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Application of Environmental Organic Petrology and Geochemistry to Fingerprint Organic Pollutants in the Recent Sediments of Lake Ontario

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Abstract. Selected surface sediment samples (sediment depth 0-10 cm) collected in the Niagara basin (western Lake Ontario) were chosen for organic matter characterization using organic petrological and geochemical techniques normally reserved for the study of coal, petroleum source rock and crude oil. The study was performed to assess the effectiveness of these techniques in discriminating between natural and anthropogenic organic matter and to determine the extent of organic pollution of the lake sediments. The organic carbon contents of the samples vary from 1.5 to 3.5%, with upper layer (0-5 cm) samples have higher TOC values than those from the lower layer (5-10 cm) at each site. Relatively low Rock Eval hydrogen indices and high oxygen indices are consistent with dominance of the pyrolyzable organic matter by recent input. This is supported by the Py-GC/MS results, as on the molecular level, the pyrolyzates are complex mixtures of (predominantly short-chain) aliphatic hydrocarbons, simple phenols, abundant organonitrogen compounds, and simple monoaromatic and polyaromatic hydrocarbons, with only minor variation between samples. The organic petrologic results indicate a greater diversity, showing a predominance of amorphous organic matter (AOM) in some samples and of coaly debris and combustion residues in others. Since the latter type of organic matter typically has low pyrolysis yields, the chemical techniques employed understated its importance. Its presence is indicative of direct anthropogenic input to the lake sediment. The AOM is at least in part the result of anthropogenic perturbation of the ecosystem, being the sub-fossil remains of degraded algal and bacterial biomass whose growth had been stimulated by artificially high nutrient flux to the lake waters, particularly during the past century. The results of the study show the benefits derived from the tandem application of organic geochemical and petrologic techniques to environmental problems.

Key words: lake sediments, organic petrology, organic geochemistry, anthropogenic

Index Terms/Descriptors: biota, environmental forensics, Great Lakes, hydrocarbons, industrial waste, Lake Ontario, North America, organic matter, organic pollutants, organic materials, petroleum products, phytoplankton, plankton, pollutants, pollution, pyrolysis-gas chromatography-mass spectrometry, sediments, waste disposal, water quality

Introduction

Environmental organic petrology is a new branch of microscopic science which identifies and characterizes the proportion of natural (both recent and ancient) and anthropogenic organic matter in recent sediments from ocean and lake environments (Mukhopadhyay *et al.*, 1995; 1996). Application of this technique depends on comprehensive knowledge of the petrology of all forms of coal (from peat to anthracite), solid bitumen, crude oil, combustion residues (fly ash, char, coke, etc.), forest fire residues, kerogen, recent palynomorphs, household combustion products of wood, and an acquired knowledge of the petrology of chemical products, sewage, plastic, etc. Although the pollutants in recent sediments can be in both particulate and dissolved forms, the present study is devoted to the particulate organic matter in sediments. An excellent annotated review by Depers (1994) on environmental organic petrology makes the point that most earlier publications mainly focused on coal combustion residues, and that data on other contaminants, for example, sludges, stockpile waters, etc. are totally lacking. Data on the petrology of some specific contaminants such as crude oil, chemical, plastics, sewage effluent, etc. in recent sediments are nonexistent. In the Great Lakes, Bostick (1994) studied the petrology of anthropogenic contaminants from the Lake Michigan which he identified as derived from "coal-dust" and coal combustion products.

Lake Ontario lies at the end of a chain of five Great Lakes bordering USA and Canada (Fig. 1). The basin of Lake Ontario rests in limestone, dolomite, and shale of Upper Ordovician to Middle Silurian age (Hough, 1958). The lake axis trends 306 km east to west with a maximum width of 84 km; the maximum depth is 244 m and the lake surface is ca. 75 m above sea level. Three major sediment units are recognized: (a) glacial till and bedrock; (b) glaciolacustrine clay; and (c) post-glacial mud, sand, and silt (Thomas *et al.*, 1972 a, b). The postglacial recent muddy sediments in western Lake Ontario are the subject of this research.

The present research was initiated to groundtruth sediment acoustic mapping in 1992-1994 by scientists of the Marine Environmental Geoscience Group of the Geological Survey of Canada based at the Bedford Institute of Oceanography. The mapping by sidescan sonar and multibeam sonar revealed numerous linear reflectivity anomalies on the muddy lakebed. These anomalies commonly appear as elongated or aligned dark areas on the geophysical records representing zones of anomalous backscatter less than 20 m in width and ranging in length from several hundred meters to 2.5 km. Seismic reflection data suggest the anomalies have no surface or subsurface expression, and do not correlate with known textural changes in the surface sediments (Thomas *et al.*, 1989, 1993; Cameron and Lewis, 1994). The present research was initially undertaken to document the proportions and characteristics of the organic components in the finer fractions of surface sediments from the anomalous zones (sites 27 and 50; Fig. 1) and also from other sites not associated with the anomalies.

The larger objectives of this research are to (a) identify and quantify the proportions of natural and anthropogenic organic matter in various sample locations of western Lake Ontario; (b) show the vertical and lateral variations of natural and anthropogenic organic

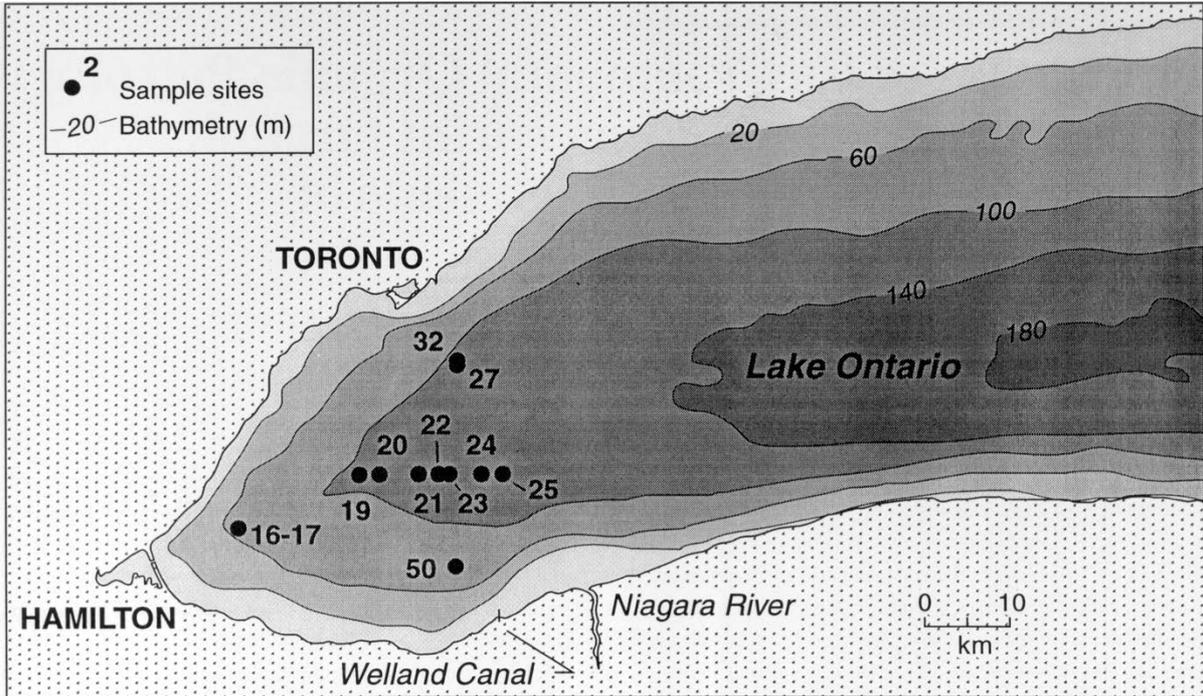


Fig. 1. Location map of sampling sites in western Lake Ontario.

matter; and (c) identify the possible sources of anthropogenic organic matter. The hypothesis proposed is that conventional organic petrologic and geochemical techniques used in fossil fuel exploration can provide critical information in environmental studies, especially given the fact that many industrial pollutants are derived from petroleum and coal.

