Technical Report No. 60

PETROLEUM HYDROCARBONS AND HEAVY METALS IN GREAT LAKES SURFACE FILMS

by

Robert M. Owen
and
Philip A. Meyers

February 1978
MICHU-SG-78-202

PETROLEUM HYDROCARBONS AND HEAVY METALS

IN GREAT LAKES SURFACE FILMS

Robert M. Owen

and

Philip A. Meyers

Department of Atmospheric
and Oceanic Science

University of Michigan

TABLE OF CONTENTS

INTRODUCTION

Petroleum added to the aquatic environment is partitioned between the water surface and the underlying sediments, with little being found dissolved or suspended in the water column. In the case of gross contamination, an obvious oil slick exists on the water surface. More commonly, low levels of petroleum hydrocarbons are found as tar balls and/or as a surface film invisible to the eye but detectable by chemical or instrumental means. Because incorporation into sediments is effective in removing petroleum hydrocarbons from the aquatic environment (Meyers, 1976), study of surface films is the most effective approach to determine the source(s) of petroleum contamination, to assess the overall magnitude of the problem, and to anticipate the potential impact on water quality.

Most investigations of organic surface films have been conducted in marine environments, and comprehensive reviews of this research have been compiled by MacIntyre (1974) and Liss (1974). A limited amount of surface film research has been done on freshwater bodies, and this work has been reviewed by Andren et al. (1975). These reviews indicate that all surface films contain analyzable lipoidal materials such as fatty acids and hydrocarbons, and non-analyzable proteinaceous materials such as polypeptides and humic acids (MacIntyre, 1974). The latter group of materials is of particular interest because they provide abundant sites for complexing specific metal ions.

Surface films represent an enhanced concentration of natural and anthropogenic organic compounds at the air-water interface

relative to subsurface levels. Similarly, heavy metals are commonly found associated with organic surface films at higher levels than in underlying waters. In general, transition metals such as copper, iron and zinc are found to be preferentially enriched in surface films (Barker and Zeitlin, 1972), and most of this enrichment appears to occur in the particulate and dissolved organic phases of the surface layers (Piotrowicz et al., 1972). A summary of concentration ratios (surface concentration/subsurface concentration) and enrichment factors (E = surface concentration/subsurface concentration - 1.0) for various organic compounds and heavy metals in different environments is given in Table 1.

It should be emphasized that the concentration ratios and enrichment factors shown in Table 1 are based upon measured film thicknesses ranging from 100 to 300 microns. This represents the thinnest layer of surface water that existing sampling procedures can collect. However, there is general agreement among workers in this field that the true surface film is probably a molecular monolayer with an actual thickness of between 0.2 and 2.0 microns (Garrett, 1967). Thus, the measured concentration ratios and enrichment factors should be multiplied by 10^3 to 10^4, indicating a pronounced enhancement of both organic compounds and heavy metals in surface films.

BACKGROUND AND OBJECTIVES OF THIS STUDY

The Great Lakes region is an area of intensive energy usage. Large volumes of petroleum fuels are transported, stored, and transferred annually and, further, considerable

volumes of crude petroleum are obtained from the Michigan basin for local refining. The various operations involving petroleum and its derivatives result in accidental introduction of these materials to the environment at chronic rates. Because these materials are unlike natural biological compounds, ecological systems adjust to them poorly, and their effects are generally deleterious.

Petroleum spillage due to transfer on or off ships or by grounding and breakup of tankers results in a direct input of petroleum products into the waters of the Great Lakes. Other direct inputs result from recreational boating and general shipping operations. However, it is probable that the greater portion of petroleum products which enters the Great Lakes is from indirect sources. Storm sewer runoff, municipal sewage effluents, and industrial wastewaters commonly carry low levels of petroleum hydrocarbons which are resistant to conventional water treatment procedures. These land-based sources of used and spilled petroleum hydrocarbons produce surface films which are transported by rivers into the Great Lakes.

As more petroleum fuels are used in response to the growing demand for energy in the Great Lakes region, indirect inputs of petroleum contaminants will undoubtedly become larger. Also, it is probable that greater volumes of petroleum will be transported on the Great Lakes by tankers, thus increasing the amounts of direct input. Finally, if petroleum production in the Michigan basin is expanded into underlake extensions of known oilfields as is being presently considered,

another direct source of potential contamination will be added.

The purpose of this investigation is to determine present-day levels of petroleum hydrocarbons and toxic heavy metals in surface films of Great Lakes waters, and to explore ways to monitor and investigate future levels. This information, in turn, should contribute toward assessing the impact of petroleum usage, transport, and handling on the overall quality of the Great Lakes aquatic environment.

This report summarizes progress made and results obtained in the first five months of the first year of a proposed three-year study. The specific objectives of the first year of this study are as follows:

1. To determine the concentrations of hydrocarbons and heavy metals in typical Great Lakes environments;

2. To measure selective partitioning of heavy metals between surface films and subsurface waters and between the dissolved and particulate phases of both locations;

3. To identify the respective contributions of petroleum and biological hydrocarbons to Great Lakes surface films; and,

4. To initiate study of the dispersal patterns of these surface films.

SAMPLING AND ANALYSIS PROCEDURES

A. Sample Stations

Surface microlayer and subsurface samples were collected from a total of 20 stations in southeastern Lake Michigan (insert map, Fig. 1) during the period between July 18 and July 21, 1977.

Sample collection was done aboard the R/V <u>Mysis</u> at stations established by ship's radar. Specific sample stations included the following: seven stations off the mouth of the Grand River (stations GH 1-7, Fig. 1); four stations along the coast between Grand Haven and St. Joseph, Michigan (stations TR 8-11, Fig. 1); two stations from the offshore area west of St. Joseph, Michigan (stations TR 26-27, Fig. 1); and seven stations off the mouth of the St. Joseph River (stations SJ 1-7, Fig. 2). The sampling patterns shown in Figs. 1 and 2 were designed so that our samples would reflect typical river mouth (point source), coastal (line source) and open lake environments. The relatively close-spaced sample clusters off the mouth of the St. Joseph and Grand Rivers were also designed to permit an initial assessment of how river plumes affected the dispersal of various parameters in the surface film and underlying waters.

B. Sampling Methods

A variety of methods have been employed by different investigators to collect surface film samples. Before the samples discussed in this report were collected, a preliminary experiment was conducted to assess the relative merits of the two sampling techniques which seemed best suited for our purposes: the meshed-screen sampler (Garrett, 1965) and the plate sampler (Harvey and Burzell, 1972). This experiment showed that the plate sampler was definitely superior, inasmuch as we could consistently obtain surface microlayer samples which averaged 125 microns in thickness as compared to an average

of 540 microns for the meshed screen sampler.

Surface film samples from Lake Michigan were collected using a rectangular plastic plate (50 x 46 x 0.25cm) attached to a nylon line. The plate was immersed perpendicular to the water surface and withdrawn slowly so that the surface film adhered to the plate by capillary action. The thin film coating both sides of the plate was then drained into a glass bottle. This procedure was repeated until approximately two liters of the surface microlayer were obtained from each sample station. The mean film thickness, T, was determined from the relation

$$T = \frac{10^4 V}{NEA}$$

where: V = volume (cm^3) of material collected;

N = number of insertions of the plate needed to collect volume V of sample;

E = the average decimal fraction of the total plate area that was covered with surface film (an efficiency factor, see below).

A = the total area (both sides) of the glass plate (cm^2); and,

T = thickness of the surface film (microns).

On the first day of sample collection the efficiency factor was determined by visual observation and was incorporated into our calculations in order to provide a conservative estimate of thickness of the surface film that was sampled. Efficiency factors used on subsequent days were calculated relative to that determined on the first day, so that the estimate error remained

constant for all calculations. The efficiency of the plate sampler ranged between 60% and 84%. The average calculated surface film thickness was 128 ± 6 microns.

