



LAKE MICHIGAN SURFACE FILMS: FATTY ACIDS AND ALIPHATIC HYDROCARBONS

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AND ALIPHATIC HYDROCARBONS

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ABSTRACT

Fatty acid and hydrocarbon contents have been measured in the particulate and dissolved phases of surface microlayer and subsurface water samples collected at 21 Lake Michigan sites. Microlayer concentrations are consistently higher than corresponding subsurface concentrations, and the surface enhancement of both fatty acids and hydrocarbons is greater than that of total organic matter. River-borne materials are important constituents of river mouth and nearshore lake environments as shown by concentration gradients which decrease with distance

from shore. These materials are removed from the microlayer and subsurface water

by settling particles and are partially replaced by lake-derived

Concentration ratios of surface-to-subsurface contents become great

open lake areas in response to physical factors favorable to microl

Petroleum hydrocarbons are present in some localities and are the r

runoff and shipping activities.

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INTRODUCTION

As indicated by Parker and Barsom (1970), MacIntyre (1974), Liss (1974), and Andren et al., (1975), organic surface microlayers are present on virtually all natural bodies of water at submillimeter thicknesses. The significance of these surface films to aquatic ecosystems, geochemical cycles, and atmosphere/hydrosphere exchanges is of wide-spread interest, yet relatively little is known about processes active in their formation, maintenance, and dispersal. Attempts to learn more about these processes are complicated by a number of analytical and sampling problems. For example, although surface films contain enhanced concentrations of analyzable substances relative to subsurface waters, the natural amounts are often at or near detection limit levels. Hence, the analytical uncertainties of these measurements can be relatively great. Furthermore, most sampling methods cannot avoid diluting microlayer material with subsurface bulk water.

Despite these limitations, there is a growing body of information about the organic constituents of surface microlayers. Most of this information describes lipid materials long considered to be important in organic film formation because of their hydrophobic nature (Garrett, 1967). Fatty acids and hydrocarbons were found to be at total concentrations of 1.4 to 3.6 times higher in a pronounced seaslick in Narragansett Bay, Rhode Island, than in water 20 cm below the surface (Duce et al., 1972). In Swedish coastal waters, Larsson et al., (1974) found that total fatty acid compositions of surface microlayers consistently differed from subsurface compositions, and that the dominant lipid constituents were triglycerides, free acids and wax esters. Particulate phase concentrations of fatty acids and hydrocarbons have been reported to be both larger and smaller than corresponding dissolved phase concentrations (Daumas et al., 1976; Marty and Saliot, 1976; Kattner and Brockman, 1978). Evidently, their relationship is highly influenced by local biological and physical factors.

The concentrations of total hydrocarbons in surface microlayer samples from 17 Sargasso Sea locations averaged 2.1 times those of subsurface water concentrations, yet the range of these surface/subsurface ratios was from 0.2 to 26.4 and showed little geographical or temporal consistency (Wade and Quinn, 1975). Evidence of weathered petroleum was found in these mid-ocean hydrocarbon distributions. In a comparison of surface films from two coastal Mediterranean sites, Daumas et al., (1976) also found indications of petroleum hydrocarbons. These were superimposed upon biogenic hydrocarbons in a polluted estuary, but only the biological components were present in an uncontaminated embayment. These studies show that identification of individual lipid components of microlayers can give indications of organic matter origins and hence provide information about surface film formation.

Additional information can be obtained through comparison of surface microlayers from different but closely related locations. Meyers (1976) reports an increase in the surface/subsurface ratio of dissolved fatty acids which accompanies increasing water depth at a coastal marine location. Similar results have been found in Lake Michigan waters for particulate acids (Meyers et al., 1980). It would appear that shallow-water turbulence works against surface film formation by mixing potential film components into subsurface water. Such mixing may explain the absence of an enhanced fatty acid concentration in microlayers from shallow coral reef waters (Meyers, 1976, 1980).

As a contribution towards furthering our understanding of microlayers, we have studied chemical properties of surface films and underlying waters from different physical environments in Lake Michigan. This report describes the characterization of fatty acids and hydrocarbons in samples from the south-eastern section of this lake. Other reports provide information about organic carbon and trace metal contents (Owen and Meyers, 1978; Meyers et al., 1980; Mackin et al., 1980) and about physical and chemical processes affecting

microlayers (Owen et al., 1979; Mackin et al., 1979),

MATERIALS AND METHODS

Sampling

A sampling scheme was designed to identify zonal differences which might indicate sources of microlayer components and suggest processes involved in the formation, maintenance, and dispersal of surface films. Twenty-one sites were chosen to reflect typical river-mouth (point source), nearshore (8 to 10 km from shore and beyond obvious river plume influences) and open lake environments in southeastern Lake Michigan.

At all of these locations, water samples representing an average microlayer thickness of 125 μm were collected with a plate-sampler (Harvey and Burzell, 1972) during July 1977. The sampler, consisting of a rectangular plexiglass sheet (50 x 46 x 0.25 cm) attached to a nylon line, was lowered in a vertical position through the air/water interface. When withdrawn from the water, the plate carried with it a thin film of surface microlayer material held onto its sides by capillary action. This material was drained into a glass bottle, and the procedure was repeated until approximately 2 liters of surface film had been collected at each station. Details of estimating collection efficiencies and calculating surface film thickness are described by Owen and Meyers (1978).

