Reprinted from ENVIRONMENTAL SCIENCE & TECHNOLOGY, Vol. *17*, Page 292, May 1983

Analyses of Organic Particulates from Boston Harbor by Thermal Distillation–Pyrolysis

Jean K. Whelan,* Michael G. Fitzgerald,[†] and Martha Tarafa

Department of Chemistry,[‡] Woods Hole Oceanographic Institution, Woods Hole, Massachusetts 02543

■ The techniques of thermal distillation and pyrolysis coupled with gas chromatography (GC) and GC–mass spectrometry (GC–MS) provide a "fingerprint" of the organic matrix of particulates collected from Boston Harbor. C_6–C_{22} pyrolysis products of particles caught in sediment traps closely resemble those of bottom sediments and are similar to those of some species of phytoplankton. GC–MS analyses indicate that these organic matrices are all lipid rich, though the lipid in the seston appears to be distinct from that in both sediment-trap and phytoplankton samples. None of these samples resemble the sewage sludge dumped into the area, suggesting rapid reworking or remineralization of the sludge material.

Introduction

Particulate organic matter plays a significant role in the biological productivity of estuarine and coastal waters (*1*, *2*), in the deposition of inorganic particles (*3*, *4*), and in the transport and fate of pollutants introduced in coastal areas (*5*). As a result, the sources, sinks, distribution, and composition of organic matter are of primary importance to the management of coastal waters.

Boston Harbor and its neighboring waters exhibit environmental problems similar to those of many bays and estuaries bordering large urban centers. Modern sediments in Boston Harbor originate primarily from anthropogenic input, biogenic production, and the resuspension and advection of bottom sediments (*6*). This study focuses on characterizing the organic matter involved in depositional processes within the harbor via the use of the technique of thermal distillation–pyrolysis (*7*). This technique has been applied extensively in petroleum-source rock studies (*8–11*) but has not previously been applied to recent marine samples. It is similar to pyrolysis–GC (which involves more rapid heating of dry samples), which has yielded valuable information about recent marine biogeopolymers in the small number of studies carried out to date (*12–14*). The purpose of this work was to obtain qualitative and semiquantitative information about various particles in Boston Harbor in order to see if, in the future, more quantitative studies of marine particles by this technique might be justified. The results showed clear and reproducible differences between different types of particles in the harbor. Because of the small amounts of polymeric material available (micrograms in the case of solids filtered from the water), thermal techniques are one of the few capable of giving chemical information about the nature of these complex materials.

Study Area

Boston Harbor covers an area of 114 km^2 in westernmost Massachusetts Bay (Figure 1). Semi-diurnal tides (mean range of 2.7 m) are primarily responsible for water exchange. Residence time in most of the harbor is slightly less than two tidal cycles. In areas with sluggish circulation, however, complete flushing presumably takes longer than two tidal cycles. Maximum current velocities approach 100 cm/s between Deer Island and Long Island but are less than 50 cm/s in most areas of the harbor. The net drift of harbor waters is not well-known but appears to be anticyclonic: waters enter President Roads, travel between the harbor islands, and exit through Nantasket Roads (*6*).

Boston Harbor receives municipal wastes from 43 communities served by the Metropolitan District Commission. Efforts to cope with these wastes led to the construction of the two existing primary treatment plants (Figure 2). The Deer Island and Nut Island facilities now contribute an average of 329 and 123 million gallons per day (mgd) of chlorinated primary sewage, respectively. Their combined discharge equals three-quarters of the average flow of all rivers emptying into the harbor. A third outfall, which discharged raw sewage from Moon Island, contributed a considerable amount of material prior to its closing in 1969. In addition, five of the older communities in the downtown area have combined sanitary and storm water sewers that overflow into the harbor at hundreds of discharge points (see Figure 2).

Approximately 100 tons of solid material from these waste-treatment plants are flushed daily into the harbor during ebb tide to enhance its dispersal into Massachusetts Bay. Evidence suggests, however, that some of this solid material accumulates in the harbor, accounting for as much as 10% of the sediment deposited (*6*).

Methods

Water samples for seston analyses were retrieved by using 5-L Niskin bottles. Surface, midwater, and near-bottom samples (Figure 3) were collected at each station. After the sample was thoroughly mixed, subsamples were taken, and those for organic matter analyses were immediately frozen. Time-series samples provide observations of tidal variation in composition and load.

Two sediment-trap arrays (Figure 3) deployed for 3 days during each cruise supplied information on the nature of particulates in flux. Locations were selected for their position relative to the Deer Island outfall and to represent different types of bottom sediment. The inner station, ST1, was located in 12 m of water over a muddy bottom, while ST2 in the outer harbor was in 11 m of water over a sandy, gravel bottom. Each array consisted of midwater (5 m above the bottom) and near-bottom (1 m above) traps. Following the recommendations of Gardner (*15*) for optimum aspect ratio, the traps were 75 cm in length with an internal diameter of 30 cm. Baffles covering the trap opening reduced turbulence. Upon retrieval, trap samples were treated with sodium azide (in order to minimize bacterial decomposition of the trap material) and sealed. Bottom sediment samples used in these analyses (grab samples in Figure 3) were taken by using a Van Veen grab. All samples were frozen between the time of recovery and analysis.

