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Analysis of Chemical Markers in Portsmouth Harbor

Report on Phase II Results

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I. Introduction

The Portsmouth Naval Shipyard (PNSY) is located on Seavey Island in the Lower Piscataqua River Estuary in Kittery Maine. This area of the estuary is the site of much industrial and urban activity (Short, 1992) and therefore this system may have received inputs of contaminants from multiple sources including the PNSY facility. The focus of the chemical markers analysis done in Portsmouth Harbor was to investigate sources of the contamination measured in the harbor sediments. The first phase of this work (*Bowen and Pruell, in Phase I report, 1994)* reported on the analysis of surface sediments for a suite of compounds used to identify contaminant sources. In a follow on study this second phase of the chemical markers work was designed to provide for a more quantitative analysis of past and present inputs of contaminants to Portsmouth Harbor from suspected sources.

This phase is comprised of five components. An attempt to use chlorinated paraffins from cutting oils as potential shipyard markers comprised the first component of the Phase II work. It was hypothesized during the Phase I work that chlorinated paraffins, sometimes used as components of cutting oils, may be useful as a specific marker needed to track the impact of shipyard practices in the surrounding sediments. The results of the Phase I analysis showed our analytical method to be a potential problem in detecting these compounds. During the Phase II study a new instrumental method (negative ion chemical ionization mass spectrometry, NCI MS) was used to further investigate this hypothesis.

The second component of this effort involved the collection of water samples in Portsmouth Harbor and their analysis for chemical markers. A sampling cruise was conducted with chemists from the Graduate School of Oceanography. During this cruise, samples of the dissolved and particulate fractions of the water column were collected for organic analysis from four stations in the Seavey Island area of Portsmouth Harbor.

The third component of the Phase II efforts involved analyses of sections from deep cores collected from areas surrounding Seavey Island. A core that was collected from Station 17, off Badgers Island was radiodated (Ward, 1994). These data indicated a predictable down core pattern in both ^{210}Pb and ^{137}Cs with a subsurface maximum in the ^{137}Cs indicative of the 1963 peak in atmospheric nuclear weapons testing. The location of this core was close by the shipyard where surface sediments had previously been analyzed for chemical markers. A sediment core that was collected from the salt marsh on the north side of Clark Island was also analyzed for chemical markers. This core was chosen for its proximity to the landfill on Seavey Island. This core was not analyzed for radionuclides, therefore, there is no information about approximate dates for the different sections analyzed.

The fourth component was a detailed analysis of source material samples from potential contaminant sources to the estuary. These materials included: sewage sludge from the Portsmouth and Kittery sewage treatment plants; road sediments from stormwater runoff drains in Portsmouth, NH; and atmospheric particulate material collected in Portsmouth, NH. These samples were analyzed for the suite of chemical markers that were measured in the harbor sediments (Table 1). This group of compounds was previously included in the analytical work for the first phase of this study. In addition to the source material analyses, six more surface sediments from the Phase I collection were analyzed to increase the total number of sediments for which a detailed chemical markers analysis was performed from 9 to 15.

The fifth component was a statistical analysis of the data from both the surface sediments collected from Portsmouth Harbor and the samples of material representing potential sources of contaminants to these sediments. This multivariate analysis focused on a principle component analysis of the chemical distributions in both of these groups of samples.

II. Methods

The analytical methods used for the analysis of sediments, sewage sludge, and seawater particulate material were those described previously for the Phase I report *(Bowen and Pruell, 1994)*. Modifications to these methods were made for the extraction of the water column foam plug samples. The compounds of interest samples were eluted from the plugs in the teflon housing used to hold the plugs during sample collection using the same 30% methanol / methylene chloride solvent mixture. This extraction technique is referenced in the ERL-N SOP 2.04.001 (ERL-N Standard Operating Procedure Analysis of Dissolved PCBs Using Foam Plugs).

Table 1. Measurements used as Chemical Markers in Portsmouth Harbor Samples.

Petroleum	
PAH128	Naphthalene
MW128 homologs	Alkyl Homologs of Naphthalene
DBTH	Dibenzothiophene
DBTH homologs	Alkyl Homologs of Dibenzothiophene
PAH178p	Phenanthrene
PAH178a	Anthracene
MW178 homologs	Alkyl Homologs of Phenanthrenes
PAH202f	Fluoranthene
PAH202p	Pyrene
PAH228b	Benz[a]anthracene
PAH228c	Chrysene
MW228 homologs	Alkyl Homologs of Chyrsenes
PAH252p	Perylene
Sum MW252 PAHs	Sum of Benzofluoranthenes, Benzopyrenes, and Perylene
Hopane	Hopane
Sewage	
Octylphenol	Octylphenol
Nonylphenol	Sum of p-Nonylphenols
Total LABs	Sum of the Linear Alkylbenzenes
Coprostanone	Coprostanone
Runoff and Atmospheric Deposition	
BZT	Benzothiazole
MTBT	Methylthiobenzothiazole
9-FLU	9-Fluorenone
ANQ	Anthraquinone
9-FLU/PAH166	Ratio of 9-Fluorenone to Fluorene
ANQ/ANTH	Ratio of Anthraquinone to Anthracene

III. Results and Discussion

A. Cutting Oil Markers

In an attempt to further investigate the use of chemical components in cutting oils used at the shipyard as source specific chemical markers, we used an analytical technique new to the laboratory, Negative Ion Chemical Ionization Mass Spectrometry (NCI/MS). Cutting oils were selected because they have been commonly used at the shipyard (Mike Dejardins, PNSY Personal Communication to R.K. Johnston, Sept. 9, 1992) and other researchers (Campbell and McConnell, 1980) have found stable components from cutting oils in marine sediments.

An investigation into the analysis of chlorinated paraffins by NCI/MS was based on previous work by several researchers. Gjos and Gustavsen (1982) analyzed samples of the commercial product CP huls 70C (C_{10} to C_{30} carbon chain lengths, 70% chlorine content) via direct insertion probe - NCI/MS and found that the resulting mass spectrum showed ion clusters over the mass range from *m/z* 380 to 580. Although no molecular ions were found, they reported prominent clusters corresponding to fragments such as $C_{11}H_{14}Cl_9^-$ and $C_{12}H_{16}Cl_9^-$. Analysis of chlorinated paraffins using gas chromatography - NCI/MS is reported by Schmid and Muller (1985) using cool on-column injection. They analyzed the commercial mixtures, Witaclor 149, 352, and 549 (C_{10} to C_{26} carbon chain lengths, 49% - 71% chlorine content) and reported mass spectra showing ion clusters from *m/z* 360 to 560. They also identified ions at *m/z* 416, 430, 465, and 487 in the selected ion monitoring mode. Analysis of environmental samples using gas chromatography - NCI/MS was reported by Jansson et. al. (1991) using a split/splitless injection port at 250°C. They did not specify the standards used but did indicate that Dechlorane 603 was used as an internal standard (monitoring the ions at *m/z* 237 and 239). For chlorinated paraffin detection they monitored ions at *m/z* 70,71,72, and 73 (corresponding to Cl_2^- and $(HCl)_2^-$ dimers); this is, however, a non-specific mode of detection as there are many interfering ions at that *m/z* in environmental samples.

For our investigation, a 30m HP-5MS column (equivalent to the DB-5MS) was used with split/splitless injection at 250°C and the MS in full scan EI mode. Initial runs showed no peaks

with either the Dechlorane or the Cereclor S52, which was assumed to be because of compound breakdown in the column itself. A modified column was constructed out of 5m of the HP-5MS column (the methods listed above used either a 5 or 15m column). Runs of Dechlorane (Figure 1) and Cereclor S52 (Figure 2)on 5m columns gave reasonable response, but in the case of the Cereclor gave several poorly resolved "peaks", which were probably mixtures of various fragments. The spectrum for the Dechlorane showed ions at *m/z* 237, 272, and 513 (the 237 ion is used for selected ion monitoring for this compound by Jansson et. al.). The Cereclor spectrum showed a prevalence of ions at lower (<100) *m/z*, probably due to fragmentation in the source of any fragments of the original compounds that managed to make it through the GC injection port and column.