In conjunction with the microlayer sampling, water samples were obtained from a subsurface depth of 1 meter at each location. A 10-liter glass carboy was lowered to the sampling depth attached to a wooden pole before being unstoppered, thus avoiding contamination from surface film material. At two nearshore stations, triplicate samples were collected at the 1 meter depth to measure natural variability of water contents, and additional samples were obtained at depths of 20 centimeters and 5 meters to compare organic matter from three different depths in the water column. The glass carboy procedure was

used for the 20 centimeter sample, and a Niskin sampler for the 5 meter one,

Sampling stations near the mouth of the St. Joseph River are shown in Owen et al., (1979) and at all Lake Michigan locations in Owen and Meyers (1978), complete descriptions of the positions, water depths, and wave heights present during sampling of all the stations are listed in Table 1. This tabulation also includes the classification of each location as river plume, nearshore or open lake and the calculated surface film thickness that was sampled.

Analysis

Surface microlayer and subsurface water samples were divided for analysis of organic materials and of heavy metals. Concentrations of total and dissolved organic carbon are reported in Owen and Meyers (1978). Results of analyses of copper, iron, manganese, nickel, and zinc in these samples are given in Owen and Meyers (1978), Owen et al. (1979), and Meyers et al. (1980).

The portion of each sample for organic matter analysis was first passed through a preignited Reeve Angel 934 AH glass fiber filter to separate particulate and dissolved phases. This was usually completed within 30 minutes of sample collection. Filters were frozen in individual aluminum foil packets and maintained at -20°C until subsequent treatment.

Particulate phase fatty acids and hydrocarbons were released through saponification of the entire filter in a 100 ml flask by refluxing for 1 hour in a mixture of 25 ml benzene and 25 ml 0.5N KOH in methanol/water, 95/1. The cooled flask contents were transferred to a separatory funnel, combined with 25 ml organic-free water, and mixed well. The resultant benzene layer was removed, and the alkaline aqueous layer extracted with two 25 ml volumes of petroleum ether. The organic extracts were combined, washed once with 25 ml organic-free water to remove traces of KOH, and concentrated for hydrocarbon analysis.

TABLE 1. Description of surface film sampling locations in Lake Michigan, July, 1977.

Station Location and Number	Lat. (N)	Position Long. (W)	Date	Classification	Film Thickness (μm)	Water Depth (m)	Wave Height (m)
Grand Haven							
1	43°01'	86°15'	7-18-77	River Plume	125	11.3	0.5
2	43°00'	86°21'	7-18-77	Nearshore	131	56.4	0.6
3	43°05'	86°22'	7-18-77	Nearshore	122	50.9	0.8
4	43°06'	86°17'	7-18-77	Nearshore	131	4.6	0.9
5	43°03'	86°18'	7-18-77	Nearshore	132	29.3	1.1
6	43°04'	86°15'	7-19-77	River Plume	127	8.2	0.5
Transect							
7	43°00'	86°20'	7-19-77	Nearshore	137	52.1	0.3
8	42°50'	86°20'	7-19-77	Nearshore	138	52.4	0.3
9	42°40'	86°20'	7-19-77	Nearshore	119	48.8	0.6
10	42°30'	86°20'	7-19-77	Nearshore	119	34.8	0.6
11	42°20'	86°30'	7-19-77	Open Lake	126	45.1	0.3
11R	42°20'	86°30'	7-21-77	Open Lake	127	45.1	0.1
26	42°20'	86°50'	7-21-77	Open Lake	127	118.0	0.3
27	42°20'	86°40'	7-21-77	Open Lake	125	69.5	calm
St. Joseph							
1	42°07'	86°30'	7-20-77	River Plume	137	7.3	0.3
2	42°08'	86°32'	7-20-77	Nearshore	129	19.8	0.3
3	42°08'	86°35'	7-20-77	Nearshore	127	26.8	0.3
4	42°06'	86°34'	7-20-77	Nearshore	135	17.7	0.3
5	42°05'	86°31'	7-20-77	Nearshore	120	9.8	0.3
6	42°09'	86°28'	7-20-77	River Plume	122	9.1	0.3
7	42°10'	86°32'	7-20-77	Nearshore	129	22.6	0.3

The alkaline aqueous layer, containing fatty acids and other saponifiable materials, was acidified with 10 ml 3N HCl and extracted with three 25 ml volumes of petroleum ether. These were combined and concentrated, and the residue methylated with a known amount of n-heptadecanoic acid with boron trifluoride in methanol (Metcalf et al., 1966). The fatty acid methyl esters were then extracted from this reaction mixture with petroleum ether.

Dissolved phase fatty acids and hydrocarbons were extracted by acidifying the sample filtrates with 6N HCl and extracting with chloroform. For the microlayer samples, usually containing 700 to 850 ml, 10 ml of acid and three 40 ml volumes of chloroform were used. Subsurface water samples were generally between 3000 and 3800 ml; to these 40 ml acid were added prior to extraction with three 80 ml chloroform volumes. These extracts were concentrated, and the residues dissolved in the saponification mixture of 25 ml benzene and 25 ml methanolic KOH. This was then heated and carried through the extraction and preparation steps described for the particulate phase materials.

Fatty acid methyl esters and hydrocarbons from the respective particulate and dissolved phase of these samples were isolated from the other lipid materials by thin-layer chromatography. Glass plates coated with Merck Type G silica gel (250 μ m thick) were developed in a solution of petroleum ether/diethyl ether/acetic acid, 90/10/1, and visualized in an iodine chamber. The separate bands containing the methyl esters and the hydrocarbons were scraped off the plates, and the isolated lipid classes extracted from the silica gel scrapings with chloroform.