Phytoplankton were cultured as described by Guillard (*16*). All cultures were unialgal and axenic and were grown in enriched seawater medium F/2. Two liters of the media

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[†] Present address: Exxon Research Production Co., Houston, TX 77001.

[‡] Contribution No. 5089.

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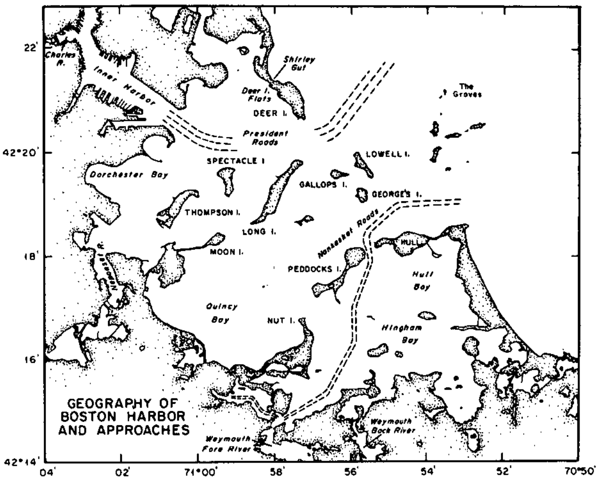

Figure 1. Geography of Boston Harbor and its approaches. Dashed lines refer to shipping lanes.

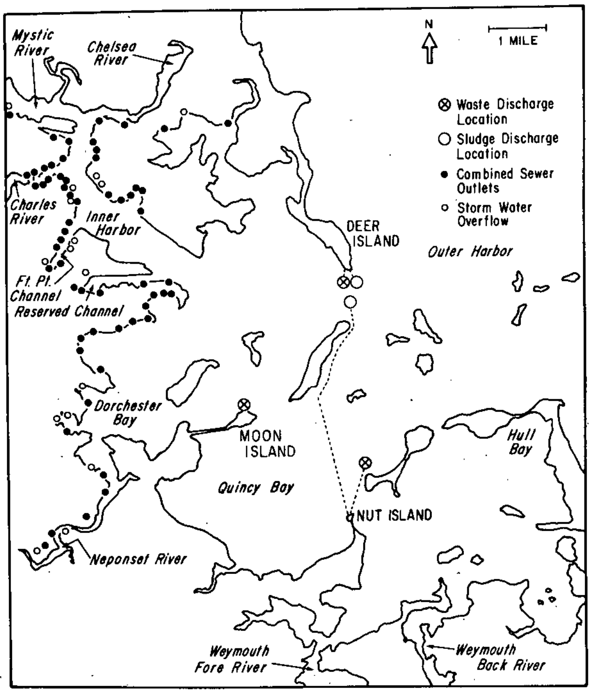

Figure 2. Map of sewer outfalls and storm sewer overflows in Boston Harbor.

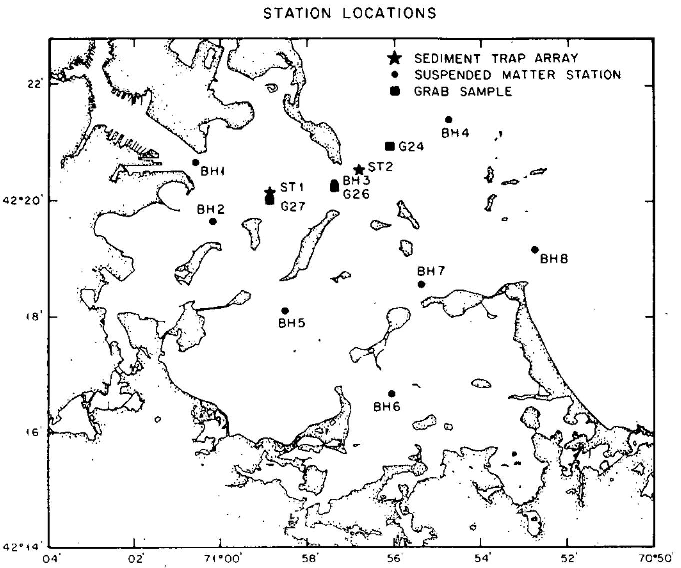

Figure 3. Station locations: sediment trap array ST1 consists of a near-bottom trap (IB) and a midwater trap (IT). Array ST2 has a near-bottom trap (OB) and a midwater trap (OT).

