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FLASH PYROLYSIS OF ANTHROPOGENIC AND NATURAL ORGANIC MATTER IN POLLUTED SEDIMENTS

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INTRODUCTION

Combustion products along with spilled petroleum and industrial chemicals contribute to environmental degradation by contaminating soils and sediments. Such anthropogenic organic matter (OM), if preserved in sediments, can serve an archival function, documenting the local history of industrial pollution. Christensen and Zhang (1993) determined the sources of polycyclic aromatic hydrocarbons (PAH) to Lake Michigan from sedimentary records, finding that coal combustion was a major source for PAHs in these sediments. Bodzek and Luks-Betlej (1993) reported that atmospheric deposition is the main source of PAH in soils of the heavily industrialized Upper Silesia region of Poland. Smith and Levy (1990) investigated the geochronology of PAH contamination in sediments of the Saguenay Fjord (Quebec). They found that the concentrations and fluxes of PAHs in these sediments track developments in the region's aluminum industry. OM in sediment samples from a 3 m core was investigated to determine the impact of industrialization on the natural environment of the study area, a polluted industrial zone near Chicago, Illinois. In an attempt to examine the extent of chemical contamination in these sediments, the present study used analytical pyrolysis-gas chromatography/mass spectrometry (Py-GC/MS) and petrography to characterize the anthropogenic and natural OM.

METHODS

A 3 m sediment core was collected using a portable vibrocoring system. Aliquots of eleven samples of dry sediment were mixed with epoxy resin and mounted into pellets for petrography. Total organic carbon (TOC) was determined for each sample. Py-GC/MS was used to chemically characterize sedimentary organic matter in these sediments. For each GC/MS run 5 mg of dry sediment contained in a quartz tube was placed in platinum coil and pyrolyzed in a flow of helium for 20 sec. at 610°C, as measured by a thermocouple in the sample holder. Prior to pyrolysis, the samples were heated at 310°C for 20 sec. to remove low molecular weight OM, which was analyzed separately and is not discussed here.

RESULTS

Petrographic analyses indicate the presence in the sediments of eight types of OM of which three have been identified as debris of natural vegetation. Other organic particles, including coal, metallurgical coke, petroleum coke, char, fly ash, and solid bitumen, are anthropogenic and related to industrial activity. Anthropogenic particles are dominant in sediments in the upper core, while plant fragments dominate OM at core bottom.

Pyrolyzates of the sediments in the top meter are dominated by chemical pollutants that are related to pyrolytic sources. These include PAHs, thioarenes, azaarenes and aliphatic hydrocarbons (Fig. 1). The aromatic hydrocarbons in pyrolyzates of the top sediments are predominantly three, four and five-ring parent PAHs. Bouloubassi and Saliot (1995) observed the prominence of such compounds in OM from pyrolytic sources in surface sediments collected in the Rhone delta. Concentrations of PAHs in pyrolyzates decrease with increasing depth to background levels by approximately 120 cm, the core depth at which we infer to record the local onset of industrialization (Fig. 3).

Various classes of sulfur compounds are present in pyrolyzates of the sediments. Among the organic sulfur compounds detected in our samples, the thioarenes (benzothiophenes, dibenzothiophenes, benzonaphthothiophenes, and their alkyl-substituted homologues) were the most abundant. The sum of their concentrations in the pyrolyzates of the sediments varied from 125 to 473 $\mu\text{m/g}$ in the top 76 cm. The concentrations of thioarenes showed trends with depth similar to those shown by PAHs. Steinhauer and Boehm (1992) reported that uncombusted fossil fuels are highly enriched in two- to three-ring PAHs and thioarenes.

Most of the nitrogen in the pyrolyzates is found to be present in aromatic forms (simple and alkylated multi-ring azaarenes), with small amounts of alkyl amine and amides. Azaarenes often have

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stronger mutagenic and carcinogenic activity than the PAHs (Tyreplen *et al.*, 1995) and thus are cause for concern. As with PAHs, concentrations of azaarenes in pyrolyzates are higher in shallower sediments. Tyreplen and others (1995) reported the presence of azaarenes (e.g. isoquinoline, acridine, and their isomers) and their alkyl derivatives in sewage sludge from treatments plants in the Upper Silesia region, Poland. Low abundances of single ring N-compounds (pyrrole and pyridine) were observed in pyrolysis products of sediments above 106 cm, whereas higher concentrations were detected in pyrolyzates of the older sediments below that depth. These compounds may arise in part from pyrolysis of proteinaceous material.