Sampling and analytical procedures

Relatively undisturbed sections of lakebed mud about 900 cm² in area and 10 cm deep were carefully raised and transferred to the decks of the research vessels in 1993 (CCGS *Griffin*) and 1994 (CCGS *Samuel Risley*) using a Van Veen grab sampler. The dark gray to black reduced mud was covered with a brown oxidized surface layer from a few mm to 1 cm thick. Subsample layers comprising the 0-5 cm and 5-10 cm intervals below the top of sediment were collected from most samples and stored at 4 °C for subsequent analysis. For the few sites (27, 32, and 50) in the acoustic backscatter zones, only the 0-5 cm layer was available for study. The remaining sample sites (16-25) comprise a transect across the zone of modern mud deposition in western Lake Ontario.

Estimates of time represented by the 5-cm sample intervals range from 15 to 45 years approximately. Relatively long-term accumulation rates, based on a rise in *Ambrosia* (ragweed) pollen content since 1850 A.D. averaged for 5 sites in western Lake Ontario, suggest that it required an average of 40-50 years to deposit 5 cm (about 0.036 g cm⁻² yr⁻¹) (Kemp and Harper, 1976). Shorter-term accumulation rates based on ²¹⁰Pb and ¹³⁷Cs radiometric measurements at one site indicate about fifteen years per five cm (about 0.075 g cm⁻² yr⁻¹). Discontinuities in ²¹⁰Pb activity profiles from this and other cores in the Great Lakes suggest that erosion and redistribution events associated with major storm surges occur periodically in the deep offshore basins of the lakes (Robbins *et al.*, 1978). Though it is assumed the sample intervals analyzed in this study represent continuous deposition over 1-2 decades, it is possible some contain hiatuses and redistributed sediment due to storm surge activity.

Of the twenty-one samples available, all were analyzed by organic petrology and 18 by Rock-Eval pyrolysis (Tables 1 and 2). Eight samples were analyzed by pyrolysis-gas chromatography/mass spectrometry (Py-GC/MS).

For the organic petrologic study, the organic matter were isolated from its inorganic matrix using the standard methods for kerogen isolation in petroleum source rock analysis (Tissot and Welte, 1984). Two types of sample preparations (polished block and smear slide) were made and all samples were studied under incident and transmitted light using white and blue light illumination. Volume percentages of various components were recorded by point counting (ASTM, 1991). Maceral or phytoclast (coal, kerogen, and bitumen) and vitrinite reflectance studies were conducted using a Zeiss Axioskop microscope with a MPM 03 photomultiplier following standard methods (Stach *et al.*, 1982; ASTM, 1991). For the identification of combustion by-products, the standard method and the methods adopted by earlier researchers were followed (ASTM, 1991; Gray and DeVaney, 1986; Bailey *et al.*, 1990; Hower *et al.*, 1994; Crelling, 1996). For the characterization of plastics and chemicals, a comparison was made based of microscopic studies of reference materials such as

styrofoam, plastic, paints, etc.

Py-GC/MS analyses of the sediment was performed using a CDS 120 pyroprobe, coupled to a HP 5890 gas chromatograph with a HP 5970 mass selective detector and a 50 m HP-1 column (0.2 mm i.d., film thickness 0.33 μm). A measured amount of dry, powdered sediment (≈ 5 mg) was pyrolyzed in a flow of helium for 20 sec in a platinum coil at 610°C, as measured by a thermocouple in the sample holder. Poly-*t*-butylstyrene was added as an internal standard. The GC oven was operated under the following program: isothermal for 5 min. at 40°C; temperature programmed at 5°C/min. to 300°C and then isothermal for 20 min. The MS was operated in full scan mode (50-550 daltons, 0.86 scans/sec., 70eV ionization voltage). Compounds were identified based on mass spectra and GC retention indices, with reference to the Wiley and U. S. National Bureau of Standards computerized mass spectral libraries and the literature (Hartgers *et al.*, 1992; Nip *et al.*, 1992; Sinnighe Damsté *et al.*, 1992a,b; Krugé and Bensley, 1994; Sicre *et al.*, 1994; Stankiewicz *et al.*, 1996).

Results and discussion

Bulk geochemistry

The organic carbon contents of the samples vary from 1.5 to 3.5% (Table 1, Fig. 2), within the range of 1 to 4% determined by Thomas and coworkers (1972a,b) to be typical for Lake Ontario sediments. The new data also show that the upper layer (0-5 cm) samples have higher TOC values than those from the lower layer (5-10 cm) at each site (Table 1, Fig. 2), consistent with previous work in eastern Lake Ontario documenting decreasing TOC contents with increasing sediment depth (Schelske *et al.*, 1988; Schelske and Hall, 1991). The highest TOC contents were noticed in the upper layer at sites 19 and 25. Amounts of pyrolyzable organic matter (Rock Eval S₂) are relatively low (between 2 and 6 mg/g sediment), giving low hydrogen indices (118-204 mg pyrolyzate/g TOC, Table 1). The low T_{max} values of all samples (414-424 °C) suggest that the pyrolyzates are primarily produced from "low rank", recent organic matter and are not greatly influenced by the mature anthropogenic organic matter present. Thermally extractable organic matter (Rock Eval S₁) is also not abundant (0.3-0.8 mg/g sediment), but its ratio to S₂ (Rock Eval production index) is high enough (0.10-0.18, Table 1) to suggest the presence of mature petroleum products (Espitalié *et al.*, 1985) or other semi-volatile organic matter. Usually the production index of immature recent sediment (kerogen type I or II source rocks) without any allochthonous bitumen varies between 0.01 to 0.04. Relatively large amounts of CO₂ were produced upon pyrolysis, with S₃ values ranging from 3.7 to 5.2 mg/g sediment (Table 1). The resulting oxygen indices are also high (159-292 mg CO₂/g TOC).