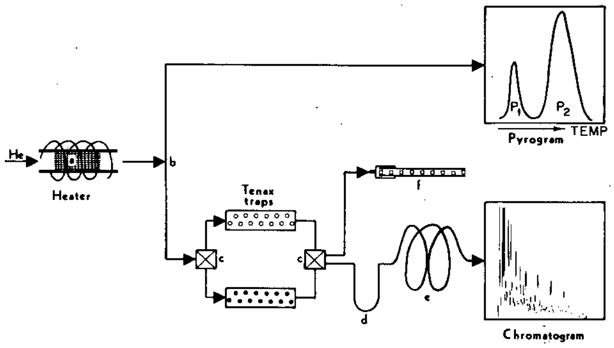

Figure 4. Diagram of thermal distillation–pyrolysis–gas chromatography apparatus: (a) wet sample in quartz tube is heated by platinum coil heater; (b) helium stream split; (c) eight-port switching valves; (d) chilled loop for concentrating sample in front of capillary GC column; (e) capillary GC column; (f) mass spectra trap.

was divided into two Erlenmayer flasks. One flask was inoculated with a particular organism, and one was maintained as a control. The control was subjected to the same growth requirements and analytical procedures as the flask containing phytoplankton and served as a blank of the analytical procedure. The flasks were incubated at 20 °C and exposed to a 14-h day cycle under ca. 2.5×10^{-2} ly/min provided by fluorescent light (Sylvania Co.). To insure against bacterial contamination, all media and glassware were autoclaved, and a standard sterile procedure was used in storing and sampling cultures for analysis. Collections and analyses of organisms and blanks were carried out in a manner identical with that for seston (described below).

Detailed information on the technique of thermal distillation–pyrolysis–gas chromatography (TDPGC) is provided by Whelan et al. (7). In brief, a small (0.1–100 mg), moist sample is placed in a quartz tube and heated (a in Figure 4) at 60 °C/min in a helium stream. In the case of suspended particulates, 300 mL of water is filtered through precombusted, glass-fiber filters (Gelman, Type A/E, 25 mm, 1-μm pore size) and $^1/_8$ of the resulting wet filter placed in the quartz tube. The helium stream is split (b in Figure 4) and part passed through a flame ionization detector to give a trace of total organic compounds evolved as a function of temperature, called a "pyrogram" in Figure 4. One peak, P_1, evolves at low temperature (100–200 °C) and represents volatile organic matter sorbed on the particles. A second peak, P_2, evolves at 350–600 °C and represents organic compounds cracked from the high molecular weight organic matrix of the particles.

The second part of the helium stream from the split at b is passed through an eight-port sampling valve (c in Figure 4) and is trapped at 25 °C in two traps (one for P_1 and one for P_2) packed with a porous polymer, Tenax (60-80 mesh, Applied Science Inc., State College, PA). By a series of heating and cooling cycles (d in Figure 4), the trapped compounds are desorbed from the Tenax and analyzed by gas chromatography (GC; in Figure 4) to give a chromatogram characteristic of the C_6–C_{15} volatile organic compound composition of the trapped mixture. A 0.0254 cm i.d. × 50 m stainless steel (OV101 WCOT) capillary GC column was used in obtaining the GC's such as those shown in Figures 5–10 (temperature program 60–200 °C at 6 °C/min). Alternatively, the Tenax traps could be desorbed into a second small Tenax trap (f in Figure 4) and stored in sealed glass ampules under nitrogen and the trapped compounds examined later by GC–mass spectrometry, which allows compound identification for some samples via comparison to standards run on the same instrument or via comparison to reference spectra.

In calibration studies of this technique, it has been determined that *n*-alkanes from C_{16} to C_{22} can be quantitatively recovered from P_1 without decomposition in experiments carried out by injecting alkanes onto the surface of various moist mineral matrices including calcite, the clay mineral kaolinite, and an organic-rich (4% organic carbon) diatomaceous sediment (*17*). The accuracy of the method is not known for compounds in the C_6–C_{14} range because of the problem of variable volatilization losses in attempted spiking experiments. The problem appears to be less severe with more organic-rich samples and if the samples are kept moist and cool during preparation.

The precision of the method is excellent in comparison with other methods of analysis. Coefficients of variation for individual *n*-alkanes and aromatic hydrocarbons for duplicate samples (including sediments, sediment traps, seston, and organisms) for both P_1 and P_2 capillary GC's averaged 24% for C_6–C_8 (1σ range 5–32%) and 8% for C_9–C_{15} (1σ range 3–12%) for levels of compounds in the range 10–500 ng of compound/g dry weight of sample. The higher variability of the C_6–C_8 compounds is probably due to greater loss during sample preparation because of higher volatilities of the lower molecular weight constituents.

These values compare very favorably with precisions reported for other methods of analyzing complex organic mixtures of natural systems where values for either total or individual constituents generally show coefficients of variation in the range of 10–30% for replicate sediment samples analyzed in the same laboratory (*18, 19*). Higher variabilities—coefficients of variation in the range of 16–68% (average value 34%)—have been reported for some halogenated and aromatic hydrocarbons in very organic-rich substances such as sewage sludge (*20*).