The types and amounts of fatty acids and of hydrocarbons present in the particulate and dissolved portions of each sample were determined by gas-liquid chromatography. A Hewlett-Packard 5710 Gas Chromatograph equipped with dual flame ionization detectors was used. Stainless steel 3m x 2.1mm 10 columns packed with 3% SP2100 on 100-120 mesh Supelcoport (Supelco, Inc., Bellefonte, PA)

were operated from 150 to 325°C at 4° per minute, Nitrogen carrier gas flow rates were adjusted daily to optimize resolution of the n-heptadecane/pristane and n-octadecane/phytane doublets and to reproduce retention times on an n-alkane mixture spanning n-tetradecane to n-hexatriacontane. Known amounts of n-tetradecane were added to each hydrocarbon sample prior to gas chromatography to enable quantification. Individual peak retention times were compared with those of authentic standards to give tentative compound identifications. Comparison of peak areas with that of the quantitative standard in each sample allowed the amounts of each component to be calculated.

RESULTS AND DISCUSSION

Fatty Acid Vertical Comparisons

Comparisons of the vertical changes in particulate fatty acids at two nearshore stations are given in Table 2. In both of these, the surface micro-layer samples contain higher total concentrations and different distributions than the underlying water samples, and the subsurface samples from different subsurface depths have virtually the same fatty acid content at each station.

At Grand Haven station 5, the three samples collected at 1m give a mean concentration of 12.2 ± 0.5 $\mu\text{gm}/\text{l}$. This is nearly identical to the mean of 12.2 ± 0.6 of all five subsurface samples at this station. The dominant fatty acid in these compositions is palmitic (16:0), and the other major acids in decreasing order of abundance are oleic (18:1), palmitoleic (16:1), myristic (14:0) and stearic (18:0). The strong similarity in both composition and concentration displayed by the five subsurface samples allows them to be considered replicates. Hence, the analytical and sampling variability at this station has a relative standard deviation of $\pm 4.9\%$ for the subsurface samples.

Particulate fatty acid concentrations are lower at St. Joseph station 2,

TABLE 2. Vertical comparison of weight percent compositions of major particulate fatty acids. Total concentrations of major acids plus unlisted minor acids given in micrograms per liter of water. Fatty acids represented by chain length: number of double bonds.

Station	Depth	12:0	14:0	16:0	16:1	18:0	18:1	Total
Grand Haven 5:								
	surface	--	17.0	38.0	10.0	16.6	17.5	55.2
	surface	14.8	11.3	27.5	5.8	27.5	11.3	67.6
	20 cm	1.8	16.6	36.1	17.6	4.6	21.7	12.9
	1 m	--	10.4	37.9	19.1	3.3	24.6	11.6
	1 m	1.4	15.5	35.9	20.6	4.0	21.3	12.6
	1 m	1.4	14.7	37.2	19.4	4.9	21.6	12.3
	5 m	--	14.7	40.1	19.3	5.5	18.6	11.5
St. Joseph 2:								
	surface	--	10.0	41.1	7.5	17.2	23.1	18.5
	20 cm	--	10.7	40.8	10.4	8.6	27.6	5.7
	1 m	--	10.3	40.4	9.9	8.2	28.6	5.9
	1 m	--	15.0	39.9	10.4	7.1	19.8	8.1
	1 m	--	15.5	39.9	11.8	5.8	21.9	6.8
	5 m	--	15.8	41.0	10.2	8.8	22.4	8.4

having a mean of 7.0 ± 1.2 $\mu\text{gm}/1$ for the five subsurface samples. These lower levels produced greater analytical uncertainties, and the relative standard deviation of $\pm 17.7\%$ of these samples reflects this. In addition to having lower concentrations, the fatty acids at this location have somewhat different compositions than at the Grand Haven station. In decreasing abundance, the major acids are palmitic, oleic, myristic, palmitoleic, and stearic. In general, relatively greater proportions of C_{18} acids are present than at the Grand Haven station.

Surface microlayer particulate acids are enriched by factors of 5.0 and 2.6, respectively, at the Grand Haven and St. Joseph stations. These are larger than the corresponding values of 1.6 and 1.5 reported by Owen and Meyers (1978) for particulate organic carbon. Evidently, a preferential surface enrichment of hydrophobic lipid material relative to bulk organic matter exists at these locations.

Dissolved fatty acid contents of microlayer and subsurface water samples from three depths at Grand Haven station 5 are compared in Table 3. As found for particulate acids, the five subsurface samples are similar to each other but different from the surface film samples in both amounts and relative proportions of acids. The mean concentration of the five subsurface samples is 9.3 ± 0.7 $\mu\text{gm}/1$, giving a relative standard deviation of $\pm 7.3\%$ for the entire sampling and analysis procedure.

The dissolved acid compositions are similar to those of the particulate acids at this station, containing in decreasing rank palmitic, oleic, palmitoleic, myristic and stearic acid. However, relative contributions are somewhat smaller for C_{16} acids and somewhat larger for C_{18} acids in the dissolved phase. As before, microlayer acids are not the same as those in the underlying water.

acids.
ograms
uble bonds.