A conventional interpretation of the hydrogen and oxygen indices (following the criteria of Espitalié *et al.*, 1985) would suggest that the Lake Ontario sedimentary organic matter is predominantly of terrestrial origin and is of extremely low rank. However, since the samples are recent sediments and not petroleum source rocks (for which the Rock Eval technique was originally developed), facile interpretations should be avoided. It can however

Sample Locations	Total Organic Carbon (wt %)	T _{max} (°C)	S ₁ (mg HC/g sediment)	S ₂ (mg HC/g sediment)	S ₃ (mg CO ₂ /g sediment)	Production Index (S ₁ /S ₁ + S ₂)	Hydrogen Index (mg HC/g total organic carbon)	Oxygen Index (mg CO ₂ /g total organic carbon)
16-Upper	2.79	420	0.85	5.69	4.46	0.13	204	160
16-Lower	2.50	417	0.52	3.88	4.29	0.12	155	172
17-Upper	2.68	420	0.56	3.88	4.39	0.13	145	164
17-Lower	2.44	418	0.46	3.31	4.22	0.12	136	173
19-Upper	3.05	421	0.62	5.18	5.18	0.11	170	170
19-Lower	2.62	421	0.43	3.98	4.70	0.10	152	179
20-Upper	2.32	414	0.69	3.15	4.35	0.18	136	188
20-Lower	1.86	416	0.41	2.54	4.10	0.14	137	220
21-Upper	1.87	424	0.31	2.72	4.38	0.10	145	234
21-Lower	1.60	421	0.25	1.88	4.67	0.12	118	292
22-Upper	1.90	421	0.30	2.44	4.49	0.11	128	236
22-Lower	1.62	419	0.32	2.08	3.66	0.13	128	226
23-Upper	2.28	419	0.41	3.17	4.24	0.11	139	186
23-Lower	1.97	419	0.32	2.46	4.04	0.12	125	205
24-Upper	2.31	420	0.42	3.15	4.34	0.12	136	188
24-Lower	1.76	416	0.32	2.11	3.89	0.13	120	221
25-Upper	3.02	422	0.68	5.13	4.79	0.12	170	159
25-Lower	2.23	419	0.39	2.92	4.22	0.12	131	189

Table 1. Total organic carbon and Rock-Eval pyrolysis data of samples from various sites, western Lake Ontario.

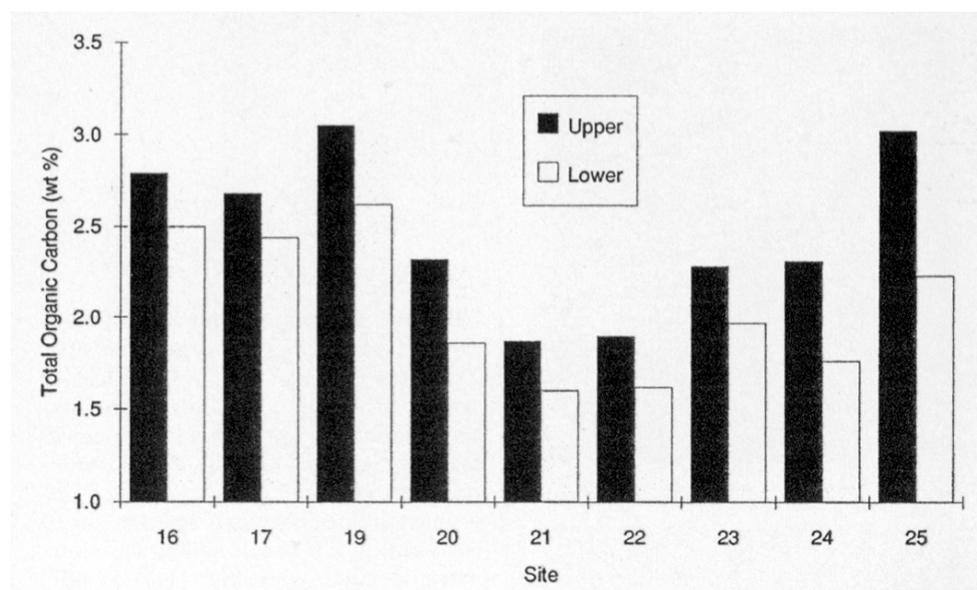


Fig. 2. Total organic carbon contents at each sample site.

be said at this point that the organic matter apparently does not have an important aliphatic component and that it has been partly oxidized during sedimentation and/or is fresh enough that it still retains abundant carbohydrates. It is noteworthy that both upper and lower samples from sites 21 and 22, as well as the lower samples from sites 20, 23 and 24 are distinguished by particularly high oxygen indices (>200 mg/g TOC) and low hydrogen indices (<150 mg/g TOC, Table 1).

Petrographic composition of organic sediments

The samples can be distinguished by the grain size of their organic components. Those from sites 27, 32, and 50 have organic fragments usually greater than 50 μm , with many fragments >100 μm . The organic particles from sites 16, 20, 21, and 22 are very fine grained (mostly <25 μm). The other samples (from sites 17, 19, 23, 24 and 25) have organic fragments intermediate in size.

The natural organic matter observed in sediments from Lake Ontario usually includes two populations of particulate components (Table 2). The first is the autochthonous population which includes phytoplankton (alginite; Fig. 3a), bacterial clusters (Fig. 3d), and fungal residues (Fig. 4a). The second population includes arboreal lignin-rich (nonfluorescent to dark fluorescent) or cellulose-rich (yellow fluorescent) humic particles (huminite; Figs. 3b, 4b), spores, pollen, resin, and suberin (exinite; Figs. 3a, 3b, and 3c), and charcoal (from forest fires). These natural components have morphologies similar to various macerals previously reported by Mukhopadhyay *et al.* (1985a) and Mukhopadhyay (1990). The second population also contains clasts of organic-rich shale and fragments of vitrinite (Figs. 4a and 4b) or inertinite (Figs. 3b, 4c). The second population is considered allochthonous, with its components derived from terrestrial vegetation in the drainage basin and the erosion of pre-existing sedimentary sequences surrounding Lake Ontario. The components have been transported to the lake with other clastics by river, wind or ice action.

The anthropogenic particulate organic matter is extremely diverse in composition (Table 2). Anthropogenic particles are mainly derived from four sources:

- Fragments of coal (all sites except Sites 22 and 23; Fig. 4f; Mukhopadhyay *et al.*, 1984), coal combustion residues such as char (Figs. 3c, 4c and 4d), coke (Figs. 4a and 4f), fly ash (Fig. 4b), and charred wood (Fig. 4h)
- Combustion products of tar or pitch (Sites 27 and 32; Fig. 4g)
- Bunker or crude oil biodegraded to solid bitumen (all sites except site 16) or refined petroleum (diesel, gasoline, etc.; all sites except sites 22, 27, and 32)
- Manufactured chemicals - dry paints, plastics, styrofoam etc. (all sites) (Figs. 3a, 3b)

The components from the first three sources could be identified properly with normal petrographic techniques. Identification of components from the fourth group is somewhat problematic because a comprehensive collection of standard reference materials is not presently available for petrographers. Furthermore, at all sites there were some components which could not be identified given our present state of knowledge in organic petrology. Sites 19 and 24 contain the highest percentages of these unidentifiable components (Table 2).