Subsurface samples from a depth of 1 meter were also collected at each sample station using a 10-liter glass bottle attached to a wooden pole. The bottle was lowered to the sampling depth before the stopper was removed to prevent contamination from surface film material. Subsurface samples from a depth of 5 meters were collected at two stations (station GH-5, Fig. 1; station SJ-2, Fig. 2) using Niskin bottles. Both Niskin bottles were lowered through the surface in an open position, and it was assumed that the flushing that occurred while they were lowered to the sampling depth would remove any surface film contamination.

That portion of each sample intended for heavy metals analysis was transferred to a one liter polyethylene bottle and three drops (0.15ml) of concentrated HNO_3 (Ultrex grade) were added to preserve the samples for later analysis. The remainder of each sample was used for organic content analysis. The initial steps in the analytical procedures for total organic carbon, dissolved organic carbon, hydrocarbons, and fatty acids were performed immediately after sample collection to minimize biological or biochemical alterations of these materials.

C. Sample Analysis

1. Heavy Metals Analysis - Each sample was separated into three fractions: (1) a particulate fraction; (2) a chloroform

extractable dissolved organic fraction; and (3) a dissolved inorganic fraction.

The particulate fraction was separated by filtering the sample through Millipore type HA filters (0.45 microns, 47mm). The filters were then transferred to 100 ml glass beakers and 3 ml of concentrated HNO_3 were added. The filters were dissolved with gentle heating and the residue was refluxed at 65°C for 45 minutes (but not taken to dryness - see below). The remaining solution was diluted to 10 ml with distilled water and retained for heavy metals analysis as the particulate fraction. In the above procedure it is important to emphasize that the HNO_3 solution was not heated to dryness. This represents a small, but significant, change in the standard procedure (Perkin-Elmer, 1973). Preliminary experiments with this technique indicated that complete drying of the HNO_3 solution resulted in irreversible sorption of heavy metals on the sides and bottom of the beaker. Thus, the standard procedure (Perkin-Elmer, 1973) causes significant sample loss if the original solution contained only small amounts (ppb level) of heavy metals, as it commonly does in surface films. Our experiments also showed that the sorption problem can be prevented if the HNO_3 solution is not completely dried.

Separation of the dissolved organic fraction was done using the method of Barker and Zeitlin (1972). A volume of 750 ml of the filtrate from the particulate filtration was added to a 1 liter polyethylene erlenmeyer flask containing 100 ml of

purified chloroform. The solution was equilibrated for 30 minutes on a mechanical shaker and then transferred to a separatory funnel. The chloroform phase, along with any interfacial material, was then drained into a 1 liter round bottom flask containing 4 ml of 5M HCl. The chloroform was distilled off and the remaining solution was diluted to 10 ml with distilled water and held for analysis as the dissolved organic fraction.

Heavy metals remaining in the aqueous phase after the chloroform extraction were concentrated using the APDC/MIBK (ammonium pyrrolidine dithiocarbamate/methyl isobutyl ketone) extraction scheme of Brooks et al. (1967) and held for analysis as the dissolved inorganic fraction.

The concentration of Cu, Fe, Mn, N and Zn in each of the separated fractions were determined using a Perkin-Elmer Model 460 atomic absorption spectrophotometer or a Model 403 spectrophotometer in conjunction with a Model HGA-2000 graphite furnace.

Enrichment factors (E) for the various heavy metals were calculated as follows:

$$E = (M_{surf}/M_{sub}) - 1$$

where:

E = enrichment factor for metal M

M_{surf} = concentration (ppb) of metal M in the surface layer

M_{sub} = concentration (ppb) of metal M in the subsurface
waters (1 meter depth unless otherwise stated).

In those cases where the concentration of a particular metal

was below the detection limit of our instrument, the detection limit was used to calculate enrichment factors.

2. **Analysis of Organic Carbon** - The amount of organic matter present in surface film and subsurface water samples was assessed by determining organic carbon levels. The procedure of Strickland and Parsons (1972) was used. This is a wet oxidation procedure using potassium persulfate as an oxidant to convert organic carbon into CO_2, which is measured by quantitative non-dispersive infrared spectrometry. This procedure is a refinement of one developed by Menzel and Vacarro (1964) and is widely used in oceanography and limnology. An Oceanography International Total Organic Carbon Analyzer equipped with an electronic integrator was used to measure the CO_2 generated from the samples.

All samples were prepared in triplicate. Total organic carbon (TOC) values were obtained by taking 5 ml aliquots of each well-mixed sample prior to filtration. Dissolved organic carbon (DOC) levels were determined by filtering each sample through a Reeve Angel 934 AH glass fiber filter retained in a Millipore filter holder before taking triplicate 5 ml aliquots. The filters had been previously combusted at 450°C for four hours to destroy organic material which could have contaminated the filtrate. Particulate organic carbon (POC) concentrations were estimated by the difference between TOC and DOC. Ampules containing the aliquots were purged with oxygen and sealed using an Oceanography International Purging and Sealing Unit.

This commonly was accomplished within 30 minutes of sample collection. Surface film samples were diluted by 50% with $KMnO_4$ - distilled water to prevent ampule breakage due to large CO_2 pressures.

3. Analysis of Petroleum Hydrocarbons - Samples were filtered through Reeve Angel 934 AH glass fiber filters as described for DOC analysis. The filters, containing the particulate fraction of petroleum hydrocarbons, were individually wrapped in chloroform-rinsed aluminum foil and frozen aboard ship. The filtrate, having the dissolved fraction, was extracted with chloroform after acidification. Surface film samples, usually between 700-850 ml in volume, were acidified with 10 ml of 6N HCl and extracted with three 40-ml volumes of chloroform. Subsurface samples were between 3000-3800 ml; these were acidified with 40 ml of 6N HCl prior to extraction with three 80-ml volumes of chloroform. These phases of sample preparation were completed aboard ship, normally within 30 minutes of sample collection.

The chloroform extracts, containing dissolved lipoidal materials including hydrocarbons and fatty acids, were evaporated using a rotary evaporator and reduced pressure. Often, a small amount of water remained after the chloroform had been entirely removed. The extract residue, plus any residual water, was dissolved in a saponification mixture composed of 25 ml benzene and 25 ml 0.5N KOH in 95% methanol. This mixture was transferred to a 100 ml flask and refluxed for 1 hour. After being cooled, the flask contents were placed in a 125 ml

separatory funnel. Then 25 ml of organic-free water, obtained from distillation with $KmnO_4$, were added and mixed well with the saponification mixture. The resultant benzene layer was removed, and the aqueous layer extracted twice with 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. The aqueous layer, containing fatty acids and other saponifiable materials, was retained for later analysis.

Hydrocarbons were isolated from the nonsaponifiable organic solvent extract by thin-layer chromatography (TLC). Silica gel G (Merck) 250µm thick on glass plates was used, and petroleum ether (30°-60°) was the developing solvent. Hydrocarbon bands were located by UV radiation of the entire plate and by the use of bromthymol blue spray reagent on co-chromatographed hydrocarbon standards. During spraying of the standards, those parts of the TLC plate containing sample hydrocarbons were pro-tected by a glass plate to minimize contamination. Alkanes and monoalkenes were isolated by this TLC procedure. They were recovered by scraping the hydrocarbon band from the plate and extracting the hydrocarbons from the silica gel with chloro-form.

Particulate hydrocarbons, retained on glass fiber filters after filtration of microlayer and subsurface samples, were treated in a fashion similar to the procedure described above for dissolved hydrocarbons. Entire filters were placed into 100 ml flasks and refluxed with the saponification mixture.

Subsequent extraction and isolation procedures were the same as those of dissolved hydrocarbons.

Hydrocarbons were characterized and quantitated by gas-liquid chromatography (GLC). A Hewlett-Packard 5830 Reporting Gas Chromatograph equipped with dual flame ionization detectors was employed. Columns were 3m x 3.1 mm OD stainless steel pack with 3% SP2100 (Supelco, Inc.) on 100-120 mesh Supelcoport and operated between 150° and 325°C at 4°/minute. Nitrogen carrier gas flow rates were optimized at around 30 ml/ minute each day using a standard hydrocarbon mixture. Samples were injected in carbon disulfide, and an internal standard of n-tetradecane was added to each sample extract prior to injection.