Figure 1. Full Scan EI Trace and Spectrum of Dechlorane 603.

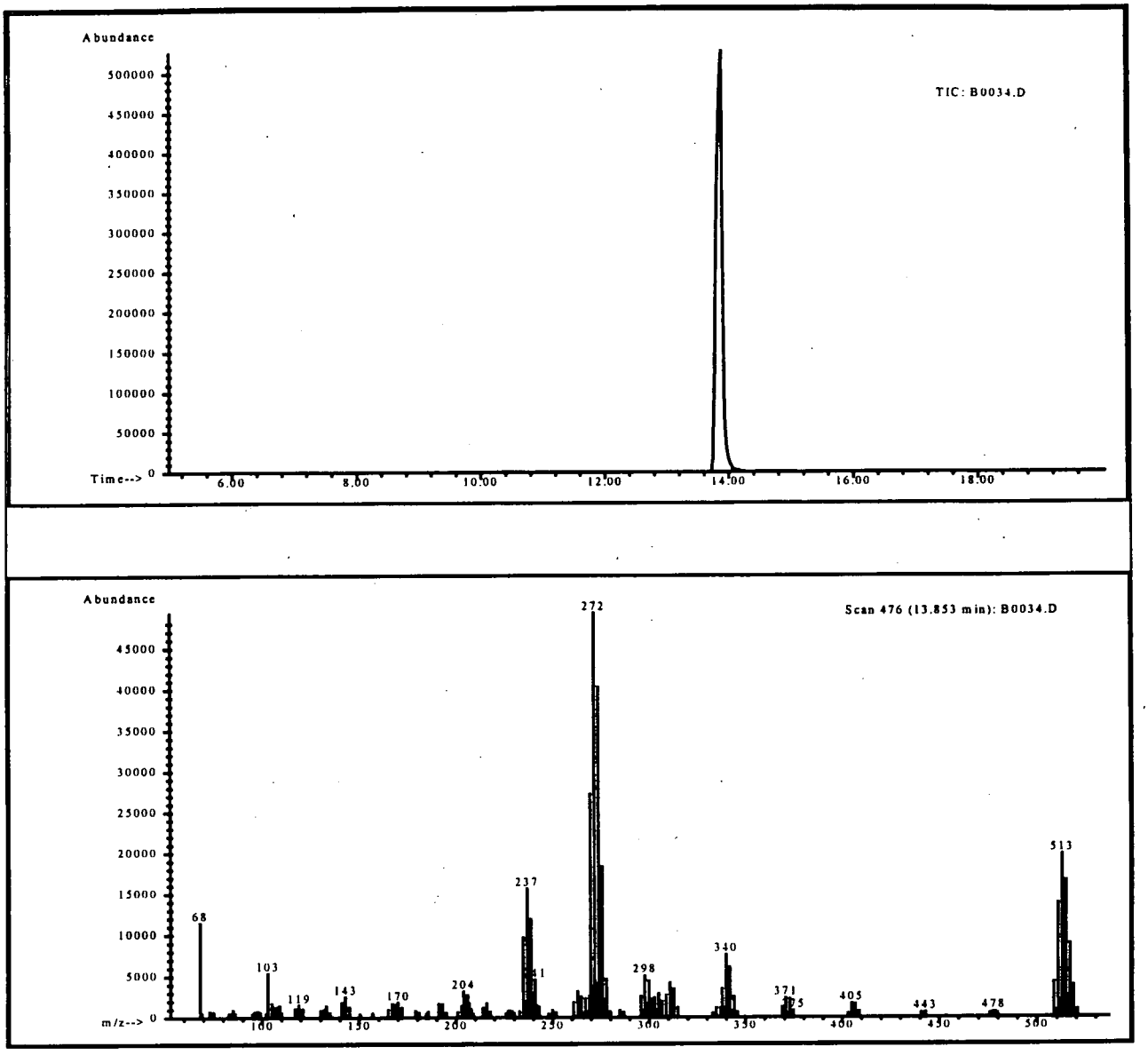
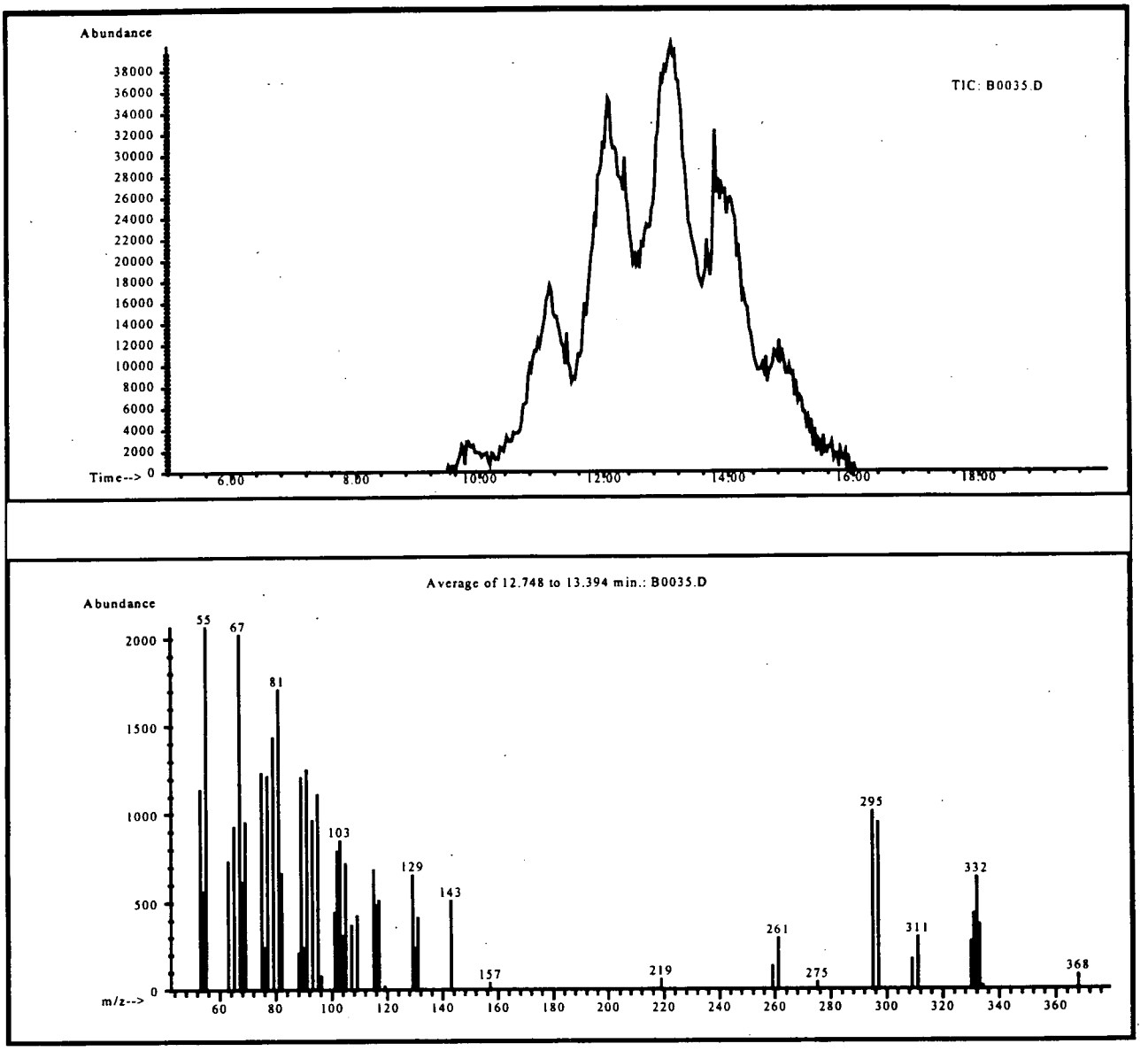