For injection into the GC–MS system, the Tenax traps are sealed at 25 °C in the injection port of the Varian 1400 GC attached to the GC–MS and are then heated to 210 °C in a helium stream for 15 min. The compounds evolved are trapped by chilling a 5-cm section of the front of the capillary GC column in liquid nitrogen. The GC analysis is then carried out as described above by using a Finnigan 1015C quadrupole mass spectrometer as the detector. The total eluant from the capillary column goes into the mass spectrometer. The mass spectrometer is interfaced with a Finnigan INCOS 2300 data system.

The term "organic matrix" used in this paper is an operational definition including all organic material not volatilized out of the sample during collection of P_1. This includes nonvolatile low molecular weight compounds (such as fatty acids, amino acids, and sugars) as well as biogenic polymers (such as proteins) and geopolymers (such as humic and fulvic acids).

Results

(A) Sediment-Trap and Bottom-Sediment Samples. GC and GC–MS analyses of P_1 capillary GC components showed a complex series of branched and *n*-alkanes, with the latter predominating. Most of the sediment-trap and bottom-sediment samples were very similar, showing a large amount of low molecular weight material (less than C_9) and a maximum in the unresolved complex mixture at C_{15} (*7*). A different pattern was exhibited by the two samples taken from close to the sewage outfall (bottom sediment sample G27 and sediment-trap sample OT from station 2 in Figures 3), which gave very few resolved peaks and showed only two unresolved broad peaks centered at C_{10} and C_{16-17}. These two samples are probably strongly influenced by the sewage material, which is very rich in adsorbed P_1 components as shown in Figure 10.

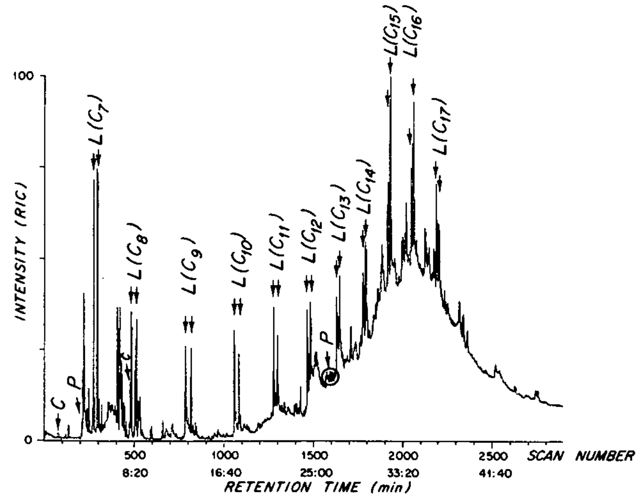

Figure 5. Typical GC–MS of pyrolysis (P_2) products from Boston Harbor sediment trap samples IB. Probable precursors of cracked products are as follows: L, lipid; C, carbohydrate; P, protein. Carbon numbers are shown for homologous 1-alkene/*n*-alkane pairs.

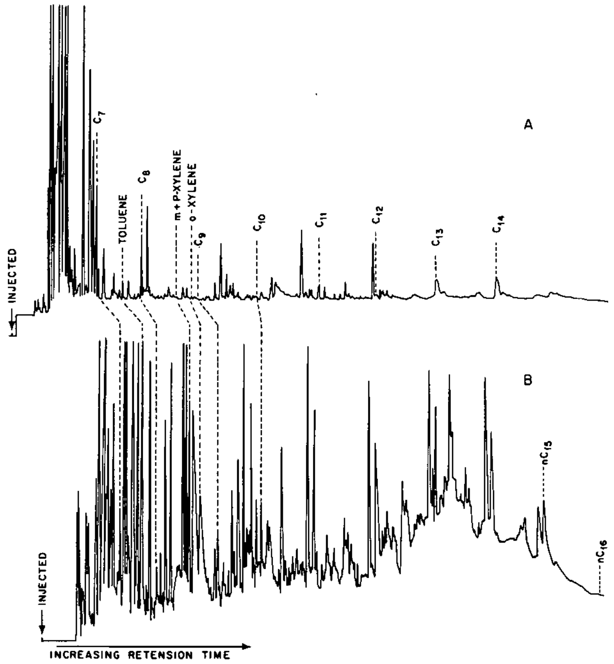

Figure 6. P_2 capillary GC patterns: seston (A) and sediment-trap particles (B).

The pyrolyzed components (see, for example, the P_2 capillary GC and GC–MS results shown in Figures 5 and 6) from all of the bottom-sediment and sediment-trap samples were very similar, suggesting that the high molecular weight, organic matrix of particles reaching both sediment traps and the bottom is fairly uniform throughout the area. These samples are also similar in mineral and elemental composition (*6*).