The sediments at most sites contain coaly fragments. However, it was observed that

Sample Number	Anthropogenic Origin										Mixed Origin					Natural Origin		
	Coal	Oil	Solid Bitumen	Fly Ash	Coke/Char	SemiCoke/Char	Plastics and Chemicals	Unknown	Amorphous Matter	Organic	Vitrinite	Inertinite	Huminite	Exinite	Alignite	Fungi	Unknown	
16-Upper	1.5	5.0		1.5	8.5	0.5	1.0	1.0	43.5	3.5	6.5	1.5	3.5	7.5	10.0	5.0		
16-Lower		3.5		1.0	12.0	2.5	4.5	1.0	44.0	6.5	3.0	3.5	2.5	4.0	8.0	4.0		
17-Upper	0.5	0.5	3.0	1.5	11.0	4.5	1.5	2.0	50.0	3.5	6.5	2.5	3.5	2.0	4.5	6.0		
17-Lower	0.5	1.0	6.0	2.0	24.5	8.5	6.5	2.0	12.5	14.5	7.0	5.0	3.5	3.0	2.5	1.0		
19-Upper	0.5	1.0	2.5	3.0	23.0	10.0	8.0	17.0	2.0	13.0	5.0	3.5	5.5	4.0	2.0			
19-Lower	2.0	1.5	3.5	1.5	15.0	8.5	3.0	16.0	4.5	15.0	10.5	6.0	5.0	3.5	2.0	2.5		
20-Upper	0.5		3.5	3.0	8.5	3.5	3.0	2.0	61.0	4.5	4.5	1.0	1.5	4.0	2.5	0.5		
20-Lower		0.5	3.5	2.5	2.0	0.5	2.0	1.5	56.5	0.5	2.0	2.5	8.0	6.0	8.5	4.0		
21-Upper	1.0		3.5		3.5	0.5	3.5	4.5	62.0	3.0	0.5	1.0	2.5	5.5	4.5	4.0		
21-Lower			3.5	1.0	1.0		2.5	2.5	50.0	7.5	3.5	5.0	11.0	5.5	7.0			
22-Upper		2.0		1.0	1.5	1.0	1.0	1.5	70.0	3.5	2.0	5.0	1.0	0.5	7.0	8.0		
22-Lower			4.5	0.5	2.0	1.0	7.0	3.0	33.0	7.0	2.5	6.0	16.5	11.5	5.5			
23-Upper		0.5	3.0	1.5	32.5	5.5	6.0	15.5	0.5	16.0	7.0	4.0	2.0	3.5	2.5			
23-Lower	2.0	1.0	3.5	1.0	17.5	7.5	2.5	9.0	5.5	17.0	16.0	4.0	6.0	6.5	1.0			
24-Upper	1.5	1.5	1.5	1.5	18.5	10.0	3.0	10.0	7.0	20.0	11.0	2.5	3.5	2.5	4.0	2.0		
24-Lower	0.5		1.5	0.5	3.5	2.5	5.0	2.0	47.5	11.5	4.5	3.5	5.0	2.0	9.5	1.0		
25-Upper	2.0	4.5	2.0	0.5	13.5	3.5	4.0	13.0	6.0	11.0	17.0	5.5	4.5	4.0	6.5	2.5		
25-Lower	2.0	4.0	4.5	4.5	13.5	10.5	5.5	8.5	2.5	12.5	11.5	7.5	4.0	5.5	3.5			
27-Upper	10.0		5.5	4.0	32.5	20.5	2.5	6.0	3.5	3.5	2.5	3.0	3.5	2.5	0.5			
32-Upper	17.5		3.5	7.5	32.0	11.0	1.0	1.0	1.0	12.5	4.0	4.0	3.0	0.5	1.5			
50-Upper	5.0	1.0	6.0	0.5	28.5	20.0	2.5	5.5	2.5	7.5	7.0	4.5	6.0	2.0	1.5			

Table 2. Volume percentage of various natural and anthropogenic components from various sites of western Lake Ontario.

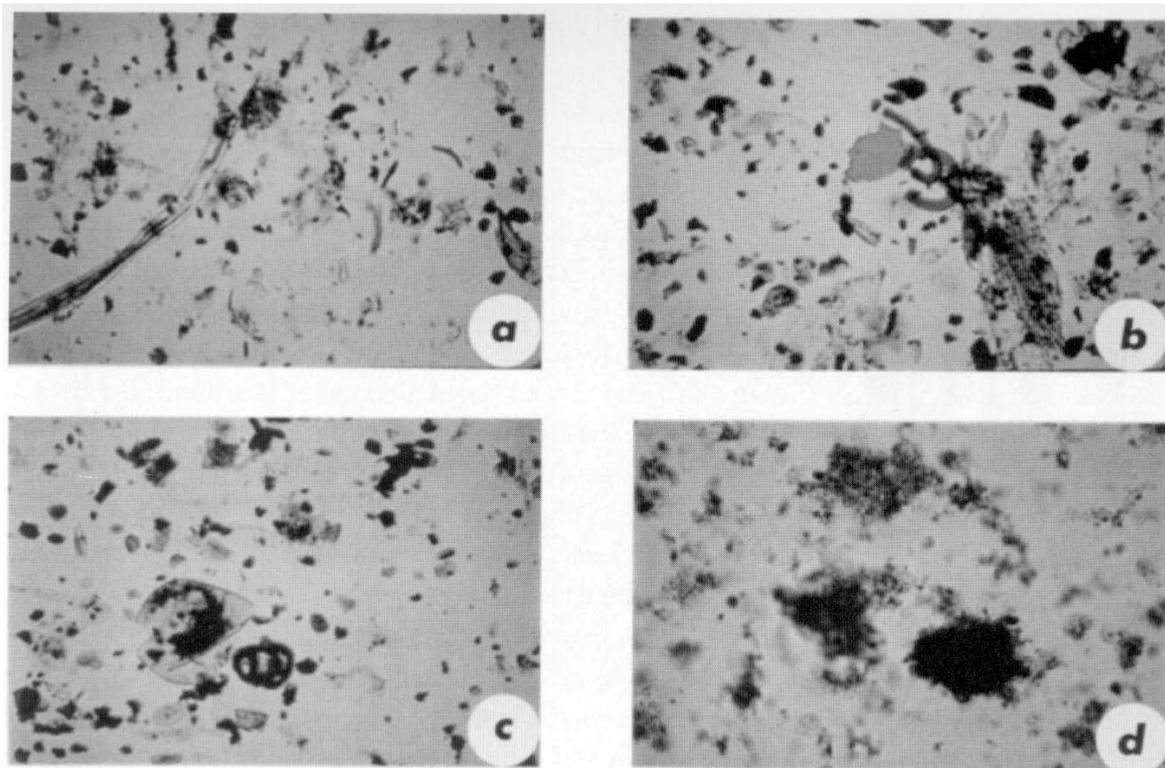


Fig. 3. Photomicrographs of natural and anthropogenic organic matter. Transmitted white light. Magnification: X400.

a. natural: phytoplankton, inertinite, huminite, vitrinite; anthropogenic: plastic. Sample: 17 (5-10 cm).

b. natural: huminite, pollen, phytoplankton, inertinite; anthropogenic: paint. Sample: 19 (0-5 cm).

c. natural: pollen, huminite, inertinite; anthropogenic: char. Sample: 19 (0-5 cm).

d. amorphous organic matter (AOM) with bacterial clusters. Sample: 16 (0-5 cm).

