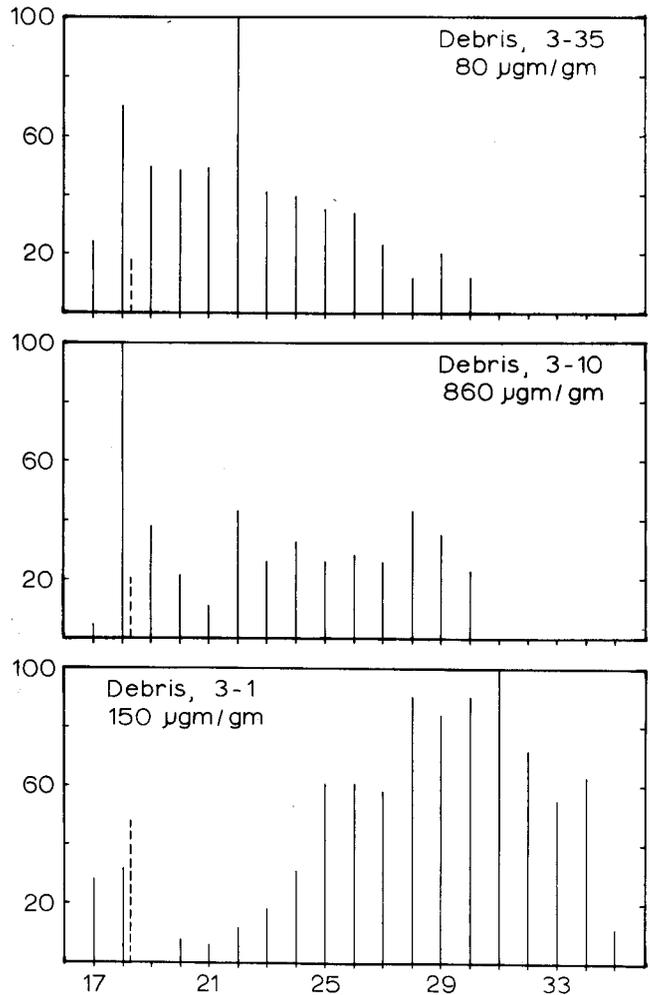


FIG. 4. Aliphatic hydrocarbon compositions of faunal debris removed from sediment trap samples. See legend of Figure 2.

types of planktonic fauna contribute to the debris in the three traps or that benthic faunal remains are found in the near-bottom trap. Hence, these hydrocarbon differences may be primarily source-related. It is also possible they may be due to different amounts of hydrocarbon degradation, inasmuch as Giger, *et al.* (1980) report preferential loss of shorter-chain n-alkanes compared to longer-chain ones under anaerobic conditions in sediments. This effect, believed to be microbially mediated, may account for the 82-m distribution since this trap appears to contain a large proportion of resuspended, and hence older, sediment.

From the measured organic component concentrations and from sediment fluxes determined by Chambers and Eadie (1980), the fluxes of TOC,

total fatty acids and total aliphatic hydrocarbons can be estimated. These data are summarized in Table 1. Although concentrations of organic materials are lower near the bottom than in the 35-m trap, the fluxes to the sediment increase progressively toward the bottom because of increase in sediment accumulation rates. However, the near-bottom trap may contain over 90% and the 73-m trap a substantial amount of resuspended bottom sediments (Chambers and Eadie 1980).

TABLE 1. Concentrations of total organic carbon (TOC), total fatty acids (TFA), and total aliphatic hydrocarbons (THC) in trapped sediment samples and estimates of fluxes to bottom sediments. Fluxes at depths of 72 m and 82 m not corrected for resuspended bottom material.

Component	35 m	73 m	82 m
TOC, mgm/gm	35.4	23.8	25.0
TFA, mgm/gm	9.8	5.3	1.7
THC, μ gm/gm	148	36	53
Sediment flux, gm/m ² /dy*	0.5	1.5	14
TOC flux, mg/m ² /dy	17.7	35.3	350
TFA flux, mgm/m ² /dy	4.9	7.9	23.2
THC flux, μ gm/m ² /dy	74	54	742

* from Chambers and Eadie (1980)

As reported by Chambers and Eadie (1980), the 35-m trap collected material at the same rate as the ²¹⁰Pb sediment accumulation rates in southeastern Lake Michigan. Hence, the fluxes at 35 m are the more accurate representations of input to the bottom. On an annual basis, these are 6.5 g C/m²/yr, 1.8 g TFA/m²/yr, and 27 mg THC/m²/yr at this Lake Michigan site.

In summary, terrigenous and aquatic sources contribute organic matter to Lake Michigan sediments, and settling particles contain varying proportions from these two main categories at different depths. Suspended sediment particles collected in the metalimnion contain organic matter characterized by fatty acids and hydrocarbons predominantly from aquatic sources. Fatty acid distributions are similar to those of surficial Great Lakes sediments (Meyers and Takeuchi 1979) yet different from Lake Michigan surface water particulate matter (Meyers, Owen, and Mackin 1980b), indicating rapid changes in organic matter character in the biologically dyna-

mic epilimnion. While diatoms appear to be an important source of lipids to surface particulates, other algae are dominant in the metalimnion. Aquatic inputs of fatty acids evidently are similar in character within the metalimnion, hypolimnion, and profundal sediments of the Great Lakes and change only in a quantitative way.

Differences in the types of n-alkanes present in suspended matter trapped at different distances from the bottom reveal changes in organic matter sources. In the metalimnion, these hydrocarbons indicate an algal or bacterial origin. A small amount of these compounds may be derived from diatoms. In addition, a portion of the hydrocarbons could be from petroleum. Closer to the bottom, resuspended sediments dilute the organic content of the trapped sediments. These particles contain predominantly land-derived hydrocarbons transported downslope in association with fine-sized sediments. These near-bottom hydrocarbon distributions resemble those of Great Lakes surficial sediments (Meyers and Takeuchi 1979).