	18:1	Total
	22.1	91.5
	22.5	82.0
	24.6	10.3
	25.7	8.9
	28.1	8.7
	24.5	9.8
	24.2	9.0

The surface enrichment of dissolved acids is 9.5 times the concentration of subsurface acids. This is nearly double the ratio found for particulate acids and over five times the dissolved organic carbon enrichment value reported by Owen and Meyers (1978) for this station. Various organic components of surface ^{microlayers exhibit different} patterns of surface/subsurface distribution, as previously described for heavy metal components (Owen et al., 1979; Elzerman et al., 1980; Meyers et al., 1980).

late and dissolved fatty acid contents shown in Figures 2 and 3 indicates the lack of chemical zonation. Similar observations have been made for total and dissolved organic matter in Lake Michigan waters (Owen and Meyers, 1978) and in other nearshore waters (Meyers et al., 1980). It is therefore possible for direct comparisons to be made between the enrichment ratios in this study which are based upon water contents from a subsurface depth of 1 meter and those of other investigators who may have used different subsurface sampling depths.

Station 6 within the visible plume of the Grand River are located south of the river mouth, and station 6, situated directly at the mouth of the river. At St. Joseph, the river plume samples are taken from the St. Joseph River and station 6, which was located 5 km north of the river mouth.

In Lake Michigan, river plumes commonly are found close to shore, and their movement relative to river mouths is controlled by the wind-generated longshore currents. These currents can completely reverse their direction in less than a day in response to changes in wind and wave patterns on the lake.

Positions of the river plume samples are listed in Table 4. In all of the subsurface samples, the major component is palmitic acid. In three of the four surface samples, the other acids in decreasing order are

previously described for heavy metal components (Owen et al., 1979; Mackinac et al., 1979; Mackinac et al., 1980).

The uniformity of particulate and dissolved organic matter in the subsurface samples in Table 4 beneath the microlayer. Similar observations have been made for total and dissolved organic matter in Lake Michigan waters (Owen and Meyers, 1978) and in other nearshore waters (Meyers et al., 1980). It is therefore possible for direct comparisons to be made between the enrichment ratios in this study which are based upon water contents from a subsurface depth of 1 meter and those of other investigators who may have used different subsurface sampling depths.

River Plume Fatty Acids

The Grand Haven samples were taken from station 1, located 5 km north of the river mouth, and station 6, which was located directly at the mouth of the river. At St. Joseph, the river plume samples are taken from the St. Joseph River and station 6, which was located 5 km north of the river mouth. In Lake Michigan, river plumes commonly are found close to shore, and their movement relative to river mouths is controlled by the wind-generated longshore currents. These currents can completely reverse their direction in less than a day in response to changes in wind and wave patterns on the lake.

Particulate fatty acid compositions are listed in Table 4. In all of the subsurface samples, the major component is palmitic acid. In three of the four surface samples, the other acids in decreasing order are

of major particulate fatty acids in river plume samples. Major acids plus unlisted minor acids given in micrograms per liter of water (once divided by subsurface concentration ratio (CR) calculated as surface concentration entrainment. Fatty acids represented by chain length:

Station	Depth	12:0	14:0	16:1	18:0	18:1	Total	CR _{PA}
Grand Haven	surface	11.3	13.6	10.8	13.0	19.4	97.5	4.9
	1 m		16.6	21.6	4.3	22.8	20.0	
	surface	10.0	15.1	13.4	11.4	16.0	76.7	2.3
	1 m	13.8	9.6	22.4	4.8	20.6	33.0	
St. Joseph	surface		17.3	38.6	22.4	4.8	33.0	
	1 m		17.3	40.0	15.7	5.4	21.6	11.4
	surface		8.3	40.4	6.5	15.0	23.5	50.4
	1 m		8.3	38.9	18.9	6.5	24.3	23.5

TABLE 4. Weight percent composition of total concentrations of major acids per liter of water (once divided by subsurface concentration ratio of double bonds)

oleic, palmitoleic, myristic, and stearic. This order is slightly modified in the St. Joseph station 1 sample by myristic acid having a larger relative contribution than that of palmitoleic acid. The three microlayer samples are similar in containing palmitic acid as the largest component, but differ in the relative amounts of lauric (12:0) myristic, palmitoleic, oleic, and stearic acids. Hence, more variability is found in the surface particulates than in the subsurface material.

River plume dissolved fatty acid contents at these stations are described in Table 5. These have even more variation in relative composition than do the particulate acids, and the two river areas are quite different from each other. As concluded by Owen and Meyers (1978) and Owen *et al.* (1979), river plume contents reflect local inputs of microlayer and subsurface water materials. They are a changing mixture of terrigenous, potamic, and lake material and can also contain resuspended bottom substances. The river plume appears to be a dynamic environment in which turbulent mixing, particulate settling, and bottom resuspension occur simultaneously and create complicated types of surface/subsurface and particulate/dissolved partitionings of water contents.

Nonetheless, several trends are evident in the fatty acid content of these river plume samples. First, the concentrations of total dissolved acids are higher at the river mouth stations (Grand Haven 6 and St. Joseph 1) than further downplume. A related observation is that the ratio of particulate acids to dissolved acids increases between the river mouth and downplume locations. A conversion of dissolved phase lipids to the particulate phase is suggested by these trends.

A second trend present in the data in Tables 4 and 5 is an increase in the concentration ratio (CR), or ratio of surface/subsurface concentrations, downplume from the river mouths. This increase is a factor of about two in all cases, indicating consistent enhancement of microlayer/subsurface partitioning

TABLE 5: Weight percent compositions of major dissolved fatty acids in river plume samples. Total concentration of major acids plus unlisted minor acids given in micrograms per liter of water. Concentration ratio (CR) calculated as surface concentration divided by subsurface concentration. Fatty acids represented by chain length: number of double bonds.