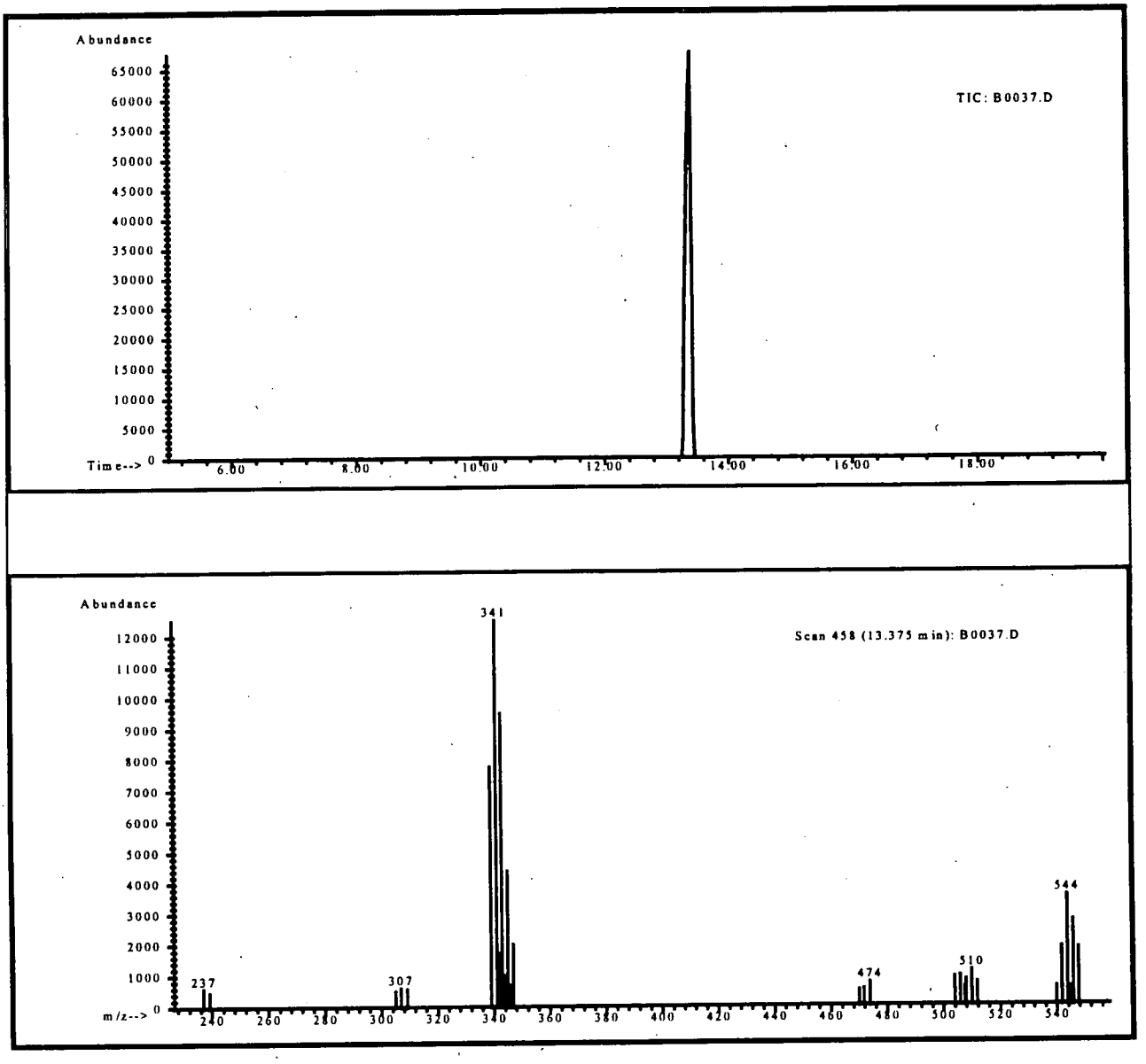
Figure 2. Full Scan Trace and Spectrum of Cerechlor S52.



Once the retention time of peaks for the mixtures had been established by EI runs, full scan NCI runs were attempted. The analysis of Dechlorane gave a single peak with a spectrum consisting of prominent ions *m/z* 341 and 544 (Figure 3). Full scan NCI analysis of Cereclor gave no peaks (Figure 4 a). In order to verify that the MS was properly tuned for NCI analysis, a standard of Aroclor 1260 was analyzed immediately after the Cereclor run, and gave a typical NCI trace and spectrum for PCBs (Figure 4 b). It would appear then that the Cereclor mixture

was either not making its way through the injection port and column in sufficiently large fragments, or that those fragments that were making their way into the CI source were not retaining a negative charge upon interaction with the CI reagent gas, and therefore going undetected.

Figure 3. Full Scan NCI Trace and Spectrum of Dechlorane 603.



Repeated runs of Cereclor S52 were made to verify lack of response, and in one case a reasonable full scan NCI spectrum was obtained (Figure 5). The spectrum obtained in this case was similar to one obtained by Schmid and Muller (1985) using on-column injection of Witaclor standards. It is not clear why the compounds should respond in this single instance, perhaps for some reason the Cereclor did not appreciably fragment upon injection, but in any case this result was not reproducible.

Figure 4. Full Scan NCI Trace of a) Cereclor S52, b) Trace of Aroclor 1260, and c) NCI Spectrum of Aroclor 1260.

