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Pyrolysis-mass spectrometry of sediment trap organic matter from Lake Michigan

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ABSTRACT

The composition of total organic matter associated with sinking particles collected by sediment traps moored at five depths in Lake Michigan has been characterized by pyrolysis-chemical ionization mass spectrometry. Concentrations of organic carbon decrease dramatically in the upper part of the water column as organic matter is remineralized. Remineralization changes the character of organic matter associated with particles as they settle, and different pyrolysate distributions are consequently obtained. Nitrogen-containing compounds are more abundant in trap contents from the epilimnion and metalimnion, whereas saccharides and humic acids are more abundant in particles settling within the near-bottom nepheloid layer. Comparison of extractable *n*-alkane distributions to the pyrolysates of bulk organic matter indicates preferential degradation of algal components during sinking of sediment particles.

Keywords: PY-CIMS, organic matter, sediment trap, sinking organic particles, sediment resuspension.

INTRODUCTION

Sediment trap studies in lakes and oceans have documented that dramatic changes in concentration and composition occur to particulate organic matter as it sinks through the water. Eadie *et al.* (1984) show that 96% of the organic carbon produced in the photic zone of Lake Michigan is remineralized to CO₂ before it can sink to bottom sediments in water depths of only 100 m, a degradational value nearly as great as those reported in markedly deeper marine locations (*e.g.*, Cobler and Dymond, 1980; Knauer *et al.*, 1979; Suess, 1980; Knauer and Martin, 1981; Martin *et al.*, 1987). The early stages of particle sinking evidently are accompanied by substantial recycling and biological utilization of organic matter.

Selective destruction of some components and preservation of others alters the composition of the total organic matter associated with sinking particles. For example, lipid material contributed from aquatic organisms is destroyed more quickly than is total organic matter in sediment trap contents from Lake Michigan (Meyers *et al.*, 1980, 1984; Meyers and Eadie, 1993), the coastal ocean (Prah *et al.*, 1980), and open-ocean areas (Wakeham *et al.*, 1980; Wakeham, 1982; Wakeham and Lee, 1989). Lipid biomarker compounds have been employed to

trace the origins and alterations of organic matter, yet their preferential degradation that is evident in sediment trap studies brings into question how accurately they represent total organic matter. Moreover, extractable lipid components typically constitute only a few percent of total particulate or sedimentary organic matter. Molecular characterization of bulk organic matter consequently is a preferable approach to trace cycling of organic carbon in natural systems, but it is not easily attained.

We report here characterizations of organic matter contents of sediment trap samples using pyrolysis-chemical ionization mass spectrometry (PY-CIMS). The advantages of this approach are that it provides a measure of the composition of total organic matter, not a minor fraction of it, and that it also assesses the bulk molecular structure of this material (*cf.* Zsolnay and Harvey, 1985; Schulten, 1987; Zsolnay, 1991). In addition, we compare extractable *n*-alkane biomarker indicators to the pyrolysate characterizations of organic matter sources and degradation.

SAMPLES AND PROCEDURES

We obtained samples from the archived sediment trap materials that have been regularly collected by the NOAA Great Lakes Environmental Research Laboratory since 1978. The sediment traps that

Table 1 General characteristics of sediment trap material from Station 8 in southeastern Lake Michigan. Deployment of the trap string was from July 24 to October 23, 1980.

Water depth	Lake zone	Mass flux (g m ⁻² day ⁻¹)	TOC (%)	CaCO ₃ (%)	n-Alkane C ₁₇ /C ₂₉
15 m	epilimnion	0.21	29.0	37	10.0
35 m	metalimnion	0.12	4.8	35	5.0
60 m	hypolimnion	0.54	8.1	36	1.1
80 m	nepheloid	1.7	6.0	50	2.1
95 m	nepheloid	5.6	2.8	44	0.2