Station	Depth	12:0	14:0	16:0	16:1	18:0	18:1	Total	CR
Grand Haven									
1	surface	25.0	22.9	26.2	8.7	6.3	10.3	77.4	6.0
	1 m	3.3	15.1	32.7	20.6	6.6	19.9	12.9	
5	surface	14.4	19.1	28.0	7.6	10.8	19.5	96.7	3.8
	1 m	8.8	12.6	28.1	14.2	11.7	21.7	25.3	
St. Joseph									
1	surface	--	5.4	38.0	3.7	29.6	4.4	37.6	7.0
	1 m	--	4.7	20.9	23.7	21.6	24.6	5.4	
6	surface	--	2.2	16.4	7.4	19.5	5.0	18.2	15.2
	1 m	--	4.2	5.8	--	20.0	7.5	1.2	

of both particulate and dissolved acids with distance from the river mouth. This agrees with earlier suggestions that hydrodynamic factors are important in surface microlayer formation (Owen et al., 1979).

Nearshore Fatty Acids

Table 6 lists particulate acid compositions, concentrations, and concentration ratios in the microlayer and subsurface waters at the 13 nearshore stations. These locations, situated between 8 and 10 km from shore, include varying amounts of coastal and open lake characteristics. Hence, considerable variability in biological and chemical contents and in physical parameters is present in this zone. This is reflected in the ranges of film thickness, water depth, and wave height for the nearshore stations in Table 1; these are greater than for the river plume or open lake zones. The variation in particulate acid content presented in Table 6 is also considerable.

Concentrations of total acids, for example, vary between 18.5 and 103.8 $\mu\text{gm/l}$ in the microlayer samples, and between 5.2 and 27.8 $\mu\text{gm/l}$ in the subsurface water. CR values range from 2.4 to 10.0 and are not related to distance from shore or water depth in any obvious fashion. The dominant particulate phase acid is palmitic, and in most of the samples oleic acid is the second-most abundant component. The relative rankings of the other four major acids differ among the compositions at these thirteen locations. These variations indicate that the nearshore zone is a region of transition between lake zones dominated either by potamic influences or by pelagic influences.

Dissolved fatty acids in the nearshore samples also reflect the transitional nature of this zone. Total concentrations range from 2.8 to 86.7 $\mu\text{gm/l}$ in the surface film and from 2.3 to 11.6 $\mu\text{gm/l}$ in the subsurface water. Concentration ratios are between 1.3 and 12.3 for these samples. No relationship exists between CR values in the dissolved and particulate phases. Even more variability in percent contribution of component acids is present in the dissolved phase than

Table 6. Weight percent composition of major particulate fatty acids in nearshore samples. Total concentrations of major acids plus unlisted minor acids given in micrograms per liter of water. Concentration ratio (CR) calculated as surface concentration divided by subsurface concentration. Fatty acids represented by chain length: number of double bonds.

Station	Depth	12:0	14:0	16:0	16:1	18:0	18:1	Total	CR
Grand Haven									
2	surface	11.7	13.6	24.4	8.0	19.8	20.2	62.6	7.1
	1m	1.1	16.0	38.9	18.0	4.6	19.2	8.8	
3	surface	5.1	7.9	43.6	7.2	18.4	15.8	86.7	8.9
	1m	--	17.5	38.1	17.6	6.7	19.5	9.7	
4	surface	--	14.1	43.1	15.0	10.3	16.6	103.8	3.7
	1m	1.2	12.4	45.7	19.0	3.4	16.3	27.8	
5	surface	8.2*	13.9*	32.2*	7.7*	22.6*	14.1*	61.4*	5.0
	1m	1.0*	13.6*	36.9*	19.7*	4.1*	22.5*	12.2*	
Transect									
7	surface	17.8	16.0	30.1	5.7	12.3	17.1	51.3	5.8
	1m	--	15.7	37.4	18.2	4.5	23.3	8.9	
8	surface	14.8	16.0	33.8	8.8	12.3	13.0	42.2	2.4
	1m	--	11.3	32.6	24.4	3.1	28.5	17.9	
9	surface	--	17.7	36.1	11.3	13.3	19.3	83.0	10.0
	1m	1.2	18.3	39.1	15.9	6.0	17.7	8.3	
10	surface	15.4	19.2	33.4	6.9	12.2	9.1	70.4	7.5
	1m	--	20.3	36.3	15.3	6.2	20.6	8.9	
St Joseph									
2	surface	--	10.0	41.4	7.5	17.2	23.1	18.5	2.6
	1m	--	13.8*	39.9*	10.7*	7.0*	22.9*	7.0*	
3	surface	--	7.1	41.5	5.2	24.4	18.8	22.9	4.4
	1m	--	10.6	38.8	10.4	7.5	31.5	5.2	
4	surface	--	15.3	43.1	7.8	15.3	15.9	21.0	
5	surface	--	9.7	41.9	8.3	17.4	22.7	54.9	4.7
	1m	--	12.4	37.8	11.6	7.6	30.5	11.8	
7	surface	--	15.9	42.8	8.3	14.7	16.4	20.4	2.7
	1m	--	18.9	32.5	12.9	9.2	24.7	7.6	

*Mean of replicate values

Table 7. Weight percent composition of major dissolved fatty acids in nearshore samples. Total concentration of major acids plus unlisted acids given in micrograms per liter of water. Concentration ratio (CR) calculated as surface concentration divided by subsurface concentration. Fatty acids represented by chain length: number of double bonds.