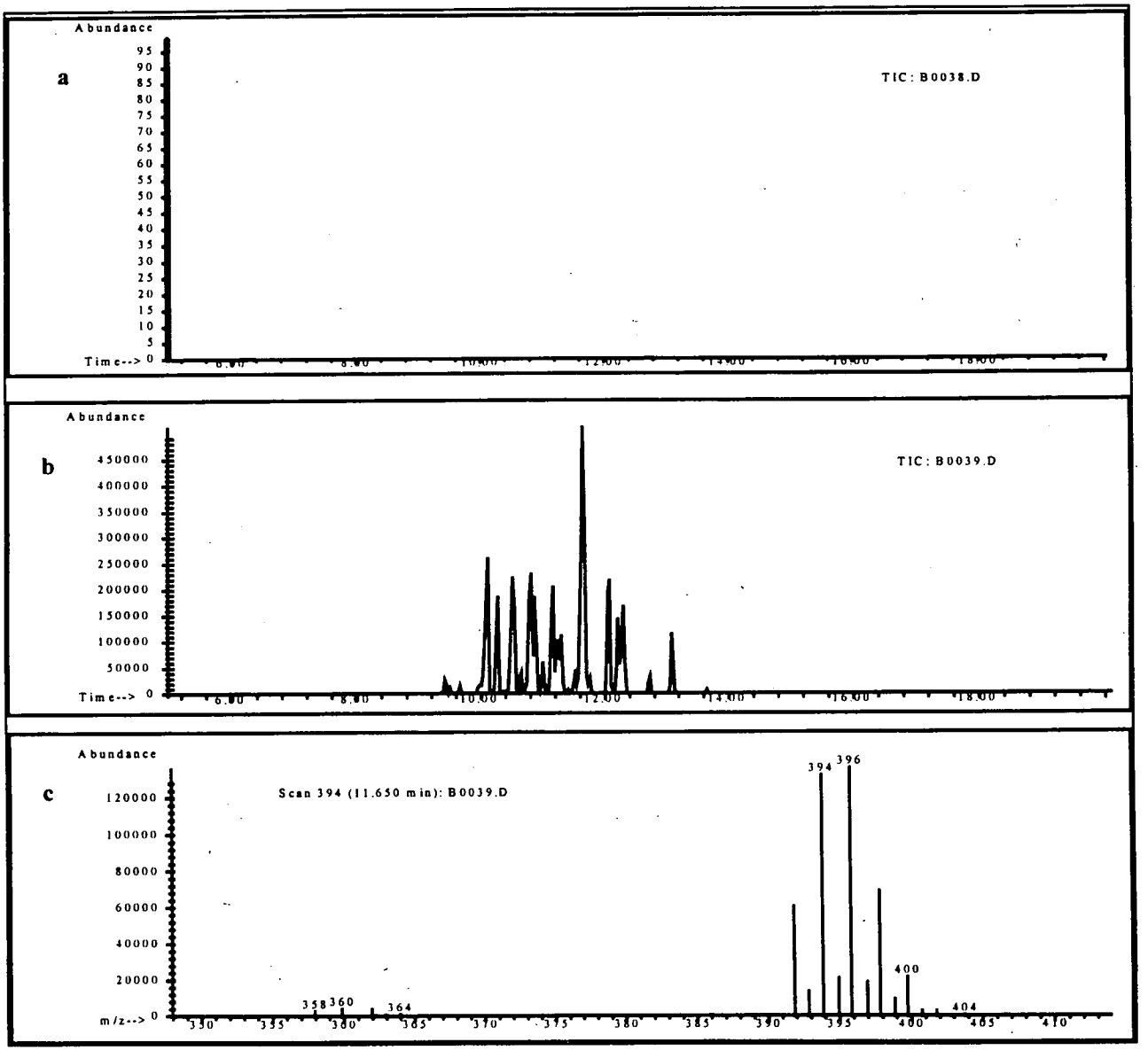
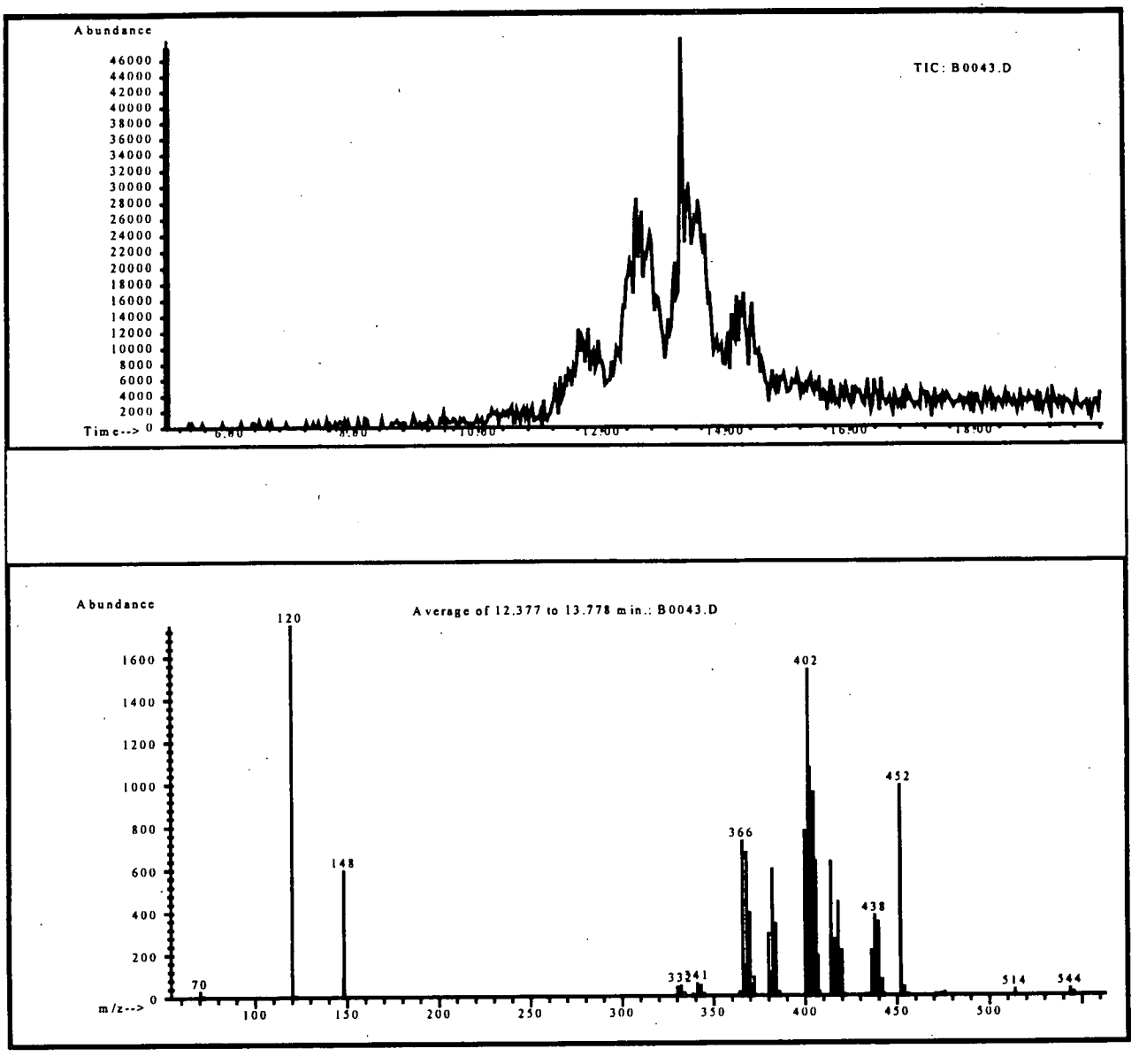


Figure 5. Full Scan NCI Trace and Spectrum of Cereclor S52.



Several other injections were attempted at different (lower) injection port temperatures, lower mass transfer line temperatures, and shorter oven temperature ramp times, but none yielded any peaks for the Cereclor S52 (during the course of these attempts, a standard of A1260 was periodically injected to verify system performance). An attempt at detection by Positive Ion

Chemical Ionization was made, in case some of the larger fragments, if able to make it through the GC, were conducive to positive charge retention. Again there were no peaks seen for the Cereclor S52.

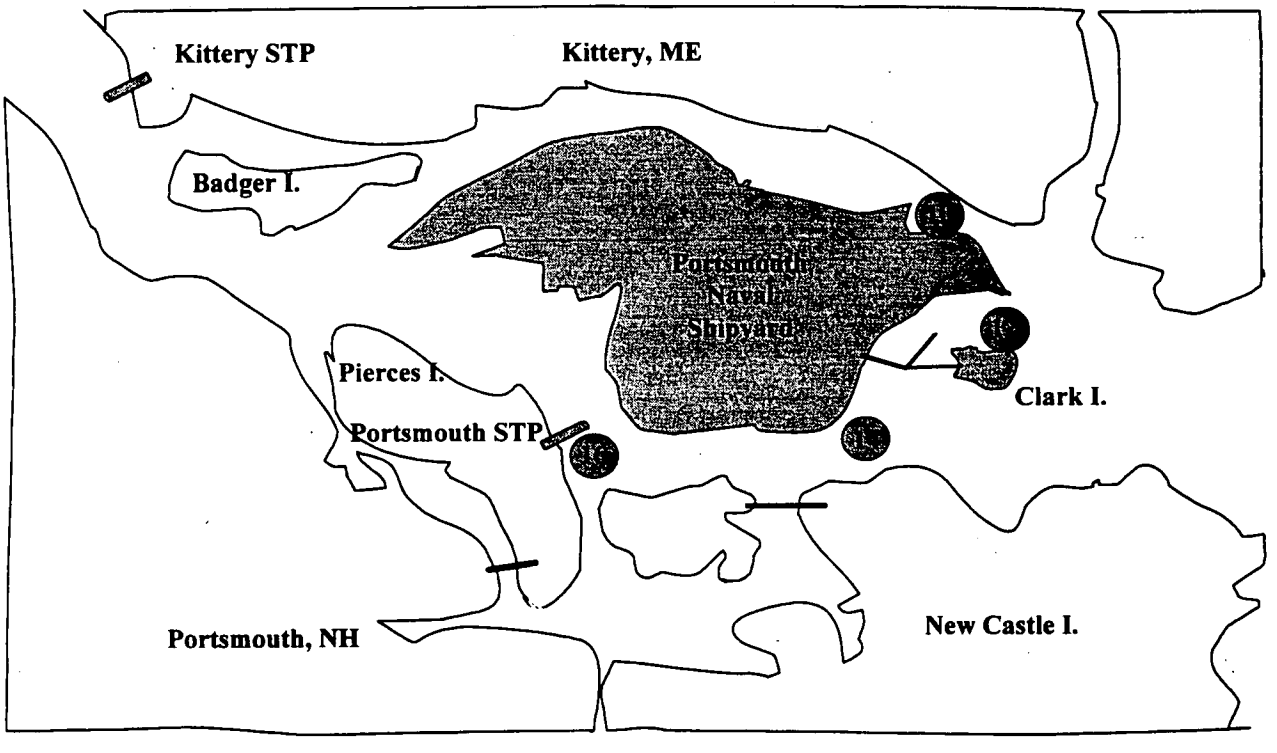
The results obtained in attempts to analyze chlorinated paraffins by GC/NCI-MS would appear to support the assumption that these compounds are labile and may not survive the elevated temperatures of the GC injection port, column, or mass transfer line. Further evidence of lability was given by the EI spectra of Cereclor S52 which showed a predominance of smaller (<100 amu) ions, indicating excessive fragmentation in the source. The two studies (Gjos and sen (1982) and Muller and Schmid (1984)) which did obtain NCI spectra used direct insertion probe and on-column injection techniques, respectively. These techniques would eliminate injection port breakdown of the thermally labile compounds. Our inability to see any peaks (not even small fragments) when analyzing the Cereclor by NCI may be explained by the possibility that smaller fragments, if indeed any made it through the GC, may not retain negative charge when interacting with the methane reagent gas (in most cases of NCI detection, increased sensitivity is gained by electron attachment of thermal electrons produced from the ionization of the reagent gas to the analyte of interest; other processes such as ion pair formation where, say, a Cl atom may dissociate from the fragment and retain the negative charge [giving an ion at *m/z* 35 which would be too low to be detected] would compete with electron attachment and result in a reduction in sensitivity). This may explain the results obtained by Jansson et. al. (1991), since by monitoring the ions at *m/z* 70 - 73 they could be looking at Cl_2^- and $(HCl)_2^-$ dimers, not a mass-specific form of detection as the MS in this case essentially functions as an generic "electron capture" detector. Based on these results we conclude that we are unable to detect these compounds by GC/NCI-MS.