RESULTS AND DISCUSSION

A. Heavy Metals - This report discusses results obtained from the analysis of the 14 surface and subsurface samples collected in the vicinity of the mouth of the St. Joseph River (Fig. 2). The data from these analyses are summarized in Tables 2 and 3, while data for the various fractions of individual samples are given in the Appendix.

1. Phase Distributions - In the surface film samples, the highest concentrations of Cu and Zn occur in the dissolved inorganic phase while Cu is most abundant in the dissolved organic phase, and Fe and Mn in the particulate phase. This

same distribution exists in the subsurface samples, with the exception of Cu, which has its highest subsurface concentration in the dissolved inorganic phase.

Copper, Fe and Mn are enriched in the particulate fraction of more than half of the surface samples. Moreover, a relatively high enrichment of Fe ($E \geq 10.4$) and the maximum average enrichment for Mn ($E = 0.81$) occurs in this phase. Heavy metals in the particulate fraction are associated with inorganic and organic detritus and with aquatic organisms and their solid waste products. Numerous investigations (cf. review by Calvert, 1976) of elemental distributions in particulate matter have shown that Fe and Mn are predominantly associated with detrital oxides and hydroxides, Cu and Ni with aluminosilicates - primarily clay minerals, and Zn with heavy minerals. In addition, significant amounts of Cu and Zn also may be present as sorbed species or in cation exchange sites on clay minerals.

Copper, Fe, Mn and Zn are all enriched in the dissolved inorganic fraction. The maximum enrichment for Mn ($E = 4.8$) and the maximum average enrichment for Zn ($E = 0.2$) occurs in this phase. Anomalously high concentrations of dissolved inorganic Mn and Ni were determined for the samples taken at the mouth of St. Joseph River, and these may reflect anthropogenic inputs. It is known, for example, that Mn in the form of $KMnO_4$ is contained in the effluent from municipal water treatment plants which drains into the river, while Ni may be associated with nickel plating operations which occur in the drainage area (R.F. Babcock, personal communication).

The dissolved organic phase contains enrichments of Cu, Ni, Fe and Mn. The maximum enrichment factor calculated for both Cu ($\geq$15.8) and Ni (2.5), and the highest average phase enrichments for Cu, Ni and Fe are associated with this phase. These enrichments arise from the presence of metal-organic complexes in the surface microlayer, where lipids (Baier, 1972), humic and fulvic acids (Ullman and Owen, 1977) and petroleum derivatives (Brinkman and Iverson, 1975) probably serve as the chelating agents. Metabolic waste products may also be important complexing agents for Fe and Mn, which serve as nutrients for aquatic microorganisms (Torrey, 1976).

2. Influence of River Plume on Enrichment Factors

While conducting the literature review which preceeded this study, we noted that other investigations of the surface microlayer had universally neglected to consider how currents, river plumes, and similar physical processes might affect enrichment factors. Although this omission is probably not serious for studies of open ocean or open lake environments, we felt it could be a significant factor in any investigation of surface films in coastal environments. For this reason, the initial suite of samples selected for analysis in this study were those collected from the vicinity of the mouth of the St. Joseph River (Fig. 2). At the time these samples were collected an obvious plume extended from the river mouth northward along the coast for a distance of approximately 5 km. Sample stations SJ-1 and SJ-6 were located within the plume, while the remainder of the sample stations shown in Fig. 2 were outside the plume.

A comparison of the results obtained for these two groups of samples (Table 3) indicates that the overall distribution of trace metals between the different phases and between the surface and subsurface layers in the water column is highly dependent on the location of the river plume. Not unexpectedly, the greatest effect of the river plume is on enrichment factors calculated for the particulate phase. These values reflect the fact that the turbulence associated with the river plume enchances its suspended sediment content relative to the more quiescent waters outside the plume.

A comparison of stations SJ-1 and SJ-6 (Table 3) shows that the enrichment factors calculated for all heavy metals in the particulate phase and for particulate organic carbon are significantly lower down-plume than at the river mouth. This trend suggests that some particulate matter in the surface film has begun to settle out as the plume extends away from the river, so that the enrichment factors at station SJ-6 are more negative. The removal of particulates from the surface layer is more pronounced for heavy metals associated with oxides and silicates (Fe and Mn) than of those associated with clay minerals (Cu, Ni, Zn), which is consistent with the known hydraulic characteristics of these mineral groups.

In summary, the data presented in Table 3 show that the relatively low enrichment factors calculated for samples within the river plume can mask the fact that the surface layer of the plume actually may contain higher concentrations of

heavy metals and organic matter than waters outside the plume. This effect could be even more pronounced if the suspended load in the river plume is augmented by resuspension and mixing of bottom sediments into the subsurface waters. In this case, the resuspended material will have had more time to equilibrate with the overlying waters and will generally contain higher concentrations of trace metals and other substances than the original river particulates (Elderfield, 1976).

The arguments stated above are not limited to river plumes, since an analogus situation exists in all coastal environments where littoral currents or tidal currents cause prolonged suspension of particulate matter or resuspension of bottom sediments. Finally, it is noted that in some studies (cf. Barker and Zeitlin, 1972; Hatcher and Parker, 1974) the data have been reported as total enrichment factors rather than as enrichment factors for each phase. In these instances the influence of a river plume or similar process cannot be discerned and the reported enrichment factors may be quite misleading.

3. Heavy Metals in the Dissolved Organic Phase

The isolation of heavy metals in the dissolved organic fraction is accomplished by extracting the aqueous sample with chloroform. This extraction routinely results in the formation of a small amount of "interfacial material" between the aqueous and organic phases. Inasmuch as the interfacial material probably consists of incompletely extracted organic compounds, it is common practice (cf. Piotrowicz et al., 1972) to add this material to the organic phase for the subsequent heavy

metals analysis. Thus, the reported concentrations of heavy metals in the dissolved organic fraction include any heavy metals associated with the interfacial material.

During the analysis of our samples it was noted that the amount of interfacial material which formed after the chloroform extraction was somewhat variable, and that the highest heavy metal concentrations in the dissolved organic fraction were associated with those samples which formed the largest amounts of interfacial material. Unfortunately, we could not recover a sufficient amount of this interfacial material from our sample to perform an adequate chemical analysis (sample sizes of about 50 liters would be required).

The exact chemical nature of the interfacial material is unknown. Khalov (1968) has speculated that it may consist of humic and fulvic acids which have an abundance of functional groups acting as complexation sites for heavy metals. Our observations, which are admittedly limited, do not support this contention because samples taken from the river plume — where humic and fulvic acid concentrations should be high — formed relatively small amounts of interfacial material during the chloroform extraction. Another possibility is that interfacial material consists of petroleum compounds and their microbial decomposition products, which can also form metal-organic complexes (Brinkman and Iverson, 1975). Because this latter possibility is relevant to petroleum and heavy metal pollution problems, we plan to conduct future experiments

designed to characterize the nature of the interfacial material.

4. Comparison with Other Studies

The heavy metal enrichment factors determined for Fe,
Mn, Zn and Cu in this study are in reasonable agreement
with freshwater values for these elements determined by
Andren et al. (1975) and Hatcher and Parker (1974). (Compara-
tive data for freshwater Ni surface enrichment were not
available.) A comparison of our data with those compiled by
Torrey (1976) indicates that the subsurface heavy metal
concentrations determined in this study are generally higher
than those found by other investigators who analyzed open
lake samples. Similarly, a comparison of our data with un-
published data collected by R. Rossmann indicates that the sub-
surface heavy metal concentrations determined in this study are
generally lower than those for rivers of southeastern Lake
Michigan, but higher than those for open lake samples. These
comparisons suggest that the distribution of heavy metals in
Lake Michigan can be subdivided into three provinces: (1) the
fluvial environment; (2) the nearshore or coastal environment;
and (3) the open lake environment. In future studies, we
intend to use the relative concentrations of heavy metals in
each of these three environments as an index of the dispersal
of heavy metals in the surface microlayer.