provided our samples were deployed from July 24 to October 23, 1980 at Station 8 in eastern Lake Michigan, approximately 30 km offshore of Grand Haven, Michigan. This station corresponds to the 1978 Station 4 of Eadie *et al.* (1984) and is about 7 km farther from shore than the 1978 Station 8 which provided samples for the sediment trap organic matter studies described by Meyers *et al.* (1984). Lake Michigan is thermally stratified throughout this deployment period, with the thermocline existing at around 30 to 35 m at its maximum development. As discussed in detail by Robbins and Eadie (1991), the epilimnion and metalimnion of Lake Michigan are free of resuspended bottom sediments during periods of thermal stratification. The traps, described by Eadie *et al.* (1984), consisted of 50 cm x 10 cm cylinders and were moored at depths of 15, 35, 60, 80, and 95 m. The total water depth at this location is 100 m. Mercuric chloride (0.5 g L⁻¹) was added to the sample collection bottle at the bottom of each trap to arrest bacterial and faunal activity and thereby improve the preservation of organic matter. Lee *et al.* (1992) have confirmed the effectiveness of mercuric chloride as a preservative in sediment trap studies.

Concentrations of organic carbon were measured by wet oxidation of carbonate-free samples in an Oceanography International total carbon analyzer. Inorganic carbon was determined by acidification of dried samples and measurement of the evolved CO₂ in the same system. Inorganic carbon concentrations were converted to CaCO₃ concentrations assuming all of the inorganic carbon was present as calcite. Adequate material remained available after other analyses only in the traps at 60 m and 80 m to allow determination of organic matter C/N ratios by combustion of carbonate-free samples in a Hewlett-Packard 185 CHN analyzer.

Milligram amounts of each sample were pyrolysed by rapid heating in quartz boats placed in a Chemical Data System Pyroprobe directly connected to a Finnigan 4500 mass spectrometer (Zsolnay and Harvey, 1985). A thermocouple near the sample verified that the pyrolysis temperature of 580°C was attained within 13 s.

Chemical ionization (CI) with methane was used after attempts to use low energy (30 eV) electron impact ionization of the pyrolysates proved to be too destructive to the pyrolysate fragments. Methane at a pressure of 133 Pa was ionized with

electrons at 130 eV. The charge was then transferred to the pyrolysates with little additional fragmentation, thereby better preserving the pyrolysate fragment ions in the mass spectra (*e.g.* Milne and Lacey, 1974). In general, CI with methane produces protonated pyrolysate ions (M+1). Adducts of M+29 and M+41 are also possible, but they are quantitatively minor under the conditions used (Zsolnay, unpublished).

The ions were separated with a Finnigan 4500 quadrupole mass spectrometer and counted with an electron multiplier at a scan rate of 50-260 atomic mass units per second. The were processed with a Finnigan INCOS data system. All analyses were done in triplicate, resulting in a coefficient of variation of 4% for all mass peaks larger than 1% of the base peak. Mass peaks smaller than 1% of the base peak were too variable to be counted accurately, and their data were rejected. Further analytical details are provided by Zsolnay (1991).

Solvent-extractable aliphatic hydrocarbons were obtained by dichloromethane Soxhlet extraction of the freeze-dried samples and column chromatographic separation of the resulting lipid mixtures as described by Meyers *et al.* (1984). The isolated hydrocarbon fractions were analyzed with a Hewlett-Packard 5830 FID capillary gas chromatograph and a Hewlett-Packard 5993 GC-MS equipped with an SP2100 (Supelco) capillary column.

RESULTS AND DISCUSSION

Considerable differences are evident in the material collected at the five depths at Station 8 (Table 1). Concentrations of organic carbon decrease markedly from 29% of the total weight of the material in the epilimnion trap to values that vary between 2.8% and 8.1% in the deeper traps. The fraction of calcium carbonate is nearly constant (*ca.* 36%) in the upper three traps, but it increases to about half the total material in the lower two traps. Earlier studies (Meyers *et al.*, 1980; Eadie *et al.*, 1984; Meyers *et al.*, 1984; Meyers and Eadie, 1993) have shown that relatively fresh algal biomass dominates the contents of sediment trap material from the epilimnion and that resuspended bottom sediments make up most of the material in near-bottom traps. The major source of bottom sediments to Lake Michigan is from erosion of