Station	Depth	12:0	14:0	16:0	16:1	18:0	18:1	Total	CR
Grand Haven									
2	surface	18.1	19.0	24.9	10.5	7.5	18.0	58.7	6.4
	1m	1.1	14.2	39.5	14.8	9.4	21.1	8.1	
3	surface	18.7	20.4	23.3	11.4	5.4	19.8	67.2	5.8
	1m	7.7	10.4	31.5	10.0	7.5	15.9	11.6	
4	surface	16.1	14.6	29.2	13.9	7.4	17.2	50.3	7.6
	1m	4.2	14.5	30.9	15.1	9.0	24.4	6.6	
5	surface	22.5*	18.2*	20.5*	7.0*	8.4*	22.3*	86.7*	9.5
	1m	5.1*	15.5*	26.6*	15.8*	7.8*	26.0*	9.1*	
Transect									
7	surface	2.3	2.1	39.7	2.3	15.3	37.1	47.5	5.7
	1m	8.6	16.1	28.4	11.1	9.5	24.0	8.4	
8	surface	13.0	15.4	26.0	8.9	13.7	20.1	73.4	12.3
	1m	7.5	21.8	41.0	4.9	10.7	10.6	6.0	
9	surface	14.2	15.4	26.9	10.7	11.0	19.4	28.3	4.6
	1m	4.7	14.2	28.4	8.2	9.8	27.6	6.2	
10	surface	--	20.1	34.9	19.7	8.0	14.5	42.8	7.5
	1m	--	12.3	31.6	5.3	15.8	21.1	5.7	
St. Joseph									
2	1m	--	4.8*	25.3*	10.2*	15.1*	11.8*	2.8*	
3	surface	--	10.8	23.7	9.7	19.0		2.8	1.3
	1m	--	4.9	21.1	4.5	22.9	7.6	2.2	
4	surface	--	28.6	7.8	46.7	3.2	3.9	5.7	2.5
	1m	--	4.4	21.2	17.3	17.7	4.9	2.3	
5	surface	--	7.1	22.8	0.4	21.4	6.7	13.4	11.0
	1m	--	3.3	8.2	0.8	27.9	7.4	1.2	
7	surface	--	5.4	26.8	10.0	16.2	16.2	7.4	2.0
	1m	--	2.6	13.7	4.2	13.9	6.6	3.8	

*Mean of replicate values

in the particulate. The only consistent feature in Tables 6 and 7 is that all stations have CR values greater than one. Neither total organic matter (Owen and Meyers, 1978) nor heavy metals (Owen et al., 1979) are consistently enriched in the nearshore microlayer. Thus, selective surface film enrichment

Table 8. Weight percent composition of major particulate fatty acids in open lake samples. Total concentration of major acids plus unlisted minor acids given in micrograms per liter of water. Concentration ratio (CR) calculated as surface concentration divided by subsurface concentration. Fatty acids represented by chain length: number of double bonds.

Station	Depth	12:0	14:0	16:0	16:1	18:0	18:1	Total	CR
transect									
11	surface	10.7	16.6	32.8	6.3	18.3	10.0	58.2	6.6
	1m	2.4	17.2	35.4	11.5	12.0	20.1	8.9	
11R	surface	--	7.1	39.0	3.8	24.9	21.0	38.3	4.5
	1m	--	11.2	37.9	8.5	9.6	30.2	8.6	
26	surface	--	10.7	38.4	9.8	15.0	24.6	36.5	4.2
	1m	1.2	20.8	34.4	17.1	6.6	17.8	8.6	
27	surface	--	9.1	39.0	11.6	16.9	16.9	57.9	7.7
	1m	--	14.6	37.3	9.6	9.2	27.0	7.5	

Table 9. Weight percent compositions of major dissolved fatty acids in open lake samples. Total concentration of major acids plus unlisted minor acids given in micrograms per liter of water. Concentration ratio (CR) calculated as surface concentration divided by subsurface concentration. Fatty acids represented by chain length: number of double bonds.

Station	Depth	12:0	14:0	16:0	16:1	18:0	18:1	Total	CR
Transect									
11	surface	10.1	21.0	28.0	6.2	9.9	21.7	38.2	4.9
	1m	7.1	19.5	28.8	9.6	9.7	22.2	7.8	
11R	surface	8.4	13.9	29.7	10.4	8.1	28.3	40.2	7.6
	1m	7.7	16.8	31.3	8.3	8.7	23.6	5.3	
26	surface	6.5	13.6	30.2	10.8	7.1	29.3	35.6	8.8
	1m	6.9	23.9	41.4	2.0	12.3	5.7	4.1	
27	surface	9.9	15.3	23.3	17.8	4.8	27.3	47.8	8.3
	1m	4.0	14.2	29.5	8.3	9.5	31.4	5.8	

concentrations of total acids. Stations having high surface concentrations in one phase do not always have similarly high levels in the other. Local conditions evidently are important in influencing fatty acid contents of the open lake environment, although their variability is not as great as in the nearshore areas.

Concentration ratios are between 4 and 9 in the listings in Tables 8 and 9, showing marked surface film enrichment of both dissolved and particulate fatty acids. These are larger than corresponding CR values for dissolved and particulate organic carbon from these samples (Owen and Meyers, 1978), indicating selective surface enhancement of lipid materials.