B. Organic Substances – The 20 stations from which water
samples were collected yielded a total of 52 TOC determinations
and 52 DOC determinations, all done in triplicate. From these,
POC levels were calculated.

Concentrations of TOC, DOC, and POC found in surface films and at a depth of 1 m at each sampling location are compiled in Table 4. Enrichment factors are also listed in this Tabulation. Total organic carbon values at the surface range from 5.67 to 16.09 mgm/l and average 9.83 mgm/l. Below the surface the range is 4.11 to 18.02 mgm/l, and the mean is 5.45 mgm/l. Dissolved organic carbon concentrations are, of course, lower than those of TOC and exhibit less scatter. Their range at the surface is 2.08 to 10.20 mgm/l and below the surface is 3.21 to 4.96 mgm/l. The mean values at these locations are 7.38 and 4.06 mgm/l, respectively. Particulate organic carbon is quite variable in concentration. At the surface, POC levels range from 0.45 to 7.29 mgm/l, while at a depth of 1m their range is from 0.27 to 13.46 mgm/l. The corresponding means are 2.45 and 1.39 mgm/l.

These DOC and POC values from Lake Michigan are intermediate between typical marine levels and freshwater levels reported in the literature. Sieburth et al. (1976) report DOC levels averaging 1.10 mgm/l for 9 water samples from the North Atlantic from a depth of 15-20 cm. Gordon (1977) reports POC concentrations in the range of 14 to 42 µgm/l in water from the top 100 m of the North Atlantic. DOC concentrations averaged 15.2 mgm/l and POC 1.4 mgm/l in a survey of over 500 Wisconsin lakes (Wetzel, 1975 p. 542). Thus, the organic carbon contents of these samples of Lake Michigan water suggest the Great Lakes are unlike both the oceans and typical lakes and perhaps are appropriately called the "Inland Seas."

Enrichment factors given in Table 4 average about 0.8

for TOC, DOC, and POC. Although it can be misleading to average data from widely different locations, this approach is a useful way to compare individual stations to the pooled information. For example, the POC enrichment factors at station TR-6, at the mouth of the Grand River, and at station SJ-1, at the mouth of the St. Joseph River, are considerably larger than the mean POC enrichment factor of 0.76. However, the factors at stations GH-4 and SJ-6, both located in their river's plumes, are negative. This change may indicate settling of particulate matter transported to the lake by these rivers.

The levels of TOC in the surface and subsurface samples at stations TR-6 and SJ-1, both from river mouths, are higher than the mean TOC levels and are quite similar. This is also true for the DOC values at these locations. While TOC values at other stations are higher, the only stations having similarly high DOC levels are located either in river plumes (GH-4 and SJ-6) or close to shore (GH-1). High TOC levels can be explained by contributions of POC from patchy distributions of phytoplankton, but the DOC content of these samples suggests that rivers are an important source of organic matter to Lake Michigan.

One station, TR-11, was occupied on 19 July and again on 21 July to investigate short-term temporal variability in water chemistry. DOC values agree very closely in both the surface microlayer (7.98 and 7.75 mgm/l) and in the subsurface water (3.95 and 4.02 mgm/l). More variation is found in TOC levels, primarily due to differences in surface microlayer POC concentrations over the two day interval. This indicates that

phytoplankton patchiness may have a temporal as well as a geographical component because of the contribution of plankton to TOC. In contrast to the good agreement in DOC levels in these two samples from station TR-11, large differences were found in TOC, DOC, and POC concentrations between a sample from station GH-2 and one from TR-7 (Figure 1) collected on 18 July and 19 July, respectively. Only subsurface DOC values agreed well (3.98 and 3.92 mgm/l, respectively). These two stations were within 2 km of each other south of the Grand River mouth. It is likely the influence of the river plume contributed to variations in surface DOC and POC and subsurface POC.

Organic carbon concentrations from stations 8 through 11 along the coastal waters transect and from stations TR-26 and TR-? in the open lake were not significantly different from each other, although they were substantially lower than river mouth and river plume levels.

Organic carbon depth profiles were measured at two stations, GH-5 and SJ-2, to determine the extent of vertical variation. At both of these locations, duplicate samples were collected of the surface microlayer material, triplicate samples of subsurface water at a depth of 1 m, and single samples at depths of 20 cm and 5 m. The TOC, DOC, and POC levels of these samples are given in Table 5. Surface concentrations and enrichment factors (Table 4) at both stations are very similar, although station GH-5 has slightly higher levels of TOC and DOC. No trend towards decreasing carbon concentration appears between depths of 20 cm and 5 m. Mean DOC values of

subsurface samples are 3.92 ± 0.30 mgm/l at station GH-5 and
4.13 ± 0.24 mgm/l at station SJ-2. The coefficients of
variation around these means, ± 8% and ±6%, are less than that
(±10%) given in Table 4 for all subsurface samples, indicating
that vertical differences over this 5 meter depth range
are minor. Furthermore, enrichment factors which have been
calculated using subsurface concentrations at 1-meter depths
in this study can be compared to factors calculated by other
investigators relative to 20-cm depths.

C. Hydrocarbons - Dissolved hydrocarbon concentrations
found in the surface microlayer and in subsurface water from
seven locations off the mouth of the St. Joseph River are
shown in Table 6. Particulate hydrocarbons were below de-
tection limits in these samples. Because of serious analytical
problems caused in part by the low levels of dissolved hydro-
carbons present, it was not possible to identify individual
hydrocarbon components and became necessary instead to express
these concentrations in terms of total dissolved hydrocarbons.
However, no evidence of petroleum contamination was detected
in any of these samples.

Enrichment factors of total hydrocarbons range between
4.4 and 30.1, all values higher than those found for DOC and
TOC, and their mean is 17.5 ± 9.8. Evidently, dissolved hydro-
carbons are more concentrated in surface microlayer material
than is dissolved organic matter in general. This is borne
out by the contribution of hydrocarbons to DOC. In the surface
film, this contribution averages 4.3% while in the subsurface

water the average is only 0.5%. Hydrocarbons, being hydrophobic compounds, undergo partitioning in water and preferentially rise to the surface, contributing to formation of the organic microlayer. As shown in Table 1, other investigators have found hydrocarbon enrichments in marine waters, but literature references to data from freshwater studies are not available.

SUMMARY AND CONCLUSIONS

1. Significant enrichments of Cu, Fe, Mn, Ni and Zn in the surface microlayer have been determined. For the samples analyzed thus far, total surface enrichment ($E_{total} > 0$) was evident for Cu, Fe, Mn, Ni and Zn in, respectively, 88%, 57%, 75%, 50% and 43% of the samples. Within the separate phases, maximum enrichments (E_{max}) for Cu and Ni occurred in the dissolved organic phase, and for Fe, Mn and Zn in the dissolved inorganic phase. The greatest percentage enrichments (% of samples enriched in the phase) for Cu, Ni and Mn were in the dissolved organic phase, for Fe in the particulate phase and for Zn in the dissolved inorganic phase.

2. It is possible that anthropogenic inputs of Mn and Ni are present in the effluent from the St. Joseph River. Nickel plating operations are conducted in the drainage area, and Mn as $KMnO_4$ is present in the effluent from municipal water treatment plants which drain into the river.

3. The river plume associated with the St. Joseph River has a significant effect on heavy metal and organic carbon surface enrichment factors and, in particular, on enrichment factors calculated for the particulate phase of these substances.