GC–MS of the pyrolysis (P_2) capillary GC peaks showed a homologous series of 1-alkene/*n*-alkane pairs as the predominant components, generally with each peak of the doublet being of about equal intensity as shown, for example, in Figure 5. Minor amounts of oxygen-containing compounds, and nitrogen heterocycles were also found. These were identified by GC–MS mass scans and often appear as trailing or broad peaks as shown in Figure 5. The oxygen and nitrogen compounds are primarily car-

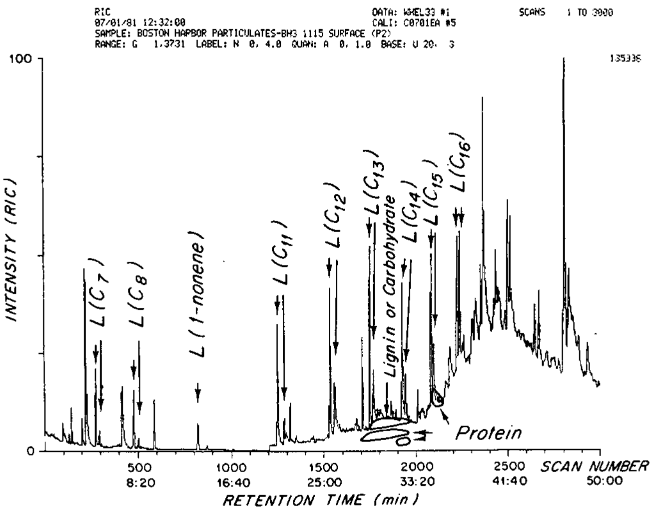

Figure 7. Typical GC–MS analysis of pyrolysis products from Boston Harbor particulates filtered from the water. Abbreviations are same as in Figure 5.

bohydrate and protein breakdown products, respectively (see Discussion).

(B) Seston (Suspended Matter). The P_2 GC pattern for suspensates was completely different from that of the coarser sediment-trap particles (Figures 6 and 7). A broad hump centered above C_{14} in Figure 7 is not present in Figure 6 due to a shorter GC run time and less efficient Tenax desportion in the latter case. Evenly spaced strong singlet peaks from C_8 to C_{14} are typical of all seston particles examined in this work. The homologous series of 1-alkene/*n*-alkane peaks are again recognized from the GC–mass spectral data. However, in almost all cases, the *n*-alkane peak, which elutes second, is considerably smaller than the 1-alkene peak. In some samples, the *n*-alkane peaks seem to coelute with other functionalized components, tentatively identified via mass spectra as ketones. These functionalized compounds cause tailing and broadening of the smaller, second peak in some cases (for example, see the C_{12} region in Figure 7). From these data, it can be concluded that the organic matrix of the fine-grained seston particles is consistently different from that of the coarser–grained samples from sediment traps discussed above.

The GC–MS of a Boston Harbor seston sample (Figure 7) shows that oxygen and nitrogen components are also present, as indicated by the peaks labeled "lignin or carbohydrate" or "protein", respectively, in Figure 7 to indicate the suspected precursors for the heterocyclic cracking compounds.

The adsorbed P_1 components for these fine particles were found to consist primarily of C_6–C_{14} hydrocarbons with total levels in the range 0.6–8 mg/L and varying roughly with tidal cycle (highest levels at low tide). The coefficient of variation for individual *n*-alkanes and aromatic hydrocarbons for duplicate samples was generally less than 14%. However, losses in these volatile components undoubtedly occur during storage and workup of these samples, so that these levels can only represent a minimum for the actual amounts originally present. The highest levels of adsorbed compounds (8 mg/L) appeared in bottom samples at low tide in sample BH3-017, where resuspension of sewage sludge material should be important. At high tide, levels decrease by an order of magnitude as expected when samples become diluted with incoming seawater.

(C) Analysis of Phytoplankton Cultures and Deer Island Sewage Sludge. To compare organic matter in the particles discussed above with some possible contributors, marine phytoplankton and Deer Island sewage sludge were subjected to the TDPGC technique (Figures 8 and 9, respectively). The GC's for different samples of the same phytoplankton species analyzed on two different days are qualitatively and quantitatively very similar in detailed peak patterns (compare Figure 8, parts A and B) if a series of broad tailing peaks (circles in Figure 8A) are ignored. The GC patterns of other species Figure 8, parts C–F) can be seen to be similar to but not identical with Figure 8, parts A and B. All are characterized by a series of *n*-alkane/1-alkene doublets as found for the sediment-trap samples. The GC–MS of one species, the same coccolithophore as that shown in Figure 8, parts A and B,