Summary of Fatty Acid Contents

Average compositions of particulate and dissolved phase fatty acids contents of river plume, nearshore, and open lake samples are presented in Table 10. These data are derived from the information in Tables 4 through 9. It must be remembered that considerable variability often is found in these tabulations, and Table 10 tends to conceal these real differences within a particular lake zone. However, the smoothed data in this tabulation are useful in comparing microlayer and subsurface fatty acid contents of the three lake environments.

Several patterns in total acid concentrations emerge from the averaged data. First, particulate acids are consistently at higher levels than are dissolved acids. This is unlike findings from a variety of marine coastal locations (Daumas et al., 1976; Kattner and Brockman, 1978). Second, concentrations generally decrease with distance from river mouth locations, suggesting riverine input of fatty acids is important to microlayer and subsurface water content. These materials evidently are removed by sinking particles. Third, concentration ratios increase with distance from shore. Decreased turbulent mixing apparently allows hydrophobic lipid materials to accumulate at the water surface and become enhanced relative to subsurface concentrations. Combined

Table 10. Averaged particulate (top) and dissolved (bottom) fatty acid compositions of river plume, nearshore, and open lake samples. Fatty acids represented as chain length: number of double bonds. Concentrations given in micrograms per liter. Concentration ratio (CR) calculated as surface concentration divided by subsurface concentration.

Classification	Depth	12:0	14:0	16:0	16:1	18:0	18:1	Total	CR
River Plume (4)	PARTICULATE PHASE								
	surface	7.1	12.3	34.2	9.3	13.1	19.6	74.9	3.4
	1m	0.6	13.7	37.5	19.7	5.3	22.3	22.0	
Nearshore (13)	PARTICULATE PHASE								
	surface	5.6	13.6	38.6	8.3	16.2	17.1	53.8	4.8
	1m	0.3	15.0	37.8	16.1	5.8	23.1	11.2	
Open Lake (4)	PARTICULATE PHASE								
	surface	2.7	10.9	37.3	7.9	18.6	18.1	47.7	5.7
	1m	0.9	16.0	36.3	11.7	9.4	23.8	8.4	
River Plume (4)	DISSOLVED PHASE								
	surface	9.9	12.4	27.2	6.9	16.6	9.8	57.5	5.1
	1m	4.0	9.2	21.9	14.6	15.0	18.4	11.2	
Nearshore (13)	DISSOLVED PHASE								
	surface	8.1	14.8	25.5	12.6	11.4	16.3	40.4	7.0
	1m	6.4	10.7	26.7	9.4	13.6	16.1	5.8	
Open Lake (4)	DISSOLVED PHASE								
	surface	8.7	16.0	27.6	11.3	7.5	26.7	40.5	7.0
	1m	6.4	18.6	32.8	7.1	10.1	20.7	5.8	

with this is a general loss of subsurface particulate materials through sinking (Owen et al., 1979) which further enhances CR values.

In addition to these physical factors, differences in the particulate phase compositions of microlayer and subsurface waters in Table 10 suggest differing biological inputs. The surface compositions uniformly contain higher percentages of lauric (12:0), palmitic, and stearic acids and lower percentages of myristic (14:0), palmitoleic (16:0) and oleic acids (18:1). These differences cannot be explained solely on the basis of solubility differences in the individual acids. A more probable explanation is that the presence of living planktonic organisms is responsible for these contrasts.

Neuston communities present in marine surface films differ significantly from phytoplankton communities in subsurface waters (Hardy, 1973) and contain large amounts of bacteria and protozoans (Seburth et al., 1976). This is probably also true in Lake Michigan. The relatively high proportions of unsaturated C₁₆ and C₁₈ acids present in the subsurface particulate acids has also been found in marine waters (Daumas et al., 1976) and agrees with published fatty acid compositions of phytoplankton (Chuecas and Riley, 1968; DeMort et al., 1972). These subsurface samples may contain proportionately more living phytoplankton cells than do the microlayer samples in which bacteria and protists dominate. These communities, while different, are probable sources of both particulate

and dissolved fatty acids

and dissolved fatty acids

enishing some of the material removed by various

lake environments, hence r

layer/subsurface differences, there are differences

physical processes.

ulate phase fatty acid compositions of the three

In addition to the mi

the sources of these fatty acids are not identical.

which exist between the pa

inant acid in all of the compositions is palmitic

provinces which suggest th

ance in all but one case by oleic (18:1). However,

As shown in Table 10, the

(16:0), followed next in a

a progressive increase occurs in the proportion of stearic acid (18:0) in both the microlayer and subsurface compositions in going from the river plume to the nearshore, and to the open lake provinces. At the same time decreases are found in the relative amounts of palmitoleic acid (16:1).

The most likely explanation for these distributions and their differences is that separate combinations of biological sources contribute to and maintain the content of these lake provinces. Evidently, most of the particulate acids transported to Lake Michigan by rivers settles out close to river mouths. This material is partially replenished by organic substances originating from aquatic communities within the lake. Because environmental factors such as temperature, light levels, availability of nutrients, and water turbulence can affect the biological communities and thus their biochemical compositions, the amounts and types of organic materials contributed to microlayers and subsurface waters will vary from one area of the lake to another.

Dissolved fatty acid compositions, although originating from particulate phase materials, differ from them in their respective lake zones in Table 10. Because they are released from living and detrital biological particles by decomposition processes, it is probable that dissolved acids are altered from their source materials during their generation. Subsequently, they may be more susceptible to biochemical and photochemical attack than would be particulate phase acids.