Our attempt at an analysis of standards of chlorinated paraffins by available techniques has shown poor results. Therefore, use of chlorinated paraffins from cutting oils as a shipyard specific chemical marker was not possible and we do not know if these compounds are found in the estuary. As noted in Phase I (*Bowen and Pruell in Phase I report, 1994*) no other unique markers of the shipyard were identified.

B. Water Samples

As part of the Phase II work effort, samples were collected by chemists from the Graduate School of Oceanography (GSO). These water samples were analyzed for trace metals as a means to validate the modeling effort done during Phase I by the University of New Hampshire group. We participated in the first of three sampling cruises on September 14th and 15th, 1993. Four stations in Portsmouth Harbor were chosen to be sampled for organic chemical markers. Sampling stations were chosen to examine the dispersion of contaminants in the lower estuary surrounding the east end of the shipyard on Seavey Island. The location of the water stations sampled are shown in Figure 6.

Figure 6. Location of Water Sampling Stations for Chemical Markers.



The sampling procedure followed ERL-N SOP 2.01.002 and used a teflon pump and a braided stainless steel hose with teflon lining to pump water through a 293mm glass fiber filter held in a stainless steel housing. The flow from the stainless steel filter housing was diverted through a teflon pipe containing four polyurethane foam plugs. The sampling hose was

positioned one meter below the surface and the end of the hose was arranged to face into the current where one existed. At each station the pumping system was used to sample 54 liters of seawater. The pump was operated at a flow rate of approximately one liter per minute.

1. Petroleum

The analytical results for the water samples show that most analytes were not detected in these samples (Table 2). Compounds that were detected were, for the most part, the alkyl homologs of the polycyclic aromatic hydrocarbons (PAHs) and naphthalene (PAH128). This result might suggest a petroleum source, particularly near Station 16 where the compound hopane was also detected.

Table 2. Concentrations of Petroleum Markers in Water Samples (ng/L, values in parenthesis are Method Detection Limits (MDLs) where the analyte was not detected).

Station	10	12	14	16
PAH128	0.68	1.20	1.73	1.12
MW128 homologs	56.7	111	406	887
DBTH	(0.55)	(0.55)	(0.55)	(0.55)
DBTH homologs	7.68	4.18	4.42	7.37
PAH178p	0.35	(0.51)	(0.51)	0.36
PAH178a	(0.59)	(0.59)	(0.59)	(0.59)
MW178 homologs	23.3	13.2	12.4	25.2
PAH202f	1.11	0.61	0.79	1.19
PAH202p	1.01	0.58	0.51	1.21
PAH228b	(0.49)	(0.49)	(0.49)	(0.49)
PAH228c	(0.48)	(0.48)	(0.48)	(0.48)
MW228 homologs	6.29	3.99	2.12	7.90
PAH252p	(0.53)	(0.53)	(0.53)	(0.53)
Sum MW252 PAHs	1.16	(0.59)	(1.64)	1.99
Hopane	(0.85)	(0.85)	(0.85)	0.64

2. Sewage

Results from the analysis for sewage markers was less successful (Table 3). None of the compounds used as markers of sewage contamination were quantifiable in the samples analyzed from Portsmouth Harbor.

Table 3. Concentrations of Sewage Markers in Water Samples (ng/L, values in parenthesis are MDLs where the analyte was not detected).

Station	10	12	14	16
Octylphenol	(0.55)	(0.55)	(0.55)	(0.55)
Nonylphenol	(6.15)	(6.15)	(6.15)	(6.15)
Total LABs	(8.28)	(8.28)	(8.28)	(8.28)
Coprostanone	(59.8)	(59.8)	(59.8)	(59.8)

3. Runoff and Atmospheric Deposition

These water samples were also analyzed for a group of compounds used to indicate inputs from road runoff and atmospheric deposition. As with the other markers these compounds were marginally detected at the stations sampled (Table 4). The road runoff marker benzothiazole was found at a concentration of 20.2 ng/L at Station 12, which is located outside the entrance to the Clark Cove Embayment and at a much lower concentration (0.79 ng/L) at Station 14.

Table 4. Concentrations of Runoff and Atmospheric Markers in Water Samples (ng/L, values in parenthesis are MDLs where the analyte was not detected, ND means the value was not determined).

Station	10	12	14	16
BZT	(0.97)	20.2	0.79	(0.97)
MTBT	(1.33)	(1.33)	(1.33)	(1.33)
9-FLU	(0.87)	(0.87)	(0.87)	(0.87)
ANQ	(2.06)	(2.06)	(2.06)	(2.06)
9-FLU/PAH166	ND	ND	ND	ND
ANQ/ANTH	ND	ND	ND	ND

C. Sediment Cores

Two sediment cores were sectioned and analyzed for chemical markers. One of these cores was collected from Station 17 (off Badgers Island) and the other core was collected from a marsh on the north side of Clark Island (Figure 6). The collection and sectioning of these cores are described elsewhere (Ward, 1994).