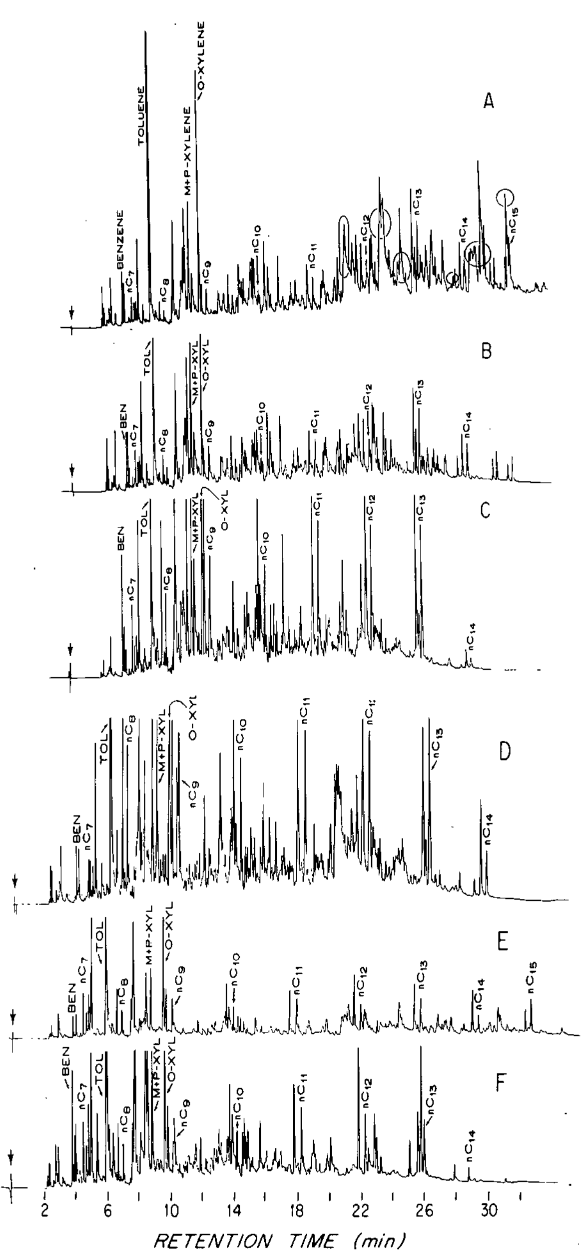

Figure 8. TDPGC analyses of various species of marine phytoplankton cultures (A–F). A and B show the same culture analyzed on consecutive days. Circles in A represent peaks that are present in A but not in B. Organisms are as follows: A and B, *Emiliania huxleyi*, class Haptophyceae, clone BT6, (coccolithophore, no calcium carbonate shell); C, *Emiliania huxleyi*, class Haptophyceae, clone MCH-1, (coccolithophore, with calcium carbonate shell); D, *Chroomonas salinas*, class Cryptophyceae, clone 3-C; E, *Synechococcus bacillaris*, class Cyanophyceae, clone Syn (blue green algae); F, *Thalassiosira* sp., class Bacillariaphyceae, close 298-1 (diatom).

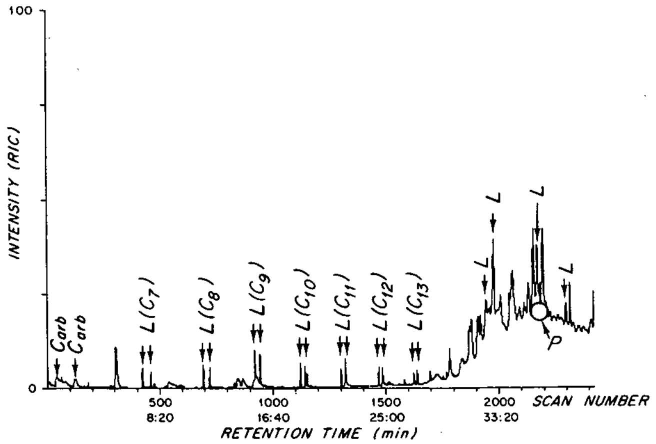

Figure 9. GC–MS analysis of pyrolysis products of a phytoplankton grown in culture (coccolithophore BT6 as shown in Figure 8, parts A and B).

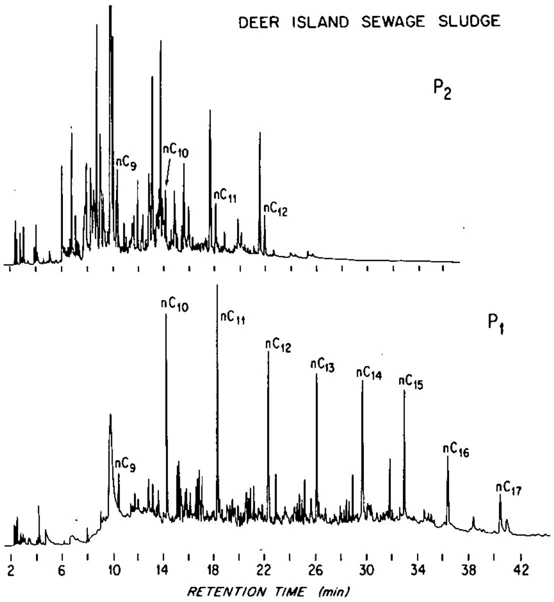

Figure 10. Capillary GC's from P_1 and P_2 of TDPGC analysis of Deer Island sewage sludge.

is shown in Figure 9. The alkane/alkene peaks (labeled L) dominate as in the sediment-trap samples. However, minor amounts of oxygen-containing (labeled C in figures) and nitrogen-containing (labeled P in figures) components are also present. Little or no adsorbed P_1 component was present in any of the organisms shown in Figure 8. Since similar results have been obtained with unpolluted organic-rich recent sediments containing primarily the remains of these and related organisms (*7*), phytoplankton organisms apparently do not contribute significantly to adsorbed P_1 components detected in the Boston Harbor samples.