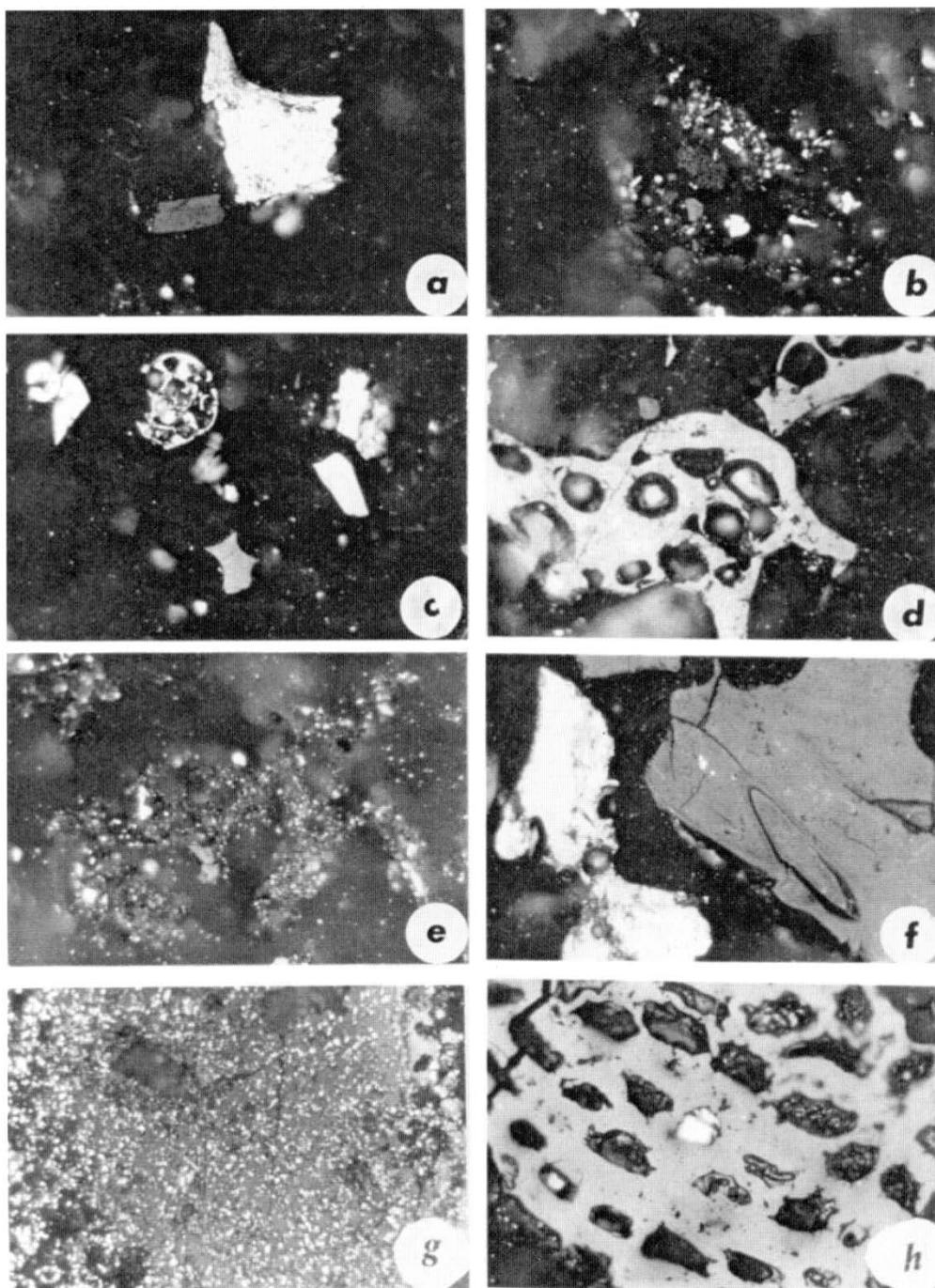


Fig. 4. Photomicrographs of natural and anthropogenic organic matter. Incident white light. Magnification X500.

- a. Natural: huminite, fungi; Anthropogenic: coke. Sample: 17 (5-10 cm).
- b. Natural: huminite, vitrinite, inertinite; Anthropogenic: unknown. Sample: 17 (5-10 cm).
- c. Natural: inertinite; Anthropogenic: char and coke. Sample: 17 (5-10 cm).
- d. Natural: none; Anthropogenic: large char grain. Sample; 50 (0-5 cm).
- e. Natural: amorphous organic matter (AOM), vitrinite; Anthropogenic: coke (fine grain), oil. Sample: 22 (0-5 cm).
- f. Natural: none; Anthropogenic: coke, large coal high volatile bituminous fragment. Sample: 50 (0-5 cm).
- g. Natural: none; Anthropogenic: partially combusted tarry products. Sample: 32 (0-5 cm)
- h. Natural: none; Anthropogenic: home combustion product of wood. Sample: 50 (0-5 cm).

there is no coal basin close to Lake Ontario which could be a local source of these coaly particles. Therefore, all coaly fragments identified in the samples are considered anthropogenic (Table 2). However, the provenance of isolated particles of vitrinite and inertinite cannot be assigned unambiguously. They may originate from anthropogenic coal debris or have been weathered out of clastic sedimentary rocks in the drainage basin by natural processes.

The abundance of amorphous organic matter (AOM) is notable in Lake Ontario sediments (Figs. 3d, 4e). AOM (or bituminite or sapropelinite; Teichmuller and Ottenjann, 1977; Mukhopadhyay *et al.*, 1985b) can be derived from the natural degradation of palynomorphs by bacteria and fungi. It can also be derived from sewage or agricultural refuse which contain bacteria and fecal pellets. AOM, whether derived from either natural or anthropogenic sources, has a characteristic texture, i.e. fluffy and granular with a yellow to brown fluorescence (Figs. 3d and 4e). The absence of anoxic bottom water within the lake suggests that the AOM is mostly derived from aerobic bacterial alteration of "natural" components, such as algae from the photo zone. However, the "natural" vs. "anthropogenic" distinction is obscured in this case as the nutrient supply to the lake has been artificially increased since the advent of European settlement in the drainage basin (Schelske *et al.*, 1988; Schelske and Hall, 1991). Therefore, these components are likely to be due to the natural response to a human perturbation of the ecosystem and are therefore classified as being of "mixed" derivation in Table 2.

In contrast to the organic carbon data (Fig. 2), there is no regular increase or decrease in the relative volumes of individual components with sediment depth (Table 2, Figs. 5a, 5b). Individual sites may have distinguishing features, however. Site 17 has several particles of yellow-fluorescing solid bitumen. The lower part of site 16 has abundant highly fluorescent patches typical of crude oil (considered as possible refinery product in this case). Upper and lower sediment samples from sites 19, 23, and 25 contain a high proportion of char and coke structures which are less than 50 μm in size, whereas sites 27, 32, and 50 have char, coke and coal fragments which are often greater than 100 μm (Figs. 4d, 4f). Sites 27 and 32 have combustion residues which are possibly derived from the combustion of a tarry petroleum product (Fig. 4g). Plastic and possible dry paint are common in minor proportions in all samples.