1. Station 17 Core

a) Petroleum

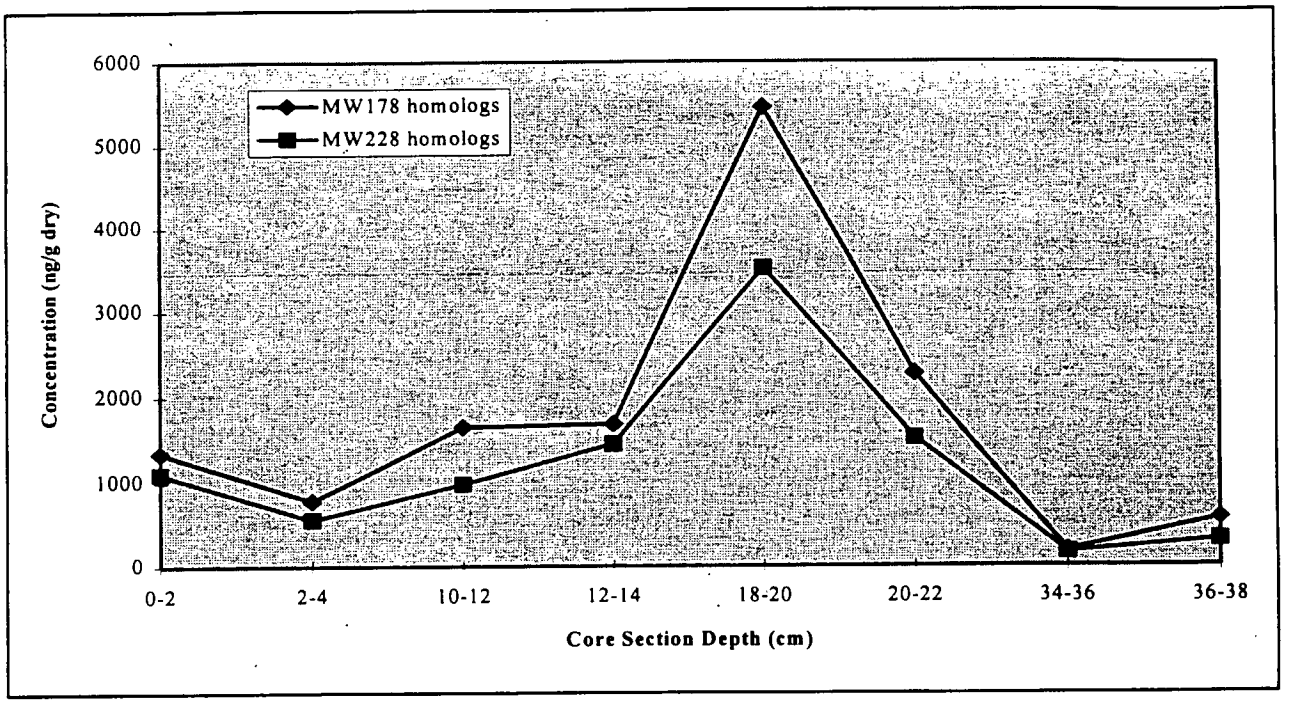
The results for the station 17 petroleum marker analysis (Table 5) show that all compounds were detected down the entire length of the core (38cm). The PAH concentrations increase (moving up core) in the 20-22 cm section and show a subsurface maxima in the 18-20 cm section. This area of the core is from the time frame encompasing the early 1920's to late 1930's (personal communication, L. Ward) and may represent a period of increased shipyard

activity. The concentrations of the alkyl homologs of phenanthrenes and chrysenes (MW178 homologs and MW228 homologs, Table 1) increase down core with a maximum in the 18-20 cm section (Figure 7). This subsurface maximum is not collocated with the subsurface maximum in the concentrations of the lower molecular weight homologs of naphthalene (MW128 homologs) or that of hopane (Figure 8).

Table 5. Concentrations of Petroleum Markers in Core Sections from ST. 17 (ng/g).

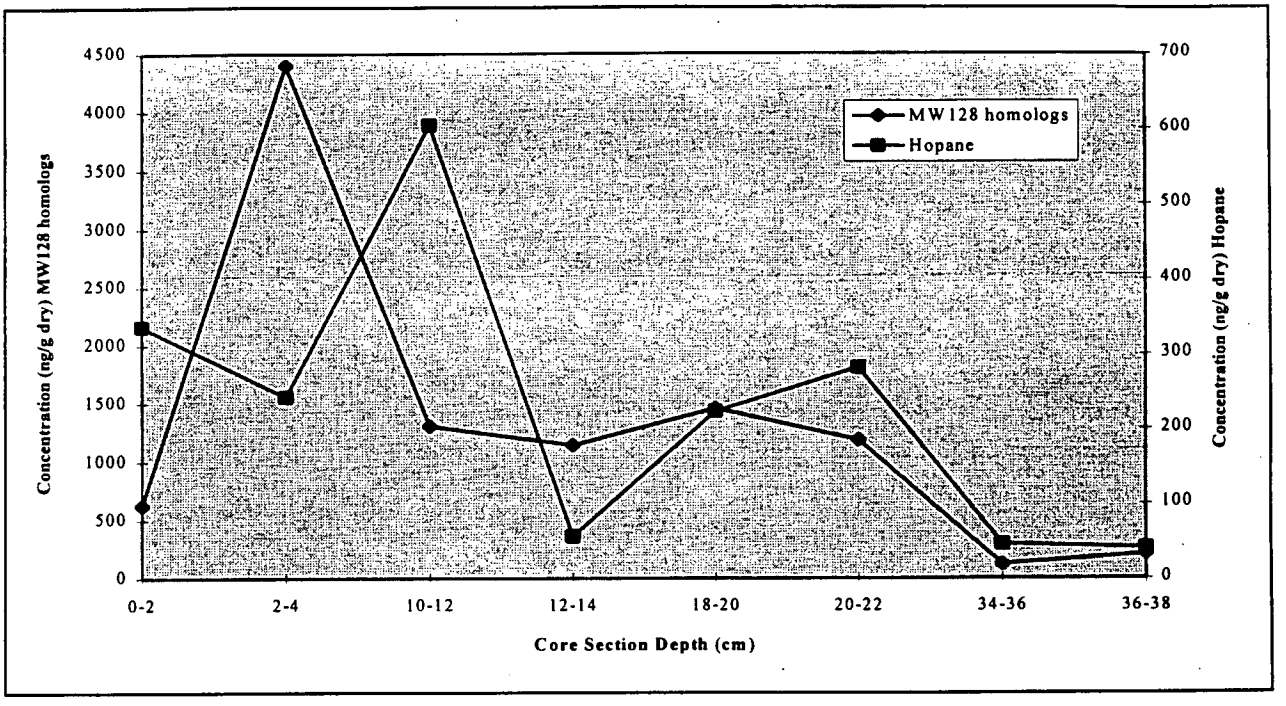
Section Depth (cm)	0-2	2-4	10-12	12-14	18-20	20-22	34-36	36-38
PAH128	86.2	269	101	86.7	166	76.9	17.9	23.7
MW128 homologs	629	4400	1310	1140	1460	1190	123	210
DBTH	28.8	17.0	39.5	26.7	46.0	39.6	1.72	5.72
DBTH homologs	191	78	262	105	355	183	14.3	45.3
PAH178p	630	480	985	611	1270	1120	40.5	105
PAH178a	280	231	421	392	775	621	20.8	32.5
MW178 homologs	1350	779	1650	1680	5450	2270	182	567
PAH202f	1650	1150	2230	841	3520	1930	79.0	220
PAH202p	1880	1110	2770	1520	6660	2250	268	681
PAH228b	1010	733	1070	697	2650	1210	65.0	190
PAH228c	797	543	752	729	1610	1050	57.1	110
MW228 homologs	1100	556	981	1450	3510	1520	160	308
PAH252p	277	138	319	261	524	289	33.7	67.8
Sum MW252 PAHs	4320	2620	4640	5130	10200	5450	538	637
Hopane	336	242	605	56.3	223	282	46.0	41.3

Figure 7. Alkyl Homologs of MW178 and MW228 PAHs in the Core Sections from St. 17 (ng/g dry).