Fatty acid content of the suspended sediments reflects active microbial reworking of contributed organic matter. Hydrocarbon distributions seem to have been little altered by this activity, probably because the periods of time required for the changes observed in laboratory degradations of hydrocarbons (Cranwell 1979, Giger *et al.*, 1980) are not available during the settling times of these sediments.

ACKNOWLEDGMENTS

We thank A. Robertson, M. J. Barcelona, C. P. Rice, and R. Carpenter for their thoughtful and constructive comments on earlier versions of this paper. Portions of this study were supported by the Earth Sciences Division of the National Science Foundation (Grant No. EAR7822432). Acknowledgment is made to the donors of the Petroleum Research Fund administered by the American Chemical Society for partial support. Great Lakes Environmental Research Laboratory Contribution 231.

REFERENCES

- Ackman, R. G., and Hooper, S. N. 1970. Analysis of fatty acids from Newfoundland copepods and sea water with remarks on the occurrence of arachidic acid. *Lipids* 5:417-421.

- Boutry, J. L., and Barbier, M. 1974. La diatomee marine *Chaetoceros simplex calcitrans* Paulsen et son environnement, I. *Mar. Chem.* 2:217-227.
- Blumer, M., Mullin, M. M., and Thomas, D. W. 1963. Pristane in zooplankton. *Science* 140:974.
- Chambers, R. L., and Eadie, B. J. 1980. Nepheloid and suspended particulate matter in southeastern Lake Michigan. *Sedimentology* In press.
- Cranwell, P. A. 1973. Chain-length distribution of n-alkanes from lake sediments in relation to post-glacial environmental changes. *Freshwater Biology* 3:259-265.
- _____. 1974. Monocarboxylic acids in lake sediments: indicators, derived from terrestrial and aquatic biota, of paleoenvironmental trophic levels. *Chem. Geol.* 14:1-14.
- _____. 1979. Decomposition of aquatic biota and sediment formation: bound lipids in algal detritus and lake sediments. *Freshwater Biology* 9:305-313.
- Crisp, P. T., Brenner, S., Venkatesan, M. I., Ruth, E., and Kaplan, I. R. 1979. Organic chemical characterization of sediment-trap particulates from San Nicolas, Santa Barbara, Santa Monica and San Pedro Basins, California. *Geochim. Cosmochim. Acta* 43:1791-1801.
- DeMort, C. L., Lowry, R., Tinsley, I., and Phinney, H. K. 1972. The biochemical analysis of some estuarine phytoplankton species - I. Fatty acid composition. *J. Phycol.* 8:211-216.
- Douglas, A. G., and Eglinton, G. 1966. The distribution of alkanes, pp. 57-77. In T. Swain (ed.), *Comparative Phytochemistry*, Academic Press, London.
- Giger, W., and Schaffner, C. 1977. Aliphatic, olefinic, and aromatic hydrocarbons in recent sediments of a highly eutrophic lake, pp. 375-390. In R. Campos and J. Goni (eds.), *Advances in Organic Geochemistry 1975*, ENADIMSA, Madrid.
- _____, _____, and Wakeham, S. G. 1980. Aliphatic and olefinic hydrocarbons in recent sediments of Greifensee, Switzerland. *Geochim. Cosmochim. Acta* 44:119-129.
- Jeffries, H. P. 1970. Seasonal composition of temperate plankton communities: fatty acids. *Limnol. Oceanogr.* 15:419-426.
- Lewis, R. W. 1969. The fatty acid composition of Arctic marine phytoplankton and zooplankton with special reference to minor acids. *Limnol. Oceanogr.* 14:35-40.
- Menzel, D. W., and Vaccaro, R. F. 1964. The measurement of dissolved organic and particulate carbon in seawater. *Limnol. Oceanogr.* 9:138-142.
- Meyers, P. A., and Quinn, J. G. 1971. Fatty acid-clay mineral association in artificial and natural sea water solutions. *Geochim. Cosmochim. Acta* 35:628-632.
- _____, and _____. 1973. Association of hydrocarbons and mineral particles in saline solution. *Nature* 244:23-24.
- _____, and Takeuchi, N. 1979. Fatty acids and hydrocarbons in surficial sediments of Lake Huron. *Org. Geochem.* 1:127-138.
- _____, Bourbonniere, R. A., and Takeuchi, N. 1980a. Hydrocarbons and fatty acids in two cores of Lake Huron sediments. *Geochim. Cosmochim. Acta* 44:1215-1221.
- _____, Owen, R. M., and Mackin, J. E. 1980b. Organic matter and heavy metal concentrations in the particulate phase of Lake Michigan surface microlayers. In S. J. Eisenreich (ed.) *Atmospheric Input of Pollutants to Natural Waters*, Ann Arbor Science Publishers.
- Platt, H. M. 1979. Sedimentation and the distribution of organic matter in a sub-Antarctic marine bay. *Estuar. Coast. mar. Sci.* 9:51-63.
- Prahl, F. G., and Carpenter, R. 1979. The role of zooplankton fecal pellets in the sedimentation of polycyclic aromatic hydrocarbons in Dabob Bay, Washington. *Geochim. Cosmochim. Acta* 43:1959-1972.
- Simoneit, B. R. T. 1977. Organic matter in eolian dusts over the Atlantic Ocean. *Mar. Chem.* 5:433-464.
- Soutar, A., Kling, S. A., Crill, P. A., Duffrin, E., and Bruland, K. W. 1977. Monitoring the marine environment through sedimentation. *Nature* 266:136-139.