Deer Island sewage sludge presents a different picture (Figure 10). GC–MS data were not obtained for this sample. However, the GC data clearly show a much different composition for both P_1 and P_2 than for any other samples analyzed in this work. P_2 does not show any material of larger molecular weight than C_{12}. The 1-alkene/*n*-alkane doublets are again present, but the *n*-alkane component is only about one-third of the size of the 1-alkene component (the large peaks just preceding the *n*-alkanes). On the other hand the sludge is very rich in adsorbed P_1 components as shown by the series of *n*-alkanes in the P_1 GC (Figure 10).

Discussion

Strong differences exist between the organic matrix of seston and that of sediment-trap material (and bottom sediments) in Boston harbor (Figure 6). These differences suggest that the formation of large sediment-trap particles probably does not involve simple agglomeration of suspended particulates. Comparison of the P_1 and P_2 GC patterns of phytoplankton, sediment-trap particles, and Deer Island sewage sludge suggests several things about the role of each of this environment. The Deer Island sludge has a very large P_1 component and a smaller P_2 component. No particles or sediments examined in this work showed a similar pattern, suggesting that the sludge is rapidly altered (perhaps by organisms) once it is discharged into the water. The P_1 component in all the sediment-trap and bottom-sediment particles is considerably less than the P_2 component and differs in composition from the sewage sludge. In contrast, the P_2 GC patterns are fairly uniform for all of the sediment-trap/bottom-sediment samples. These patterns, in turn, resemble those of phytoplankton more than those of sewage sludge (which has a smaller P_2 component), suggesting that the organisms play an active role in the deposition of particulates (*4*, *21*).

The adsorbed P_1 components appear to be derived primarily from the sewage sludge and its breakdown products together with other anthropogenic compounds, since analysis of phytoplankton raised in culture or from nonpolluted recent sediments from areas other than Boston Harbor show the presence of almost no adsorbed P_1 material. The P_1 component may be similar to the petroleum-like material found in both sewage-sludge and some surface sediments in a previous study of this area (*22*). These workers found this material to be absent in parts of the estuary not affected by sewage sludge. In this work, the changes in P_1 GC patterns are consistent with what is known about movement of the discharged sludge in the harbor. The sludge is discharged on an ebbing tide, but instead of being carried out to sea, it reverses its courses as the tide turns and is partially deposited in the sediments of the inner harbor (*6*). Most of the bottom-sediment samples show very similar complex mixtures of hydrocarbons in the P_1 GC patterns. The compounds would appear to represent an "average" characteristic of organic material sorbed to particles in the harbor including that produced by advection/resuspension of bottom sediments from other parts of the harbor. Bottom-sediment G27 and sediment-trap OT show a different unique P_1 GC pattern, which probably represents rapid biodegradative changes that take place in the sewage sludge soon after dumping. This material appears in the shallowest outer Harbor sediment trap (OT from St2 in Figure 3) but not in a deeper trap (OB) at the same location. These data are consistent with the fact that the sludge tends to remain in surface waters of the outer Harbor as it is initially carried out with the tide (*6*). However, it then reverses its course as the tide turns and is eventually deposited in the bottom around the site of sediment grab sample G27 (see Figure 3).

A qualitative idea of the types of biopolymers contributing to the organic matrices of these particles can be obtained by examining the pyrolysis products present in P_2 via GC–MS. Two excellent studies of this type have been carried out in other areas—one on water particulates from Chesapeake Bay (*12*, *13*) and the other on sediments and particles from the Rhine Delta (*14*). Both groups have found that pyrolysis of lipid material produces primarily alkenes and alkanes while proteins and carbohydrates give

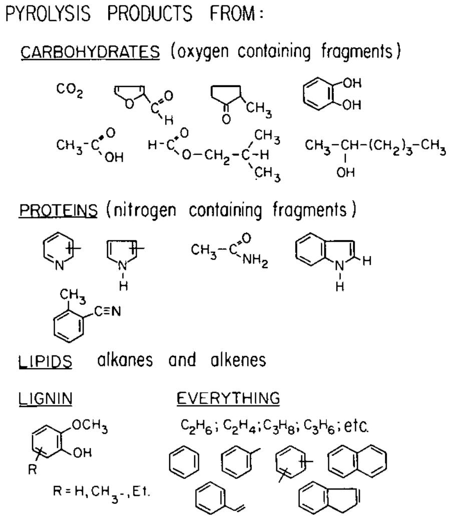

Figure 11. Some pyrolysis products typical of various biopolymers (*12–14*).