In general, despite high concentrations of heavy metals in the surface film of the river plume, calculated enrichment factors are relatively low because of the large amount of suspended material associated with the river plume. The magnitude of surface enrichment factors becomes even more diminished if bottom sediments are resuspended and become part of the suspended load. In marine coastal environments, the suspended load associated with littoral currents and tidal currents should have a similar effect to that of a river plume. For this reason, data summaries which report only total enrichment factors can be quite misleading, and data should always be reported as enrichment factors for each of the separate phases.

4. Trace metal concentrations in the dissolved organic phase are proportional to the amount of "interfacial material" which forms in this phase during the chloroform extraction. This interfacial material may consist of petroleum compounds, although further studies are needed to characterize its chemical composition.

5. Standard procedures (Perkin-Elmer, 1973) employed during the separation of different phases were found to result in sorption of heavy metals on glassware and consequent sample loss. A small modification in these procedures, whereby acid digestions are not taken to dryness, can prevent this problem.

6. Organic matter, indicated as organic carbon, is significantly enriched in surface microlayers in comparison to subsurface water. This is equally true for river mouth, nearshore, and

openlake locations. A considerable amount of variation exists in surface concentrations of both dissolved and particulate organic carbon. This probably reflects patchiness of planktonic populations which can contribute to these organic matter fractions. Subsurface levels of dissolved organic carbon are fairly uniform and average 4 mgm/l except in river plumes, where higher values are found. In contrast, particulate organic matter varies widely between locations and in some cases appears to be composed largely of settling mineral particles or organic detritus.

7. Enrichment factors of dissolved aliphatic hydrocarbons are greater than those of dissolved organic matter by one order of magnitude. This class of hydrocarbon is an important component of crude and refined petroleum, as well as a product of biological synthesis. Therefore, these materials can be expected to accumulate at the water surface in both petroleum-contaminated and pristine areas and to participate in the concentration of trace metals in surface microlayers. Furthermore, it is probable that hydrocarbon compositions of surface microlayers are sensitive indicators of low-level petroleum contamination of Great Lakes waters.

REFERENCES

Andren, A.W., A.W. Elzerman, and D.E. Armstrong, 1975. Chemical and physical aspects of surface organic microlayers in freshwater lakes. Proc. First Specialty Symposium on Atmospheric Contribution to the Chemistry of Lake Waters, J. Great Lakes Res. 2, Supp. 1:101-110

Baier, R.E., 1972. Organic films on natural waters: Their retrieval, identification, and modes of elimination. J. Geophys. Res., 77:5062-5075.

Barker, D.R. and H. Zeitlin, 1972. Metal-ion concentrations in sea-surface microlayer and size-separated atmospheric aerosol samples in Hawaii. J. Geophys. Res., 77:5076-5086.

Brinkman, F.E. and W.P. Iverson, 1975. Chemical and bacterial cycling of heavy metals in the estuarine system, in T.M. Church (ed.) Marine Chemistry in the Coastal Environment, American Chemical Society, pp. 319-342.

Brooks, R.R., R.R. Presley, and I.R. Kaplan, 1967. APDC-MIBK extraction system for the determination of tracemetals in saline waters by atomic absorption spectrophotometry. Talanta, 14:809-816.

Calvert, S.E., 1976. Mineralogy and geochemistry of near-shore sediments, in J.P. Riley and R. Chester (eds.), Chemical Oceanography, 2nd ed., v. 6, pp. 187-280.

Duce, R.A., J.G. Quinn, C.E. Olney, S.R. Piotrowicz, B.J. Ray, and T.L. Wade, 1972. Enrichment of heavy metals and organic compounds in the surface microlayer of Narragansett Bay, Rhode Island. Science, 176:161-163.

Elderfield, H., 1976. Hydrogenous material in marine sediments; excluding manganese nodules, in J.P. Riley and R. Chester (eds.), Chemical Oceanography, v. 5, pp. 137-216.

Elzerman, A.W. and D.E. Armstrong, 1975. Enrichment of Zn, Cd, and Pb in the surface microlayer of Lake Ontario and Lake Michigan. 18th Conf. Internat. Assoc. Great Lakes Res.

Garrett, W.D., 1965. Collection of slick-forming materials from the seasurface. Limnol. Oceanogr., 10:602-605.

_____, 1967. The organic chemical composition of the ocean surface. Deep-Sea Research, 14:221-227.

Gordon, D.C., Jr. 1977. Variability of particulate organic carbon and nitrogen along the Halifax-Bermuda section. Deep-Sea Research, 24:257-270.

Harvey, G.W., and L.A. Burzell, 1972. A simple microlayer method for small samples. Limnol. Oceanogr., 17:156-157.

Hatcher, R.F. and B.C. Parker, 1974. Laboratory comparison of four surface microlayer samplers. Limnol. Oceanogr., 19:162-165.

Khalov, K.M., 1968. Organic macromolecules dissolved in seawater. Geochemistry International, 5:497-503.

Liss, P.S., 1974. Chemistry of the sea surface microlayer, in J.P. Riley and G. Skirrow (eds.), Chemical Oceanography, v. 2. Academic Press.

MacIntyre, F., 1974. Chemical fractionation and sea-surface microlayer processes, in E.D. Goldberg (ed.), The Sea, v. 5, pp. 245-300. Interscience.

Marty, J.C., and A. Saliot, 1976. Hydrocarbons (normal alkanes) in the surface microlayer of seawater. Deep-Sea Research, 23:863-873.

Menzel, D.F., and R.F. Vaccaro, 1964. The measurement of dissolved organic and particulate carbon in sea water. Limnol. Oceanogr., 9:138-142.

Meyers, P.A., 1976. Dissolved fatty acids in seawater from a fringing reef and a barrier reef at Grand Cayman. Limnol. Oceanogr., 21:315-319.

Perkin-Elmer Corporation, 1973. Instructions, HGA-2000 graphite furnace (Norwalk).

Piotrowicz, S.R., B.J. Ray, G.L. Hoffman, and R.A. Duce, 1972. Trace metal enrichment in the sea-surface microlayer. J. Geophys. Res., 77:5243-5254.

Sieburth, J. McN., P.J. Willis, K.M. Johnson, C.M. Burney, D.M. Laboie, K.R. Hinga, D.A. Caron, F.W. French III, P.W. Johnson, and P.G. Davis, 1976. Dissolved organic matter and heterotrophic microneuston in the surface microlayer of the North Atlantic. Science, 194:1415-1418.

Strickland, J.D.H., and T.R. Parson, 1972. A Practical Handbook of Seawater Analyses, Fish. Res. Bd. Canada Bull. 167 (2nd edition).

Torrey, M.S., 1976. Environmental status of the Lake Michigan Region, Volume 3. Chemistry of Lake Michigan, ANL/ES-40.

Ullman, W.J. and R.M. Owen, 1977. Heavy metal-humic acid associations in Little Traverse Bay, Lake Michigan. 20th Conf. Great Lakes Res., abstract only.

Wade, T.L., and J.G. Quinn, 1975. Hydrocarbons in the Sargasso Sea surface microlayer. Mar. Poll. Bull. 6:54-57.