It was noted that the organic particles from sites 16, 20, 21, and 22 are finer grained compared to sites 17, 19, 23, 25, 27, 32, and 50. Compositionally, the finer grained samples tend to have relatively more AOM and less combustion residues (Table 2, Figs. 5a, 5b). Using the combustion residues as indicators for unambiguous input of anthropogenic pollutants, it is evident that the sites with the coarser grained organic sediments have suffered greater direct contamination. Among the "coarse-grained" samples, it was mentioned above that the combustion residue particles from sites 23, 25, 27, and 50 were especially coarse, which suggests that these were actual dumping sites for the pollutants. The combustion residues in sites 17 and 19, being somewhat less coarse, were possibly transported from their actual dumping sites by lake water circulation and fragmented. Alternately, they could have been transported from the power plant stacks or ship chimneys as air pollutants.

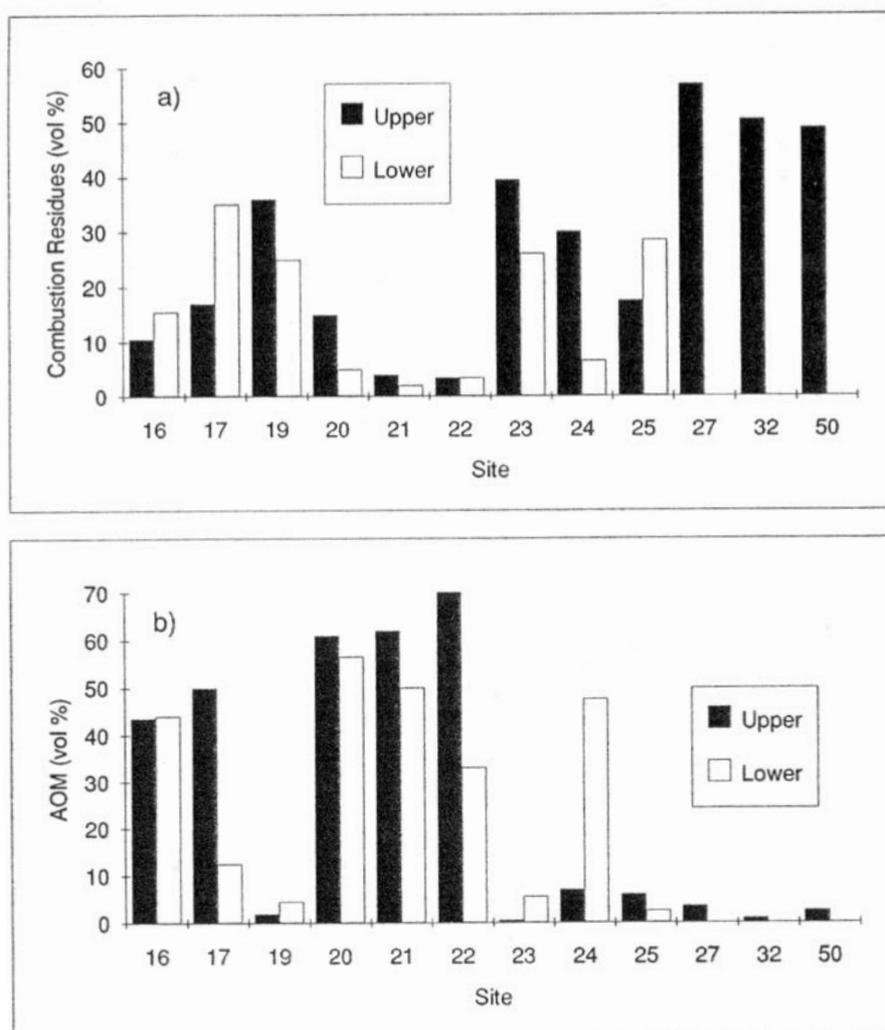


Fig. 5. Distribution of selected organic components (volume %) as determined by quantitative petrographic examination. a. Combustion residues. b. Amorphous organic matter (AOM).

Sample Site	Huminite	Vitrinite	Coal	Inertinite	Semichar/Coke	Char	Coke	Bitumen/Pitch
17-Upper	0.15–0.40	0.57–0.82	0.56–0.76	1.52–2.09	1.05–2.63	3.42–5.83	5.05–7.22	
17-Lower	0.18–0.30	0.64–0.87	0.53–0.70	1.05–2.21	1.51–2.56	3.34–5.07	4.70–6.35	
25-Upper	0.20–0.46	0.59–0.86	0.56–0.82	1.95–2.87	1.14–3.96	3.09–4.85	4.56–6.52	0.35
25-Lower	0.20–0.30	0.59–1.24	0.58–1.40	1.85–2.36	1.21–3.76	3.49–5.95	5.85–7.40	
27-Upper		0.48–1.43	0.71–1.00	0.95–2.2	0.77–3.36	3.3–5.22	4.45–6.45	2.01
32-Upper	0.42–0.45	0.43–0.75	0.68–0.96	2.32–2.67	1.05–1.27	2.02–4.84	2.38–4.42	0.36 (dark) 2.56–3.12
50-Upper	0.22–0.30	0.54–0.74	0.67–1.95		1.36–2.13	2.58–4.07	3.44–6.71	0.36

Table 3. Range of reflectance of various components from different sites of western Lake Ontario.

Table 3 shows the range of reflectance values for various components, including the upper and lower parts of the cores from sites 17 and 25 and the uppermost sediment at three other sites. The reflectance of vitrinite was measured on both single vitrinite grains and in the vitrinite part of coaly fragments. The huminite reflectance suggests that these components were derived from the degradation of peat and lignite. The maturation of vitrinite grains within the coaly fragment suggests that these coals have a rank range from high volatile bituminous C to low volatile bituminous. The low reflectance ($< 2.0\%$ R_O) of semi-char or semi-coke suggests incomplete combustion or combustion of wood. The reflectance of char in all samples is lower than for coke. The combustion residue of the tarry product has two types of components: one which is dark, with a reflectance of 0.36% R_O , and one which is yellowish-white having a reflectance of 2.56 to 3.12% R_O .

The drainage area of western Lake Ontario supports a large human population (nearly 3 million) and several industries including oil refining, cement manufacture, coal-fired power generation, steel making, and sewage processing at various locations between Hamilton and Toronto and in the Buffalo area, upstream along the inflowing Niagara River (Fig. 6). Figure 6 also illustrates the main shipping routes in the lake, which is heavily used by bulk cargo-carrying vessels. Over 16 million tons are processed annually at nine ports around western Lake Ontario and in the Welland Canal, two thirds of which is moved to and from Hamilton. Of this amount, a Canadian Coast Guard-sponsored study estimates that 280,600 kg are spilled annually into the open lake (Melville Shipping Ltd. and LGL Ltd., 1993). Accordingly, the main organic pollutants probably came from: (a) ship traffic in western Lake Ontario; and (b) industrial plants around Toronto, Hamilton, and Buffalo whose effluents were transported offshore by the circulation of air and water. (c) atmospheric dispersal of home heating combustion products. The abundance of large size ($>100 \mu\text{m}$) coal, ash fragments, and incomplete combustion products as observed in sediments from sites 27, 32 and 50 suggest that combustion residues and coal fragments were dumped by ships near these locations. Coal and coke fragments, for example, could be sweepings and debris trails from bulk cargo-carrying ships which commonly use the lake. Other chemical products such as plastic and paints may have also come from ships.