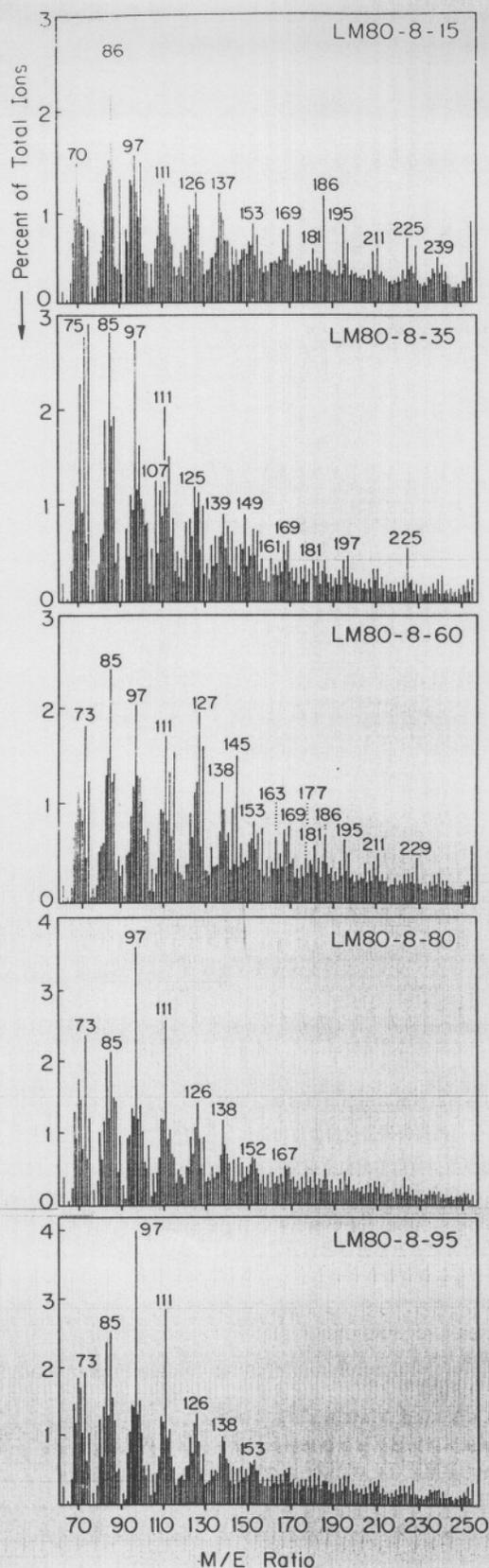


Figure 1 Pyrolysis-chemical ionization mass spectra of organic matter in sediment traps from five depths at Station 8 in southeastern Lake Michigan. Note that compositions change with depth and that the two deepest trap samples are similar in pyrolysate composition.

shoreline glacial moraines, and the surficial sediments typically contain only 1-2% total organic carbon (Rea *et al.*, 1981). The glacial till contributes a significant fraction of dolomitic limestone to the bottom sediments, and the increase in carbonate content of the two deep traps probably results from resuspension of this fine-grained clastic component. As organic matter associated with the sinking particles is remineralized and is progressively diluted by resuspended sediments at deeper depths, the proportion of organic carbon declines.

The mass spectra show that the bulk composition of the organic matter associated with the sinking particles changes with depth. Important spectral patterns are clear in Figure 1. Moreover, the lack of difference between the spectra of the two deepest samples is noteworthy, inasmuch as resuspension of bottom sediments is postulated to dominate their characteristics and thereby to impose similarities on these samples.

The sinking particles from the epilimnion contain organic matter which is distinctively different from what is found in the deeper traps, a finding that is consistent with earlier studies using biomarker fractions to conclude that algal material dominates sinking particles in the epilimnion of this lake (Meyers *et al.*, 1980, 1984; Meyers and Eadie, 1993). The ion having an m/z of 86, which is a large contribution to the 15 m spectrum, is probably a nitrogen-containing fragment (Zsolnay and Harvey, 1985). Absence of major contributions of m/z 86 in any of the deeper trap samples indicates that the source material of this pyrolysate fragment is a reactive component of organic matter and has been destroyed during the short time that accompanies sinking of the particles. Hedges *et al.* (1988) found from sediment trap studies in Dabob Bay, Washington, that amino compounds were preferentially remineralized during sinking. The m/z 86 peak consequently may represent proteinaceous matter that is particularly sensitive to recycling in the upper water column.