Wetzel, R.G., 1975. Limnology, Saunders, Philadelphia, 743 pages.
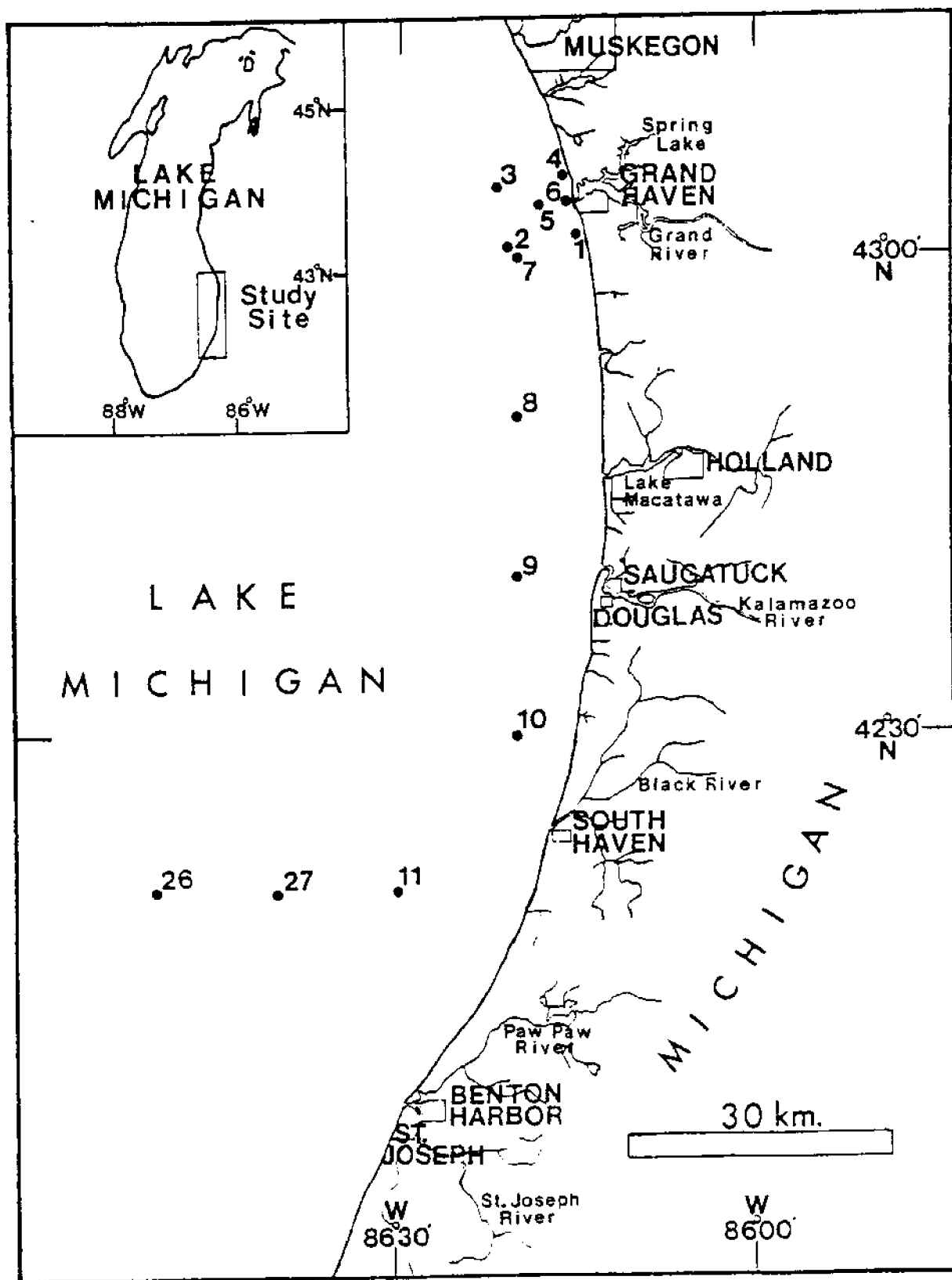
FIGURE 1. Location of samples collected off Grand Haven and between Grand Haven and St. Joseph. Samples 1-6 are prefixed GH- and samples 7-11 and 26-27 are prefixed TR- in the text and tables.
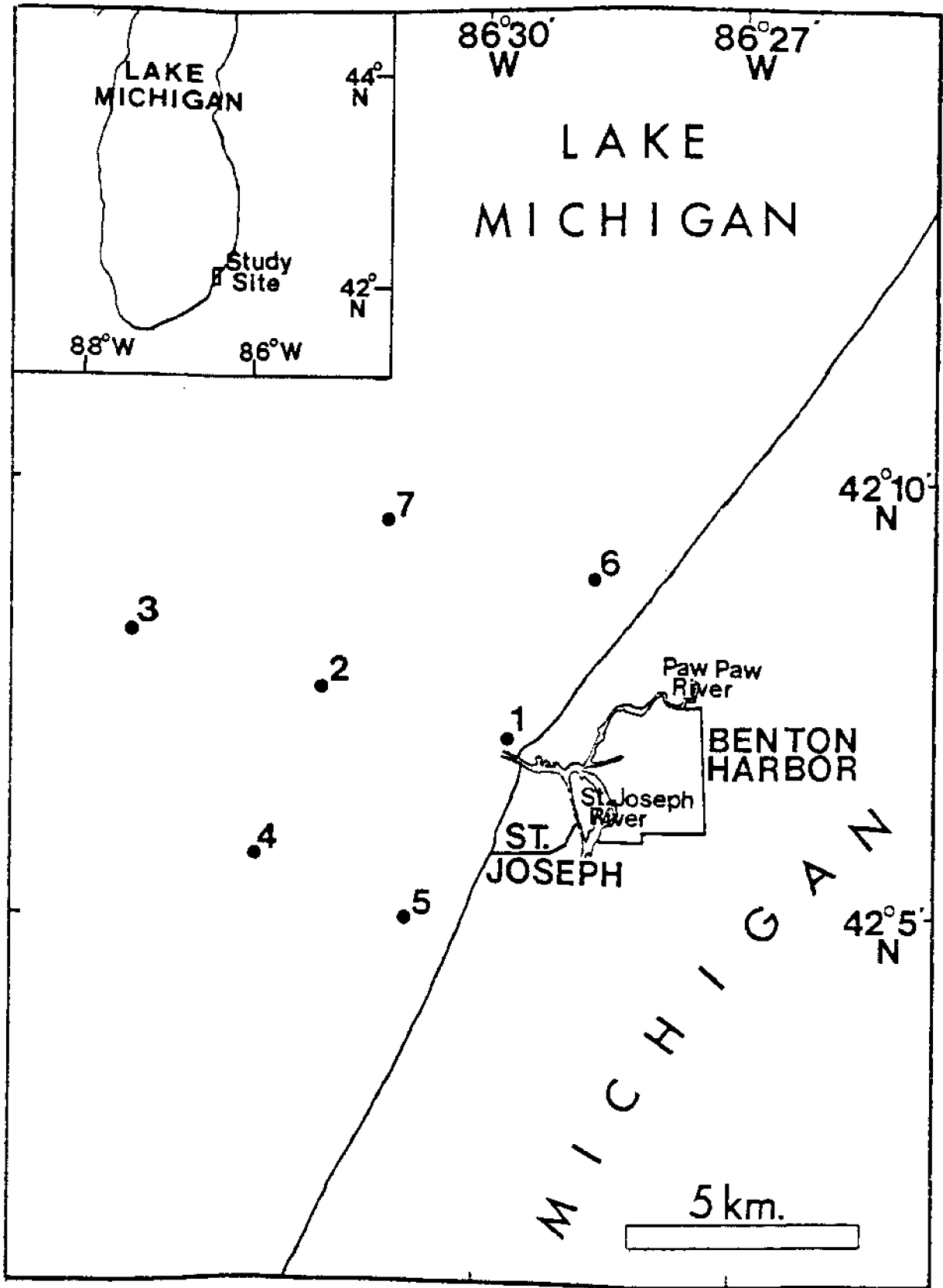
FIGURE 2.   Location of samples collected off mouth of St. Joseph
River.   These samples are prefixed SJ- in the text and tables.

TABLE 1. Reported enrichments of heavy metals and organic compounds in the surface microlayer.