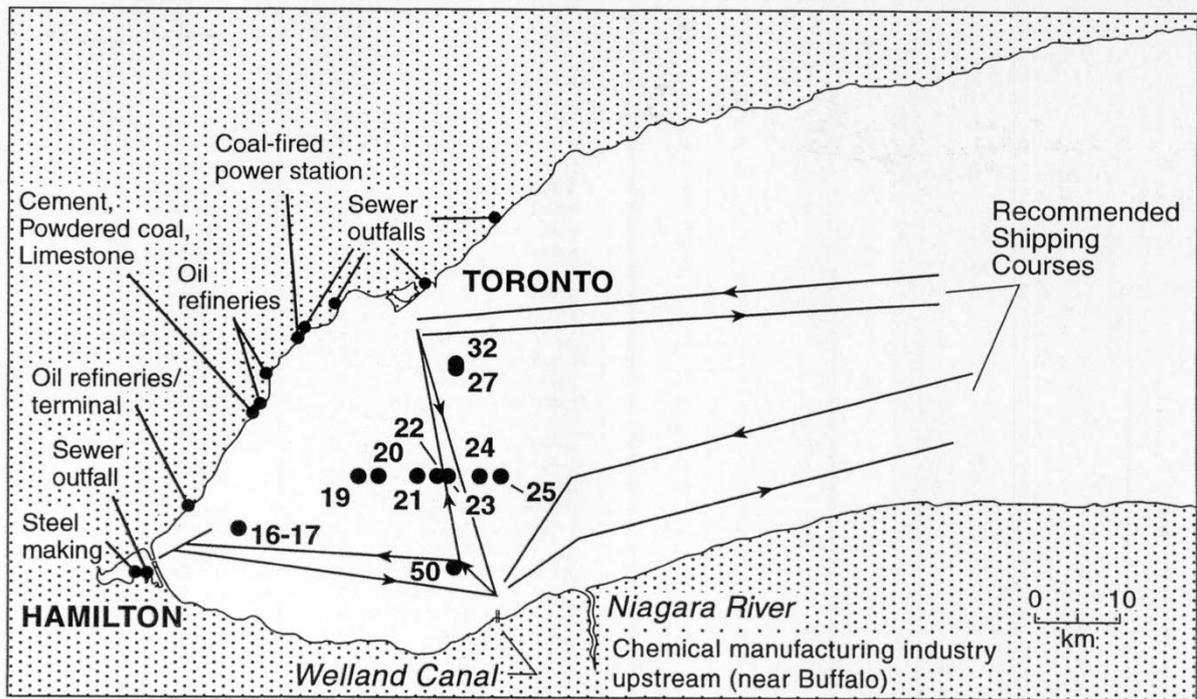


Fig. 6. Possible sources of organic pollutants surrounding western Lake Ontario.

Molecular characterization

The pyrolyzates of all samples analyzed (upper and lower core sections from sites 17, 19, 21 and 25) show strong similarities, with only subtle differences. They are complex mixtures of monoaromatic, polyaromatic and aliphatic hydrocarbons, phenols and organonitrogen compounds. The pyrogram produced from the upper sediments at site 25 is shown as a representative example (Fig. 7). The distribution of aliphatics in the pyrolyzates (*n*-alkanes and *n*-alk-1-enes with *n*-C₉ to *n*-C₂₃ predominating) suggests multiple precursors, including the lipid portions of algal and bacterial biomass, as well as possibly petroleum asphaltenes. The distribution of alkylbenzenes in the pyrolyzates shows a clear predominance of toluene [3] over the more highly alkylated [9, 10, 12, 19, 21, 23]. This is consistent with a derivation from aquatic organic matter (Peulvé *et al.*, 1996) or possibly inertinite (Stankiewicz, 1995; Kruge *et al.*, 1994). C₂-C₄ alkylbenzenes would have been relatively more abundant in the pyrolyzates of petroleum asphaltenes (e.g., Kruge *et al.*, 1996) and vitrinites of bituminous rank (Krugue and Bensley, 1994). (Numbers in square brackets refer to peak numbers in Fig. 7.) The presence of styrene [11] indicates anthropogenic input. Naphthalenes [34, 39, 40, 42, 43] are in relatively low concentrations in the pyrolyzate. Larger polynuclear aromatic hydrocarbons (PAH) [44, 49, 52, 53] are even less abundant. The distributions of the PAH isomers favor the parent and monomethylated compounds over the more highly alkylated, compatible with the pyrolysis of autochthonous organic matter (Peulvé *et al.*, 1996) and inertinite (Stankiewicz, 1995; Kruge *et al.*, 1994), rather than petroleum asphaltenes or vitrinite. The overall low abundances of the 2- and 3-ring PAH in the pyrolyzate, as well as the lack of larger PAH, precludes major contributions from fossil fuels and combustion residues to this sediment, somewhat in contradiction to the petrographic results.

Phenols are among the most important compounds in the pyrolyzates (Fig. 7), with phenol [18] and methylphenols [27] strongly predominating over the C₂-alkylphenols [30, 31] and higher homologues. Phenols are recognized to be the major pyrolysis products of vitrinite, especially of high-volatile bituminous rank, however in such cases, the relative contribution of the C₂-alkyl isomers is much greater (e. g., Kruge and Bensley, 1994). As was the case with the aromatic hydrocarbons, the phenol distributions in the pyrolyzate are more compatible with autochthonous organic matter and/or inertinite (Peulvé *et al.*, 1996, Stankiewicz, 1995; Kruge *et al.*, 1994). A few methoxyphenols were detected, but only in trace amounts. These compounds are important lignin pyrolysis products (Saiz-Jimenez and de Leeuw, 1986) and their lack in the pyrolyzates of the Lake Ontario sediments indicates a paucity of intact lignin. The phenols observed may in part arise from the pyrolysis of degraded, allochthonous lignin, in agreement with the petrographic observations. The presence of cyclopentenones [4, 15] and furancarboxaldehydes [5, 16] as relatively important pyrolysis products and the lack of levoglucosan suggests the presence of degraded polysaccharides in the sediments (Sicre *et al.*, 1994), which may derive from terrestrial or aquatic organic matter.