Moderate to low concentrations of aliphatic hydrocarbons were detected in pyrolyzates of the sediments. Concentrations of short chain *n*-alkane and *n*-alkenes (C₆-C₁₉) in pyrolyzates are highest in pyrolyzates of the top sediments, while long chain (C₂₀-C₂₉) *n*-alkanes, *n*-alkenes, and prist-1-ene are dominant in sediments at the bottom of the core. This may indicate that aliphatic hydrocarbons at the top of the core are mostly pyrolysis products of anthropogenic OM such as petroleum asphaltenes, whereas for deeper older samples, long chain aliphatics have resulted from pyrolysis of naturally occurring terrestrial higher plant OM.

Pyrolyzates of bottom sediments are dominated by lignin-derived compounds including phenols, methoxyphenols and dimethoxyphenols (Fig. 2). The lignin pyrolysis products guaiacol, syringol, and their derivatives are restricted to the bottom 2 m of the core. The presence of guaiacols and syringols in pyrolyzates of samples below 120 cm correlates with the occurrence of plant fragments, as observed under the microscope. The lack of lignin marker compounds in the upper sediments suggests a reduction in plant populations in the vicinity during the industrial period. Phenol and its alkyl-substituted forms are less specific marker compounds, occurring in pyrolyzates of all sediment samples. Their presence in pyrolysis products of the older sediments (below 106 cm) is probably due to naturally-occurring OM (terrestrial higher plants). However, phenols in pyrolyzates of the younger sediments probably derive from the abundant coal particles (vitrinite) observed petrographically.

CONCLUSION

The abundance of anthropogenic OM in pyrolyzates of sediments that correspond to the time of peak industrialization is over 10 times higher than the background levels detected in bottom sediments. It is evident that industrial activity has resulted in irreversible damage to the marshes and the wetlands of this area with the result that plant life has never recovered. Py-GC/MS analysis of organic sediments proved to be useful in determining the extent of pollution in these sediments and highlights some of the compositional features that can be used to distinguish between natural and anthropogenic OM.

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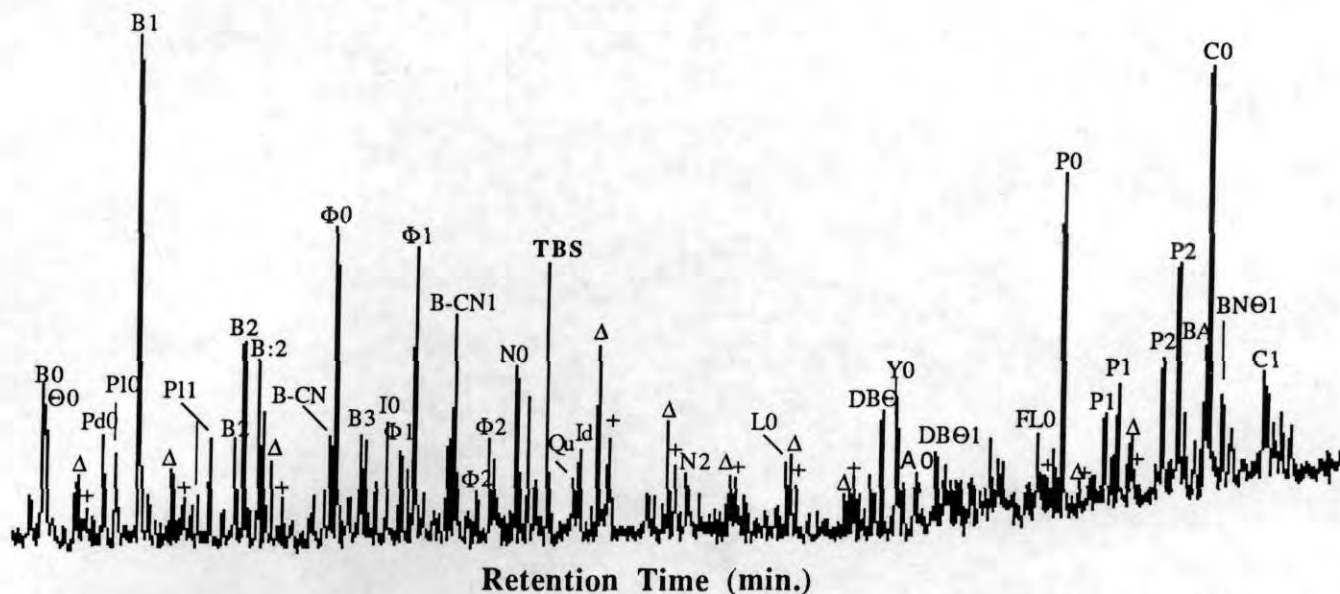