Component	Location	Concentration Ratio (G) or Enrichment Factor (b)	Reference
Fatty Acids	Narragansett Bay	1.5-3.6[a]	1
	Saginaw Bay, Lake Michigan	2.6[a]	2
	Grand Cayman	1.2-2.5[a]	9
Hydrocarbons	Narragansett Bay	1.4[a]	1
	Coastal Atlantic and Mediterranean Sea	50[a]	3
	North Atlantic	2[a]	4
Heavy Metals			
Al	North Atlantic	0.6-7.5[b]	5
Cd	Lake Mendota	-0.2-12[b]	8
	Lake Michigan	-0.3-1.5[b]	7
	Lake Ontario	-0.4-11[b]	7
Cu	Narragansett Bay	0.13-35[b]	5
	North Atlantic	0.5->57[b]	5
	Hawaii	2.1[b]	6
	Lake Michigan	0.2-6.1[b]	7
Fe	Narragansett Bay	0.89-5.2[b]	5
	North Atlantic	0.4->57[b]	5
	Hawaii	3.2[b]	6
Mn	North Atlantic	>0.0>5.0[b]	5
Ni	Narragansett Bay	0.69-49[b]	5
Pb	Narragansett Bay	0.08-15[b]	5
	North Atlantic	0.0-14[b]	5
	Lake Mendota	-0.2-36[b]	8
	Lake Michigan	-0.2-5.8[b]	7
	Lake Ontario	-0.1-10[b]	7
V	North Atlantic	>0.5->3.0[b]	5
Zn	Hawaii	5.0[b]	6
	Lake Mendota	0.3-5.8[b]	8
	Lake Michigan	0.1-10[b]	7
	Lake Ontario	-0.4-3.0[b]	7

Duce et al., 1972
Meyers (unpublished data)
Wade and Quinn, 1975
Marty and Saliot, 1976
Piotrowicz et al., 1972
Barker and Zeitlin, 1972
Elzerman and Armstrong, 1975
Elzerman and Armstrong (unpublished data)
Meyers, 1976

TABLE 2. Summary of heavy metals analysis (for stations SJ 1-7, Fig. 2).[a]

Parameter		Concentration(ppb)		Enrichment Factor	% Samples with E>0
		Surface	Subsurface		
Copper	P	≤.1-.93(.21)	≤.1-.93(.20)	-.64-.29(.05)	60
	O	≤.5-6.7(1.7)	.08-.80(.36)	-.38-≤15.8(3.7)	75
	I	≤.4-2.5(1.1)	≤.4-2.1(.81)	-.90-5.7(.35)	57
	T	.80-7.0(3.0)	.40-2.1(1.4)	-.38-2.4(1.1)	88
Iron					
	P	≤1.1-180.5(30.2)	≤.8-232.7(35.4)	-.83-≤10.4(-.15)	67
	O	≤1.0-81.0(14.5)	≤1.0-28.8(8.1)	-.90-3.0(.79)	57
	I	≤1.0-8.9(2.6)	≤.1-2.9(1.8)	≤-.86-≤39(-44)	50
	T	2.9-180.5(47.2)	1.9-232.7(45.3)	-.67-11.7(.04)	57
Manganese					
	P	≤.1-43.8(5.8)	.18-22.1(3.2)	≤.64-2.4(.81)	75
	O	≤.1-1.5(.38)	≤.1-1.2(.33)	.18-1.5(.15)	100
	I	≤.1-26.8(4.5)	.34-14.9(2.6)	-.99-4.8(.73)	63
	T	.41-70.6(10.7)	.92037.0(6.1)	-.62-.91(.75)	75
Nickel					
	P	≤.01-1.6(.25)	≤.01-2.2(.35)	≤-.97-2.0(-.29)	25
	O	.80-5.5(2.3)	.23-2.8(1.3)	≤0-2.5(.77)	86
	I	1.9-24.3(8.1)	.78-33.6(12.7)	-.88-.82(-.36)	13
	T	3.6-26.7(10.7)	2.4-33.8(14.4)	-.78-.72(-.26)	50
Zinc					
	P	≤.1-5.1(1.7)	≤.1-37.1(6.0)	≤-.96-.16(-.72)	33
	O	≤.1-5.6(1.1)	.23-2.4(1.1)	≤-.94-.78(0.0)	33
	I	≤.1-13.7(7.3)	2.8-12.4(6.1)	-.83-1.6(2.0)	38
	T	≤.5-20.7(10.1)	6.2-42.7(13.2)	-.82-1.2(-.23)	43

a. Data are shown as range of values for 7 samples with mean value in parentheses.

b. P = Particulate Phase; O = Dissolved Organic Phase; I = Dissolved Inorganic Phase; T = Total for all Phases.

TABLE 3. Influence of river plume on enrichment factors.[a]

Parameter[b]		Outside Plume (Mean of Samples SJ 2, 3, 4, 5, 7)	In-Plume	
			Sample SJ-1 (River Mouth)	Sample SJ-6 (Down Plume)
Copper:				
	P	-.14	.29	-.29
	O	2.5	15.3	_5.3
	I	.30	5.7	-.33
	T	1.1	1.9	1.1
Iron:				
	P	2.6	-.22	-.83
	O	.92	-	-.38
	I	.13	-	_.39
	T	1.1	-.22	-.67
Manganese:				
	P	1.7	.98	-.59
	O	.52	-	-
	I	0.00	.80	1.8
	T	.23	.91	.55
Nickel:				
	P	-.58	-.27	-.56
	O	.78	2.5	-
	I	-.46	-.17	-.30
	T	-.29	-.19	-.30
Zinc:				
	P	-.80	-.16	-.46
	O	.11	_-.85	-
	I	.49	-.18	-.83
	T	-.17	-.19	-.82
Organic Carbon:				
Particulate		.84	2.0	-.29
Dissolved		.78	.97	1.2
Total		.79	1.2	.77

.. Sample locations shown in Fig. 2

. P = Particulate Phase; O = Dissolved Organic Phase; I = Dissolved Inorganic Phase; T= Total Enrichment Factor (all phases)

TABLE 4. Organic carbon concentrations in Lake Michigan waters, July, 1977. Sample locations shown in Figures 1 and 2. Concentrations given in milligrams carbon per liter. E.F. = Enrichment Factor.

Station	Total Organic Carbon			Dissolved Organic Carbon			Particulate Organic Carbon		
	Surface	Subsurface	E.F.	Surface	Subsurface	E.F.	Surface	Subsurface	E.F.
GH-1	15.28 ± 1.69	18.22 ± 0.06	-0.16	8.82 ± 0.01	4.76 ± 0.01	0.85	6.46	13.46	-0.52
GH-2	5.67 ± 0.67	4.27 ± 0.09	0.33	4.33 ± 0.39	3.98 ± 0.10	0.09	1.33	0.29	3.59
GH-3	13.31 ± 0.64	4.53 ± 0.07	1.94	8.54 ± 0.37	3.63 ± 0.37	1.35	4.77	0.90	4.30
GH-4	9.64 ± 0.19	5.29 ± 0.19	0.82	9.19 ± 0.35	4.33 ± 0.09	1.12	0.45	0.95	-0.53
GH-5	8.08 ± 0.27	4.62 ± 0.55	0.75	7.02 ± 0.16	3.94 ± 0.23	0.78	1.06	0.68	0.56
TR-6	16.09 ± 0.23	6.34 ± 0.09	1.54	8.79 ± 0.27	4.67 ± 0.24	0.88	7.29	1.66	3.39
TR-7	11.63 ± 0.44	4.22 ± 0.35	1.23	7.83 ± 0.20	3.93 ± 0.09	0.99	3.80	1.30	1.92
TR-8	8.58 ± 0.27	4.11 ± 0.59	1.09	6.90 ± 0.16	3.21 ± 0.14	1.15	1.68	0.89	0.89
TR-9	8.26 ± 0.21	4.28 ± 0.09	0.93	6.77 ± 0.29	3.86 ± 0.17	0.75	1.49	0.42	2.55
TR-10	8.28 ± 0.13	4.46 ± 0.17	0.86	2.08 ± 0.15	3.68 ± 0.18	-0.43	6.19	0.78	6.94
TR-11A	9.75 ± 1.26	4.23 ± 0.22	1.30	7.98 ± 0.23	3.95 ± 0.12	1.02	1.78	0.27	5.59
TR-11B	8.54 ± 0.19	4.46 ± 0.11	0.91	7.75 ± 0.14	4.02 ± 0.25	0.93	0.79	0.43	0.84
TR-26	9.34 ± 0.12	4.17 ± 1.24	1.24	8.64 ± 0.14	3.89 ± 0.02	1.22	0.70	0.27	1.59
TR-27	7.55 ± 0.09	4.83 ± 0.04	0.56	4.81 ± 0.03	4.18 ± 0.03	0.15	2.75	0.66	3.17
SJ-1	13.67 ± 0.86	6.25 ± 0.30	1.19	9.77 ± 0.42	4.96 ± 0.21	0.97	3.90	1.29	2.02
SJ-2	7.51 ± 0.17	4.65 ± 0.11	0.62	6.59 ± 0.31	4.02 ± 0.12	0.64	0.92	0.63	0.46
SJ-3	7.77 ± 0.09	4.32 ± 0.11	0.80	6.42 ± 0.23	3.73 ± 0.13	0.72	1.35	0.59	1.29
SJ-4	7.75 ± 0.24	5.13 ± 0.16	0.51	6.97 ± 0.20	4.20 ± 0.34	0.66	0.79	0.93	-0.15
SJ-5	8.63 ± 0.20	4.30 ± 0.34	1.01	7.80 ± 0.29	3.86 ± 0.07	1.02	0.83	0.44	0.89
SJ-6	11.48 ± 0.20	6.50 ± 0.16	0.77	10.20 ± 0.20	4.71 ± 0.17	1.17	1.28	1.79	-0.28
SJ-7	9.70 ± 0.24	4.27 ± 0.09	1.27	7.86 ± 0.19	3.75 ± 0.05	1.10	1.84	0.53	2.47
Mean, µgm/l	9.83	5.45	0.80	7.38	4.06	0.82	2.45	1.39	0.76
s.d., µgm/l	2.75	3.02	-	1.89	0.43	-	2.10	2.80	-
coeff.var.(%)	28	55	-	26	10	-	86	201	-