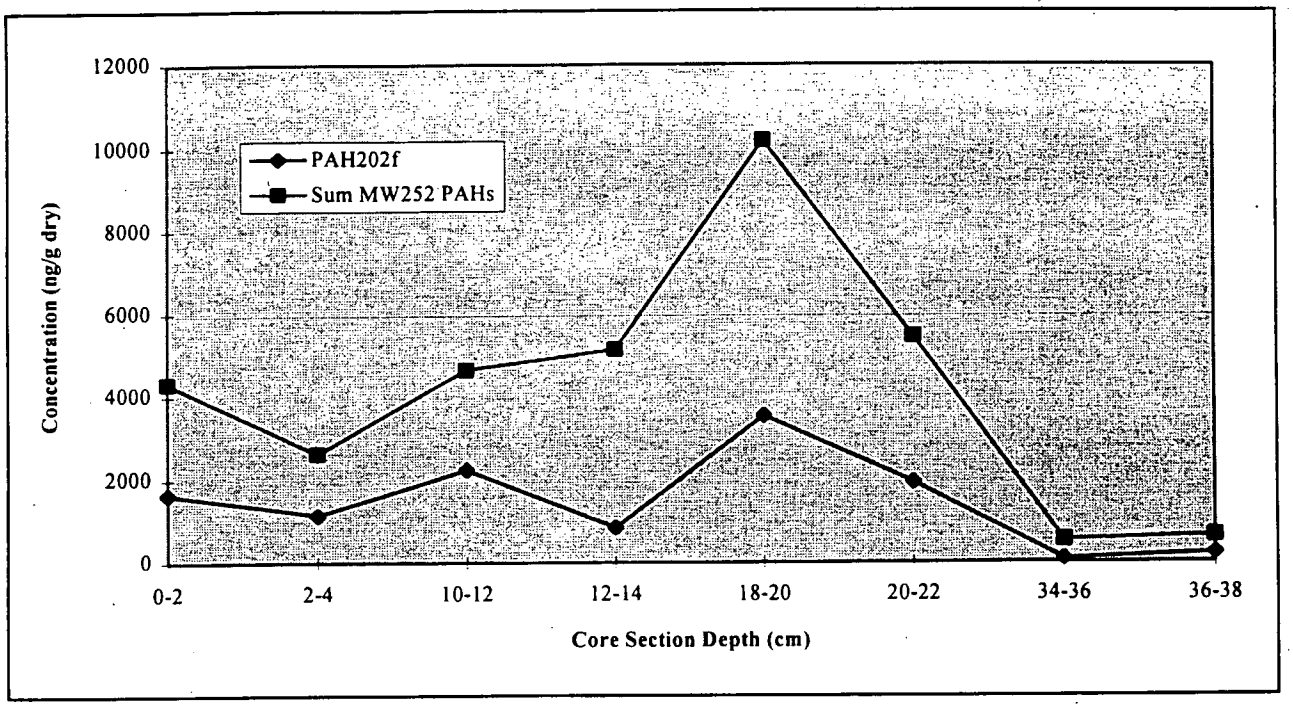
When these two figures are compared (Figure 7 and Figure 8) it appears likely that the petrogenic sources of petroleum to this area varied with time. The lower core section (18-20 cm) appears to have received a different type of petroleum, possibly a higher molecular weight or heavier oil, than the upper sections of the core.

Figure 8. Concentration of MW128 homologs and Hopane in Core Sections from St. 17 (ng/g dry).



The source of combustion derived petroleum hydrocarbons to the core appears to show an increase in relative strength in the 18-20 cm core section (Figure 9). Concentrations of both the sum of the MW252 PAHs and PAH202f (fluoranthene, Table 1) show subsurface maximums in this core section. This maxima in combustion derived material is collocated with the maxima in the down core distribution of the heavier petroleum products as shown in Figure 7 and may be the result of an increase in shipyard activities during this period.

Figure 9. Concentration of Pyrogenic PAHs in Core Sections from St. 17 (ng/g dry).



b) Sewage

The concentrations of sewage markers (Table 6) and markers of road runoff and atmospheric deposition (Table 7) were also measured in the core sections from Station 17. Coprostanone shows a declining concentration through the top three sections analyzed. None of the sewage markers are detected in the core below 12 cm. The other sewage markers are not-detected in the surface sample, however, the Nonylphenol and LAB markers are detected in the 2-4 and 10-12 cm sections and the Octylphenol is detected in the 10-12 cm section. The presence of the Octylphenol in the 18-20 cm section may be an outlier that is a result of a coeluting compound present during the analysis. The existance of this compound is not well supported by the data from the other core sections.

Table 6. Concentrations of Sewage Markers in St. 17 Core Sections (ng/g dry, values in parenthesis are MDLs where the analyte was not detected).

Section Depth (cm)	0-2	2-4	10-12	12-14	18-20	20-22	34-36	36-38
Octylphenol	(1.41)	(1.47)	2.6	(1.48)	6.3	(1.60)	(1.61)	(2.08)
Nonylphenol	(15.8)	33.9	24.4	(16.7)	(19.9)	(18.0)	(18.1)	(23.4)
Total LABs	(14.0)	51.7	29.6	(37.2)	(20.6)	(57.4)	(45.4)	(10.9)
Coprostanone	568	256	235	(162)	(194)	(175)	(176)	(228)

c) *Runoff*

The Road Runoff Markers measured in the sediment cores show a subsurface maxima (Table 7) as did the PAH alkyl homologs. The compounds BZT and MTBT (benzothiazole and methylthiobenzothiazole, Table 1) show very high concentrations in the 34-36 cm section and decrease up core with a high point in the 12-14 cm section. The high concentration of these markers deep in the core is not readily explained.

Table 7. Concentration of Road Runoff and Atmospheric Markers in St. 17 Core Sections (ng/g dry, values in parenthesis are MDLs where the analyte was not detected, ND means the value was not determined).

Section Depth (cm)	0-2	2-4	10-12	12-14	18-20	20-22	34-36	36-38
BZT	216	178	(3.92)	2140	4.41	1180	6010	5.53
MTBT	6.61	107	12.9	375	8.41	447	1280	7.96
9-FLU	11.0	14.2	12.6	24.5	11.7	15.8	(2.55)	(3.30)
ANQ	56.3	109	66.4	81.3	87.4	117	12.3	8.14
9-FLU/PAH166	0.315	0.807	0.272	0.416	0.153	0.182	ND	ND
ANQ/ANTH	0.0894	0.227	0.0674	0.133	0.0688	0.104	0.304	0.0775

d) Atmospheric Deposition

The measured concentrations of the Atmospheric Deposition Markers are shown in Table 7 in two forms. The oxidated PAHs 9-FLU and ANQ (9-Fluorenone and Anthraquinone,Table 1) and the ratio of these oxidation products to their parent compounds 9-FLU/PAH166 and ANQ/ANTH (Ratio of 9-Fluorenone to Fluorene and Ratio of Anthraquinone to Anthracene, also Table 1). A higher value of either of these ratios signifies a greater relative contribution of atmospherically derived material to that sample. The ratio 9-FLU/PAH166 varies down core with maxima at the 2-4 cm and 12-14 cm sections. The other atmospheric marker, ANQ/ANTH, has a maximum value in the 34-36 cm section of the core and also shows a maxima in the 2-4 cm section. These data may indicate an increased input in the late 1980's reflected in the 2-4 cm section results. Deeper in the core the data from the two markers are not consistant making the interpretation more difficult.

2. Clark Cove Marsh Core

The second core analyzed for chemical markers was collected from a marsh on the north side of Clark Island. This core was not part of the initially planned collection for this project and as such very little data is available for it beyond what was measured for chemical markers. It was added because the radiochem data from the other cores collected indicated they were mixed by bioturbation and therefore would not provide a good record of inputs.