heterocyclic nitrogen compounds and low molecular weight oxygen-containing fragments, respectively (Figure 11). In addition, the lignin fraction of woody plants produces a series of unique alkylphenols as shown in Figure 11. Using a pyrolysis technique similar to that utilized in this work together with GC–MS, Sigleo (*12, 13*) concluded that the seston filtered from Chesapeake Bay waters consisted primarily of a proteinaceous–carbohydrate matrix. Pyrolysis of the diatoms in the area, noted for their lack of lipids in comparison to similar organisms in other areas, showed P_2 products similar to those of the seston particles. These workers were also able to show that lignin does not contribute to these particles although it is present in river waters emptying into the Bay. Thus, they were able to conclude that lignin-containing particles must settle out of the water column rapidly upstream.

GC–MS analyses of pyrolysis products from Boston Harbor sediment-trap and particulate samples are shown in Figures 5 and 7, respectively. A GC–MS of pyrolysis products from a phytoplankton sample (the coccolithopore shown in Figure 8, parts A and B) is shown in Figure 9 for comparison. Compounds derived predominantly from lipids are marked L, from protein P, and from carbohydrate C. In all of these samples, lipids appeared to be the major components as shown by most GC–MS peaks being alkanes and alkenes. The most prominent lipid breakdown products are the homologous 1-alkene/*n*-alkane doublets in sediment-trap and phytoplankton samples (Figures 5 and 8) and homologous 1-alkenes in the case of water particulate samples (Figure 7). Thus, all of the samples examined in this work appear to be lipid rich. Small or broad peaks for protein and carbohydrate breakdown products are also present in these samples. Due to broadness and tailing of the peaks in some cases, many of these functional compounds were detected via mass scans used to search for specific compounds detected by earlier workers as discussed above. Use of fused-silica capillary columns should minimize these resolution problems in future work and may make quantitation of these protein and carbohydrate breakdown products possible.

Even though mass spectral patterns indicate that most pyrolysis products are lipid derived, there are some interesting and consistent differences that will be examined in future work. For example, the sediment trap and phytoplankton show the 1-alkene/*n*-alkane doublets in approximately equal intensities. The seston particles, on the other hand, show a series of 1-alkenes and the *n*-alkane component being either much reduced or missing. It is interesting to speculate on reasons for this difference based on data reported in the literature for thermal decomposition patterns of various kinds of lipid-like material containing a large proportion of saturated hydrocarbon groups. Pyrolysis products of the sediment-trap particles resemble those of long-chain *n*-alkanes—a series of smaller 1-alkene/*n*-alkane pairs (*23, 24*). Linear polyethylene produces this type of pyrolysis pattern (*25, 26*). Alternatively, the 1-alkene/*n*-alkane doublets observed in this work could be derived from pyrolysis of other compounds such as straight-chain fatty acids, which first break down into *n*-alkanes or *n*-alkyl radicals (*27, 28*). In contrast, the seston 1-alkenes could be derived from alcohols or esters containing a long-chain *O*-alkyl group condensed with a short-chain carboxylic acid or inorganic acid such as a sulfonate or phosphate. The pyrolysis process as well as the mass spectrometer produces "1-alkene" spectra for many organic compounds possessing a long alkane chain and a functional group at the 1-position.

These preliminary results suggest the potential of this method to detect the types of biopolymers contributing to these small particles. It may be possible, in future work, to quantify the contribution of various biopolymers to particles and organisms by integrating mass scan peaks characteristic of pyrolysis breakdown products of various materials.

Summary

Analysis of organic particulates in Boston Harbor by thermal distillation–pyrolysis–gas chromatography (TDPGC) reveal that seston has a different organic matrix than larger sediment-trap and bottom-sediment particles. This result implies that the larger particles in flux do not form by simple agglomeration of suspensates. The pyrolysis products of all the particles indicated they were comprised predominantly of lipid. However, the types of lipids seem to be quite different in the two cases.

TDPGC analyses were also carried out on Deer Island sewage sludge and various species of phytoplankton. Comparison of the P_1 and P_2 patterns of the sludge with those of sediment samples indicated the absence of unaltered sewage sludge in the sediment. Pyrolysis patterns of the particles were similar to those of phytoplankton, suggesting that organisms play an active role in depositional processes. Changes in adsorbed P_1 organic material in these particles may reflect which particles are most influenced by altered sewage sludge components.

Acknowledgments

We thank Nelson Frew for his help in obtaining mass spectra and John Farrington, Bob Meade, Jerry Glenn, and Stuart Wakeham for their careful and critical review of the paper. Clones of marine phytoplankton were obtained from the laboratory of Robert R. L. Guillard, Woods Hole Oceanographic Institution.

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Received for review February 11, 1982. Revised manuscript received December 27, 1982. Accepted January 31, 1983. This research was supported by the Department of Commerce and NOAA Office of Sea Grant under Contracts 04-7-158-4414, 04-8-M01-149, and NA 79AA-D-00102.