Total Hydrocarbon Contents

Concentrations and concentration ratios of total particulate hydrocarbons from 18 Lake Michigan stations are listed in Table 11. Dissolved hydrocarbon data for St. Joseph stations are given by Owen and Meyers (1978). Although individual compounds could not be identified by the procedures used in the present study, most of the resolved chromatogram peaks had Kovats Indices between 2500 and 3300 (Kovats, 1965). This is the range in which n-alkanes of the freshwater

Mixture; +++ indicates greatest contribution; lack of symbols indicates

Surface and subsurface samples. Concentration
 Subsurface concentration. UCM-unresolved complex
 Subsurface absence of UCM.

Location Surface UCM Subsurface UCM CR_{HC}
 µgm/l µgm/l

River Plume

Grand Haven 1 16.2 ++ 1.8
 Grand Haven 6 21.7 +++ 18.4

Nearshore (LL)

Grand Haven 2 12.6 ++ 3.3
 Grand Haven 3 10.1 +++
 Grand Haven 4 49.2
 Grand Haven 5 16.3 1.9+1.0
 transect 7 46.5 2.5
 Stansect 8 34.5 3.0 ++
 Stansect 9 10.0 5.6
 Stansect 10 36.5 2.2
 S. Joseph 2 37.6 1.8+1.2
 S. Joseph 4 11.6 1.9
 S. Joseph 7 5.0 2.6 +

Open Lake

transect 11 22.7 + 1.4
 transect 11R 7.9 2.4
 transect 26 14.8 4.6
 transect 27 12.5 + 3.7

16.2
 3.3
 3.2
 3.4

TABLE 11.

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diatom Asterionella formosa are found (Meyers et al., in preparation).

Hence, diatoms may contribute an important fraction to the particulate phase hydrocarbons in Lake Michigan waters. This is similar to the conclusion of Marty and Saliot (1976) for marine samples. Microlayer and subsurface hydrocarbon contents were qualitatively similar, unlike alkane hydrocarbons in surface film and subsurface waters from a large number of coastal Gulf of Mexico locations (Saliot and Jassby, 1976).

Concentrations of particulate hydrocarbons range from 5.0 to 49.2 $\mu\text{gm/l}$ in the microlayer samples from 1.2 to 20.9 in the subsurface. These are in the ranges reported by Marty and Saliot (1976) and Daumas et al. (1976) for marine locations considered to be unpolluted and about three orders of magnitude less than particulate hydrocarbon levels in a polluted Mediterranean estuary (Daumas et al., 1976). Thus, none of these Lake Michigan stations appears to be grossly contaminated by petroleum hydrocarbons, although evidence for their presence exists.

A significant feature in the hydrocarbon content of some of the samples is an unresolved complex mixture (UCM) of hydrocarbons underlying the resolved individual peaks on the chromatograms. This mixture is not found in hydrocarbons from biological sources and is a characteristic of petroleum-derived hydrocarbons. Hydrocarbon patterns having a large UCM similar to those found in the Grand River samples have been reported in marine microlayers (Wade and Quinn, 1975; Daumas et al., 1976) and have been interpreted as being evidence of petroleum pollution.

In these Lake Michigan samples, the UCM dominates several river plume and nearshore locations and differs in the microlayer samples from the fluvial, nearshore and open lake environments. Furthermore, a concentration gradient exists in which the UCM contribution decreases with distance from the river mouth. These observations indicate that the UCM component of the particulate

hydrocarbons originates from land or riverine sources and is transported to the lake by river flow. Once in the lake, these particulate materials evidently sediment out fairly quickly, probably in association with mineral particles. It appears that the UCM component does not have a major aquatic or atmospheric source in Lake Michigan, except from ship activity. Evidence for a shipping source is implied by data from open lake station 27 in Table 11. Samples from this station, which is offshore of St. Joseph, Michigan, have surprisingly high UCM components whereas the nearshore St. Joseph stations are free of this feature. The most likely source is not the river, but from ship activities.

An interesting contrast exists between the nearshore Grand Haven and St. Joseph hydrocarbon contents in Table 11. Several of the Grand Haven stations show the presence of a large UCM. These locations were sampled during and after a period of heavy rain. In comparison, the St. Joseph stations are free of UCM contribution and were sampled after a rainless period of over 24 hours. Wakeham (1977) has concluded that most of the hydrocarbon input to Lake Washington is from urban stormwater runoff from roads and other paved surfaces. The contrast shown here may illustrate the major source of petroleum hydrocarbons to Lake Michigan is indeed river-borne land runoff.

SUMMARY AND CONCLUSIONS

1. Concentrations of fatty acids and hydrocarbons in the particulate and dissolved phases of microlayers and subsurface waters are highest in river plume environment and decrease progressively towards the open lake. These patterns indicate that potamic sources are important to the fatty acid and hydrocarbon contents of Lake Michigan waters.
2. An unresolved complex mixture is a significant feature of the particulate phase hydrocarbons in river plume samples and some nearshore and open lake samples. This mixture is diagnostic of a petroleum

hydrocarbon input to these locations. The major source of these materials appears to be from land runoff.

3. Removal of particulate and dissolved fatty acids from microlayers and subsurface waters evidently occurs soon after these materials are carried to the lake by rivers. Settling of mineral particles appears to be the primary removal mechanism. Hydrocarbon concentrations

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