TABLE 5. Vertical profiles of organic carbon, Lake Michigan,
July, 1977.

Depth (meters)	Station GH-5			Station SJ-2		
	TOC	DOC	POC	TOC	DOC	POC
0	7.89	7.00	0.89	7.20	6.36	0.83
0	8.28	7.06	1.22	7.82	6.74	1.08
0.2	4.58	4.23	0.35	4.51	4.04	0.46
1	5.27	3.69	1.58	4.54	4.00	0.54
1	4.22	3.94	0.28	4.72	4.07	0.64
1	4.38	4.18	0.19	4.70	4.00	0.69
5	4.27	3.54	0.73	5.21	4.55	0.66

TABLE 6. Dissolved hydrocarbon concentrations and enrichment factors at the mouth of the St. Joseph River. See Figure 2 for station locations.

Total Dissolved Hydrocarbons

Station	Surface (ugm/l)	Subsurface (ugm/l)	Enrichment Factor
SJ-1	92	n.d.	n.d.
SJ-2	575	30*	18.2
SJ-3	108	20	4.4
SJ-4	446	19	22.5
SJ-5	529	17	30.1
SJ-6	300	n.d.	n.d.
SJ-7	227	17	12.4

* mean of triplicate measurements
n.d. not determined

APPENDIX

Summarized below are the heavy metal data for stations SJ 1-7. All concentrations are reported in ppb. Subsurface concentrations are from 1 m depth. I = dissolved inorganic phase; O = dissolved organic phase; P = particulate phase; T = total for all phases.

Sample	Lat.(N)	Long.(W)	Microlayer Thickness (μm)	Cu	Fe	Mn	Ni	Zn
SJ-1:	42°07.0'	86°29.6'	137					
Surface:								
I				1.4	<1.1	26.8	24.3	2.3
O				1.3	<1.0	<.1	.81	<.1
P				1.2	180.5	43.8	1.6	5.1
T				3.9	180.5	70.6	26.7	7.4
Subsurface:								
I				.21	<1.1	14.9	29.2	2.8
O				.08	<1.0	<.1	.23	.67
P				.9?	232.7	22.1	2.2	6.1
T				1.?	232.7	37.0	31.6	9.6
SJ-2A	42°07.6'	86°32.5'	129					
Surface:								
I				1.8	1.8	1.8	16.4	9.0
O				<.7	4.7	<.7	<2.0	.67
P				.10	11.0	.40	.19	2.9
T				1.9	17.5	2.2	16.6	12.6
Subsurface:								
I				.67	1.1	.31	17.3	9.4
O				.40	4.0	<.4	2.0	2.0
P				.28	2.8	.28	.23	2.5
T				1.4	7.9	.59	20.0	13.9
SJ-2B	42°07.6'	86°32.5'	129					
Surface:								
I				.13	4.5	<.7	4.2	10.7
O				.67	13.3	<.7	3.3	2.7
P				<.1	12.3	.41	<.01	.31
T				.80	30.1	.41	7.5	13.7

Sample	Position Lat.(N)	Long.(W)	Microlayer Thickness (μm)	Cu	Fe	Mn	Ni	Zn
SJ-2B	42°07.6'	86°32.5'	129					
Subsurface:								
I				.90	1.6	.95	33.6	4.2
O				.40	5.6	<.4	<1.2	1.6
P				<.1	9.5	.19	.15	.38
T				1.3	16.7	1.1	33.8	6.2
SJ-3	42°08.25'	86°35.3'	127					
Surface:								
I				2.5	1.3	<.1	9.3	10.0
O				<.5	2.0	1.0	3.5	<.1
P				<.1	6.0	.20	.11	3.6
T				2.5	9.3	1.2	12.9	13.6
Subsurface:								
I				1.1	1.7	.48	5.1	4.0
O				.80	20.8	.40	2.8	1.6
P				<.1	<.8	.19	.05	37.1
T				1.9	22.5	1.1	8.0	42.7
SJ-4	42°05.6'	86°33.5'	135					
Surface:								
I				.95	<1.0	.20	1.9	13.7
O				2.0	81.0	1.5	5.5	5.0
P				.10	9.1	.51	.03	1.4
T				3.1	90.1	2.2	7.4	20.1
Subsurface:								
I				<.4	7.3	<.4	2.3	5.3
O				.80	28.0	1.2	2.0	2.8
P				.10	<.8	.29	<.01	1.4
T				.90	35.3	1.5	4.3	9.5
SJ-5	42°04.9'	86°31.1'	120					
Surface:								
I				.22	<.7	1.2	2.1	<.3
O				6.7	11.3	<.7	1.5	<.1
P				.11	1.1	<.1	<.01	<.1
T				7.0	12.4	1.2	3.6	--
Subsurface:								
I				2.1	2.9	1.6	4.4	7.9
O				<.4	<2.8	<.4	.80	<.1
P				<.1	.94	.28	.30	<.1
T				2.1	3.8	1.9	5.5	7.9

Sample	Position Lat.(N)	Long.(W)	Microlayer Thickness (μm)	Cu	Fe	Mn	Ni	Zn
SJ-6	42°08.8'	26°28.2'	122					
Surface:								
I				1.0	4.0	5.6	6.2	1.6
O				2.5	3.0	<.5	<1.0	<.1
P				.20	6.1	.91	.10	.20
T				3.7	13.1	6.5	6.3	1.8
Subsurface:								
I				1.5	<.1	2.0	8.8	9.5
O				<.4	4.8	<.4	<1.6	<.1
P				.28	35.4	2.2	.23	.37
T				1.8	40.2	4.2	9.0	9.9
SJ-7	42°09.6'	86°31.5'	129					
Surface:								
I				.66	8.9	.47	.73	11.4
O				.50	<2.0	.50	4.0	.50
P				<.2	15.2	.61	<.01	<.1
T				1.2	24.1	1.6	4.7	11.9
Subsurface:								
I				<.4	<1.0	.34	.78	6.0
O				.40	<1.6	.40	2.4	.80
P				<.3	1.9	.18	.02	<.1
T				.40	1.9	.92	2.4	6.8