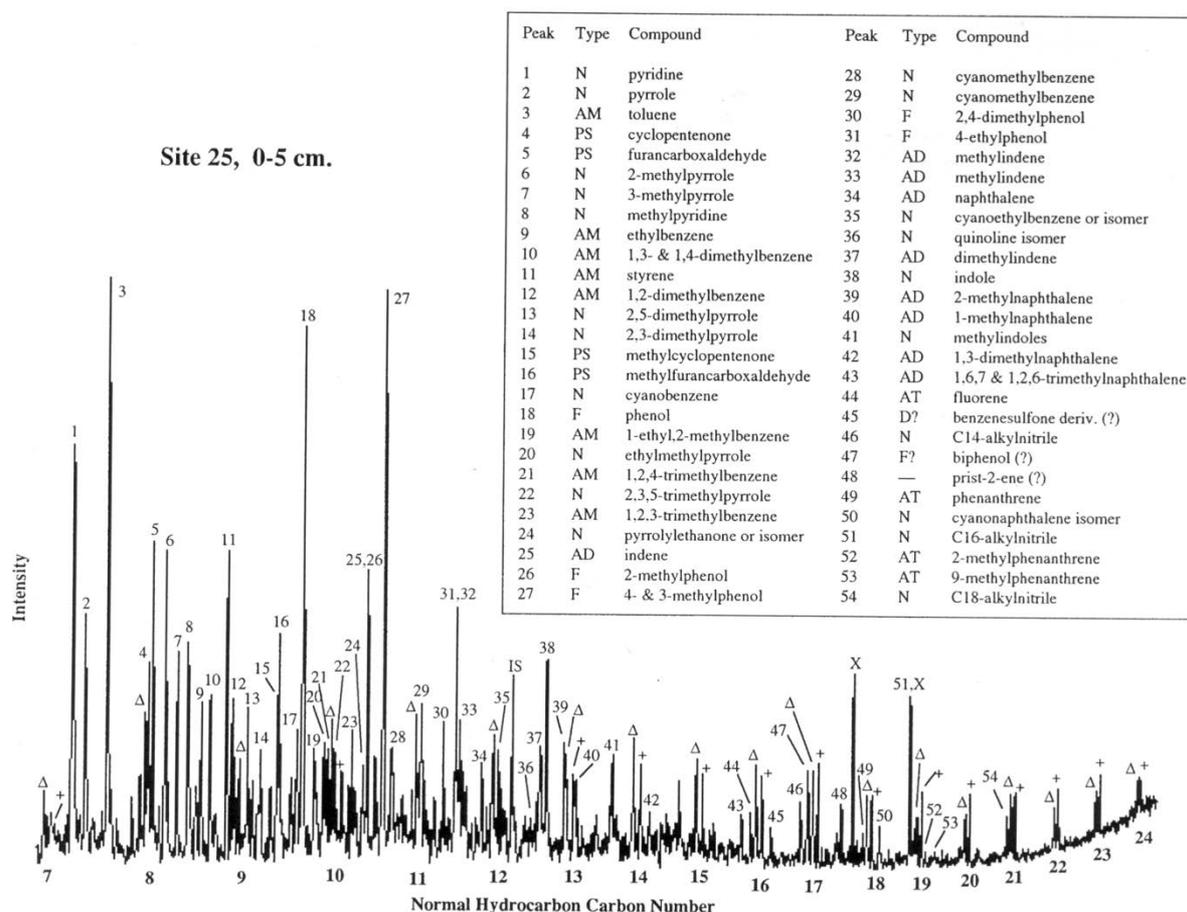


Fig. 7. Total ion chromatogram of the pyrolyzate of a representative Lake Ontario sediment sample (station 25, 0-5 cm sed. depth). Identifications for numbered peaks given at right, for which compound types are monoaromatic hydrocarbons (AM), diaromatic hydrocarbons (AD), triaromatic hydrocarbons (AT), phenols (F), polysaccharide pyrolysis products (PS), organonitrogen compounds (N) and detergent (D). Other compounds: *n*-alk-1-enes (Δ), *n*-alkanes (+), internal standard (IS), silane contaminants probably introduced during analysis (X).

One of the most striking features of the pyrogram (Fig. 7) is the high relative abundance and diversity of organonitrogen compounds. These include pyridines [1, 8], pyrroles [2, 6, 7, 13, 14, 20, 22], cyanobenzenes [17, 28, 29, 35], a quinoline isomer [36], indoles [38, 41] and C₁₄, C₁₆ and C₁₈ alkylnitriles [46, 51, 54]. All but the alkylnitriles indicate the presence of degraded proteinaceous material in the sediment (Sicre *et al.*, 1994; Peulvé *et al.*, 1996) from autochthonous sources (algae, bacteria) and/or sewage, in agreement with the petrographic results. The occurrence of the three alkylnitriles has been noted before in pyrolyzates of recent marine sediments and tentatively ascribed to a bacterial origin (Sicre *et al.*, 1994) or to an as yet unknown amide biopolymer (Peulvé *et al.*, 1996). In the present case, they most likely derive from autochthonous lacustrine organic matter. In general, high concentrations of nitrogen in lacustrine organic sediments indicate a predominance of aquatic, rather than terrestrial organic matter (Meyers and Ishiwatari, 1993). The unknown compound tentatively identified as a benzenesulfone derivative [45] would indicate the presence of detergent pollution if the identification is correct.

While the petrologic results point to a volumetric predominance of industrial organic matter residues in many of the samples, the pyrolysis products are predominantly those of autochthonous and allochthonous natural organic matter. The populations of algae and bacteria, while nominally "natural", have been influenced by the anthropogenic disruption of the nutrient balance in lake through the addition of sewage and agricultural wastes. The long-term rise in aquatic productivity in Lake Ontario after the arrival of European settlers in the region has previously documented in paleolimnological and geochemical studies (Bourbonniere and Meyers, 1996a,b; Silliman *et al.*, 1996). The apparent discrepancy between the petrologic and the geochemical results is explained by the relatively much greater yield of pyrolysis products from algal and bacterial organic matter than from coaly and especially charred material.

Summary and conclusions.

A reconnaissance study of recent sediments from western Lake Ontario by organic petrologic and molecular characterization revealed the nature and concentrations of natural and anthropogenic organic matter. Petrologically, huminite, vitrinite, inertinite, clasts of organic-rich rocks, spore, pollen, cutin, algae and fungi were identified within the natural organic component. Fragments of coal (lignite to low volatile bituminous), combustion residues (fly ash, char, and coke), petroleum products (solid bitumen, light refinery products and tar), and chemical products (plastic, paint, etc.) were identified as anthropogenic components. A major part of anthropogenic components in sites 19 and 24 could not be identified and is considered unknown. It is evident that the petrologic data point to distinct variations in industrial and natural organic matter, whereas the pyrolysis products identified are predominantly those of the autochthonous and allochthonous natural organic matter.

A major sediment component at many sites is amorphous organic matter (AOM). This is thought to be transitional between anthropogenic and natural sources because it may be derived from enhanced bacterial alteration of natural components supported by the addition of human and agricultural wastes from sewage treatment plants and inflows around western

Lake Ontario.

Some combustion residues may originate with home heating by residents around the lake (Fig. 4h). Components derived from the combustion of coal and petroleum products are possibly discharged by ships traveling in Lake Ontario. The refinery products may be derived from ships or from the refineries themselves. The large particle size of coal and combustion residues at some sites within the fine-grained sediments, clearly points the actual dumping of pollutants. Coal and coke particles, for example, could result from deposition of the sweepings and debris from bulk cargo vessels. Elongated concentrations of the largest particles could cause the linear acoustic backscattered anomalies observed on sidescan sonar records.

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