Figure 1 Total ion current of the pyrolyzates (610°C) of raw sediments at 30 cm. Key for peaks- TBS: internal standard Bn: (alkyl)benzenes, Φ n: (alkyl)phenpls, Θ n: (alkyl)thiophenes, DB Θ n: (alkyl)dibenzothiophenes, BN Θ n: (alkyl)naphthothiophenes Pln: (alkyl)pyrroles, Pdn: (alkyl)pyridines, Idn: (alkyl)indole, Qun:(alkyl)quinolines, In: (alkyl)indenes, Nn: (alkyl)naphthalenes, Ln: (alkyl)fluorenes, Yn: (alkyl)phenanthrenes, An: (alkyl)anthracenes, Fln: (alkyl)fluoranthenes, Cn: (alkyl)chrycenes, Pn: (alkyl)pyrenes, where "n" indicates the extent of substitution (0:none, 1:methyl, 2:dimethyl or ethyl, ect.), Δ : n-alkenes, +: n-alkane.

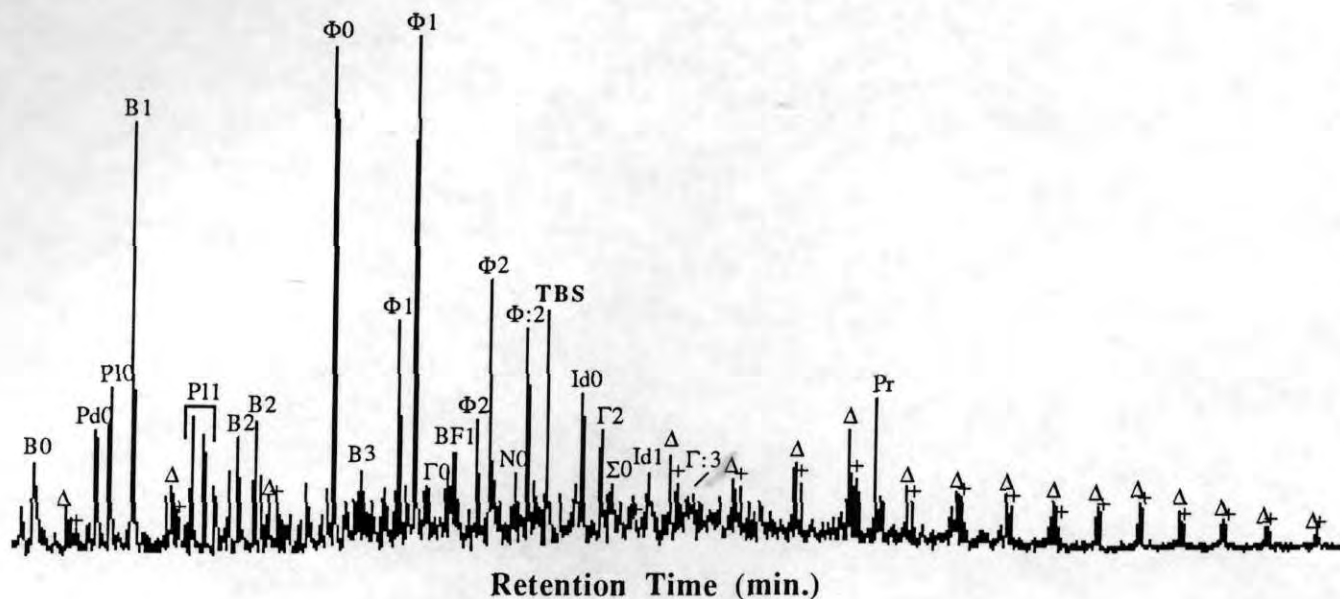


Figure 2. Total ion current of the pyrolyzates (610°C) of raw sediments at 307 cm. Key for peaks- TBS: internal standard, Bn: alkylbenzenes, Φ n: (alkyl)phenpls, Γ n: (alkyl)guaiacol, Σ n: (alkyl)syringol, Pln: (alkyl)pyrroles, Pdn: (alkyl)pyridines, Idn: (alkyl)indole, Qun:(alkyl)quinolines, Fn: (alkyl)furan, BFn: (alkyl)benzofuran, In: (alkyl)indenes, Nn: (alkyl)naphthalenes, where "n" indicates the extent of substitution (0:none, 1:methyl, 2:dimethyl or ethyl, ect.), Δ : n-alkenes, +: n-alkane, Pr: prist-1-ene