According to the m/z assignments of Leinweber *et al.* (1992), the m/z 85 and m/z 97 fragments are derived from saccharides. The presence of a relatively large proportion of this material in the trap samples is in good agreement with the results of Benner *et al.* (1992), who found that polysaccharides compose up to 50% of the colloidal fraction of organic matter in seawater. A similar bulk organic matter composition may hold true in the open waters of Lake Michigan. The m/z 97 fragment dominates the spectra of the two deeper traps. This fragment also dominated the pyrolysate spectra of surficial sediments from the Venezuela Basin (Zsolnay, 1991). The second-most abundant ion in the spectra from the 80 m and 95 m samples is m/z 111, which Zsolnay and Harvey (1985) found to be one of the fragments indicative of humic, as opposed to fulvic, acid contributions. As concluded from biomarker analyses by Meyers *et al.* (1984), the organic matter associated with near-bottom resuspended sediments is dominated by

land-derived material. These pyrolysate data support the hypothesis that the deeper traps collect predominantly resuspended bottom sediments (Eadie *et al.*, 1984). The large increase in sediment flux rates in the near-bottom traps (Table 1) also suggests substantial resuspension of bottom sediments.

Progressive degradation of organic matter during sinking is also indicated by the ratios of C_{17}/C_{29} biomarker *n*-alkanes (Table 1). This ratio represents the relative proportions of aquatic vs. vascular land plant contributions of lipids (*cf.* Giger *et al.*, 1980; Meyers and Ishiwatari, 1993). The value of 10 in the material from the epilimnion trap indicates a dominance of algal hydrocarbons in particulate matter from the upper waters of Lake Michigan. The ratio decreases rapidly with depth. This decrease implies rapid destruction of the contribution from lake algae to total extractable hydrocarbons. The destruction evidently involves algal organic matter in general in view of the large decrease in organic carbon concentrations that occurs with greater water depth (Table 1). The progressive decrease in the C_{17}/C_{29} ratio with depth confirms that preferential remineralization of lake-derived organic matter continues into the hypolimnion. Furthermore, the low C_{17}/C_{29} ratio found in the lowermost nepheloid layer sample (Table 1) indicates resuspension of bottom sediments (Meyers *et al.*, 1984; Robbins and Eadie, 1991; Meyers and Eadie, 1993), consistent with the findings from the pyrolysate data.

There is also a possibility that lateral delivery of detrital land-derived material contributes to lowering the C_{17}/C_{29} ratio in the lower three traps. The C/N ratios of the 60 m and the 80 m organic matter are 7.1 and 8.0, respectively. These are close to the value of 8.9 found in suspended fluvial particulate matter collected at the mouth of the Grand River and are substantially different from the value of 19 in suspended particulate matter from surface waters collected 20 km offshore in Lake Michigan (Meyers *et al.*, 1984). The detrital matter may be transported in the thermocline region as a turbidity flow associated with the river-borne sediments. The pyrolysate mass spectrum from the 35 m trap at the thermocline contains large contributions of probable nitrogenous materials (m/z 74 and 76 in Figure 1), whereas the spectrum from the 60 m trap below the thermocline lacks these ions and instead has a large m/z 127 contribution which is indicative of saccharides (Leinweber *et al.*, 1992). These differences imply a larger proportion of land-derived, cellulosic organic matter in the 60 m trap than in the 35 m trap.

SUMMARY AND CONCLUSIONS

Pyrolysis-chemical ionization mass spectrometry of the total organic matter associated with settling particles reveals new information about the changes that occur during the earliest phases of organic matter sedimentation in Lake Michigan.

Comparisons of pyrolysate mass spectra of material intercepted at progressively deeper water depths show that organic matter derived from algal production experiences massive destruction in the upper parts of the water column. In particular, the mass spectral patterns indicate that proteinaceous material is selectively lost in the earliest stages of particle sinking. Ratios of C_{17}/C_{29} *n*-alkanes similarly reflect major losses of algal contributions during sinking of particles through the epilimnion. Organic matter in near-bottom sediment traps appears to contain predominantly humic acid-like material and has *n*-alkane compositions dominated by land-plant components. The organic matter in these deeper traps appears to consist mostly of contributions from resuspended bottom sediments and to be principally derived from land plants.

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