a) Petroleum

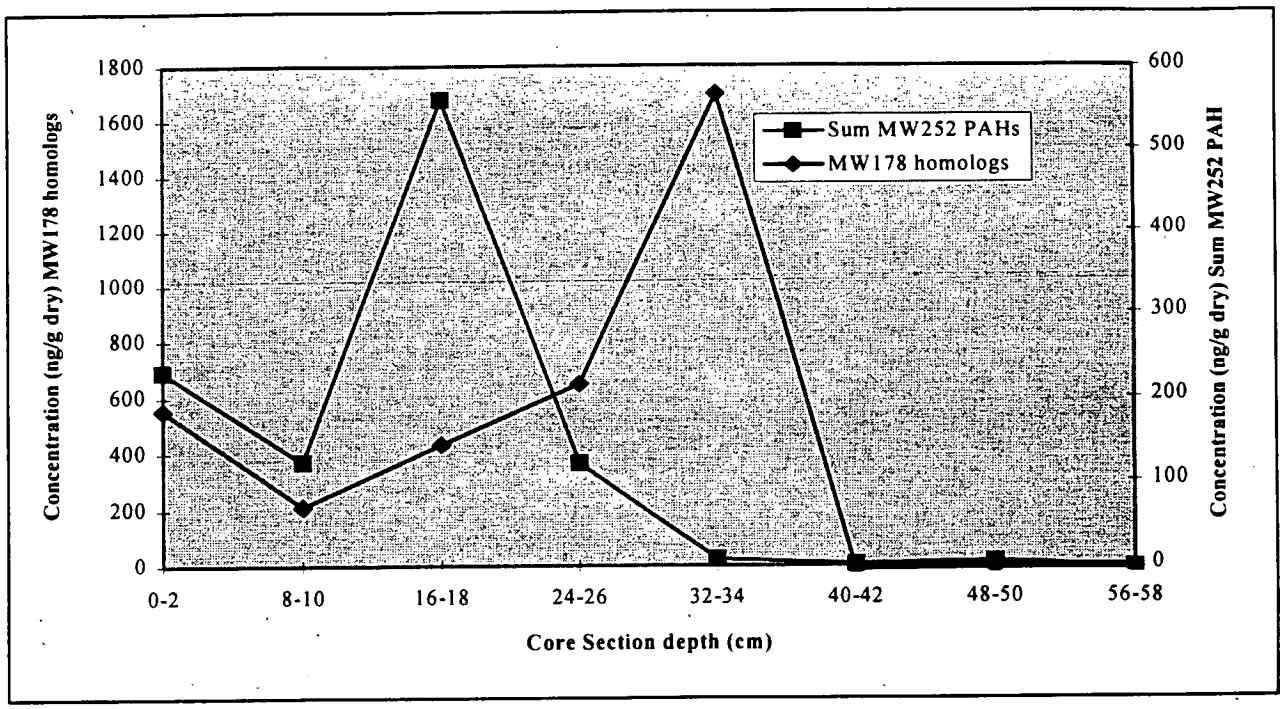
The concentrations of petroleum markers in these core sections are shown in Table 8. Naphthalene was quantified in each of the core sections and show a general decrease down core from a surface maximum. The other PAHs show surface maximums and a subsurface maxima in the 16-18 cm section. This trend is especially prevalent in the PAH202f and PAH202p (fluoranthene and pyrene, Table 1) compounds where the concentrations more than double in

comparison with the concentrations in the 8-10 cm section. The concentration of the Sum MW252 PAHs decreases steadily after the subsurface maximum at 16-18cm (Figure 10) and becomes equal to the PAH252p (perylene, Table 1) compound that makes up part of the Sum MW252 PAHs. The compound perylene may have a small natural source that contributes to its distribution in these sediments along with the combustion source that contributes to the other MW252 PAHs. These data, along with the non-detectable lower molecular weight PAHs, corroborate the lack of a combustion source contributing to the core below the 32-34 cm section.

Table 8. Concentrations of Petroleum Markers in Clark Cove Marsh Core Sections (ng/g dry, values in parenthesis are MDLs where the analyte was not detected).

Section Depth (cm)	0-2	8-10	16-18	24-26	32-34	40-42	48-50	56-58
PAH128	107	36.5	35.1	31.9	24.4	4.18	1.91	1.84
MW128 homologs	243	61.7	63.1	84.9	33.6	(3.59)	(3.08)	1.69
DBTH	8.53	3.11	2.79	1.98	(2.05)	(1.14)	(0.97)	(0.96)
DBTH homologs	38.3	16.3	19.1	20.1	5.00	(3.41)	(2.92)	(2.87)
PAH178p	187	41.7	54.7	19.6	12.0	(1.05)	(0.90)	(0.89)
PAH178a	26.7	10.8	19.2	9.28	3.94	(1.21)	(1.04)	(1.02)
MW178 homologs	185	70.8	144	216	566	(4.51)	(3.87)	(3.80)
PAH202f	389	149	394	95.9	11.3	(0.95)	(0.81)	(0.80)
PAH202p	332	124	316	79.9	12.6	(0.92)	(0.79)	(0.77)
PAH228b	123	34.9	102	69.9	5.38	(1.33)	(1.14)	(1.12)
PAH228c	145	39.8	92.1	47.2	5.50	(1.28)	(1.10)	(1.08)
MW228 homologs	150	27.7	73.8	121	35.0	(3.91)	(3.35)	(3.30)
PAH252p	35.0	11.9	42.6	19.0	16.5	4.31	12.6	(1.71)
Sum MW252 PAHs	692	369	1680	365	24.3	4.31	12.6	(7.59)
Hopane	440	72.3	(4.75)	16.8	(5.88)	(3.25)	4.90	6.48

Figure 10. Alkyl Homologs of MW178 PAHs and Sum of MW252 PAHs in Core Sections from the Clark Cove Marsh (ng/g dry).



b) Sewage

The concentrations of sewage markers in the Clark Cove Marsh core are shown in Table 9. The Octylphenol, Nonylphenols and LABs were not detected in any of the core sections analyzed. Coprostanone was detected in the top four sections of this core. The concentration varies extensively with a subsurface maximum in the 8-10 cm section and another maxima in the 24-26 cm section.

Table 9. Concentrations of Sewage Markers in Clark Cove Marsh Core Sections (ng/g dry, values in parenthesis are MDLs where the analyte was not detected).

Section Depth (cm)	0-2	8-10	16-18	24-26	32-34	40-42	48-50	56-58
Octylphenol	(4.60)	(1.54)	(1.80)	(2.08)	(2.23)	(1.23)	(1.06)	(1.04)
Nonylphenol	(51.7)	(17.3)	(20.3)	(23.4)	(25.1)	(13.9)	(11.9)	(11.7)
Total LABs	(112)	(3.87)	(11.0)	(17.6)	(36.3)	(4.15)	(1.97)	(0.84)
Coprostanone	1820	2700	755	1660	(244)	(135)	(116)	(114)

Table 10. Concentrations of Road Runoff and Atmospheric Deposition Markers in Clark Cove Marsh Core Sections (ng/g dry, values in parenthesis are MDLs where the analyte was not detected, ND means the value was not determined).

Section Depth (cm)	0-2	8-10	16-18	24-26	32-34	40-42	48-50	56-58
BZT	357	79.5	25.2	19.0	16.0	7.86	(2.16)	(2.13)
MTBT	44.2	7.91	(5.05)	(5.85)	(6.26)	(3.46)	(2.97)	(2.92)
9-FLU	20.0	4.89	3.56	5.10	(3.54)	(1.96)	(1.68)	(1.65)
ANQ	121	28.2	28.7	15.1	(8.40)	(4.65)	(3.99)	(3.92)
9-FLU/PAH166	1.98	ND	ND	ND	ND	ND	ND	ND
ANQ/ANTH	0.65	0.68	0.53	0.77	ND	ND	ND	ND

c) *Road Runoff and Atmospheric Deposition*

The concentrations of Road Runoff and Atmospheric Deposition markers in the Clark Cove sediment core sections are shown in Table 10. The down core distribution of the runoff marker BZT shows a trend of decreasing with depth to become non-detectable below the 40-42 cm section. No subsurface maxima is evident in this compound's distribution. While the data show a down core maxima in the ANQ/ANTH atmospheric depostion marker in the 24-26 cm section, the difference may not be outside of the variability in the analysis. Replicates were not done for this study.

3. Summary of Sediment Cores

Results from the analysis of two sediment cores from Portsmouth Harbor for chemical markers indicate different patterns. The core collected at Station 17, at the west end of the Portsmouth Naval Shipyard on Seavey Island, shows evidence of inputs from different petroleum sources coming at different depths in the core. Petroleum inputs in the Clark Cove Marsh core

appear high at depth. While the down core distribution of the road runoff marker shows a consistant down core gradient in the Clark Cove Marsh core, it shows a puzzling trend in the Stations 17 core. The extremely high concentration of BZT deep in the Station 17 core is not explainable given the behavior of the other compounds in this core. There is down core evidence of inputs from sewage material in both of the cores, however, only in the Station 17 core are there detectable levels of any of the sewage markers besides Coprostanone. It is difficult to suggest an input history of sewage derived material from this sparse data set. Contributions of atmospherically derived material are evident in the Station 17 core throughout its depth (38 cm). The Clark Cove Marsh core shows a higher relative input strength in the surface section (compared to Station 17) and inconsistant results below the surface.

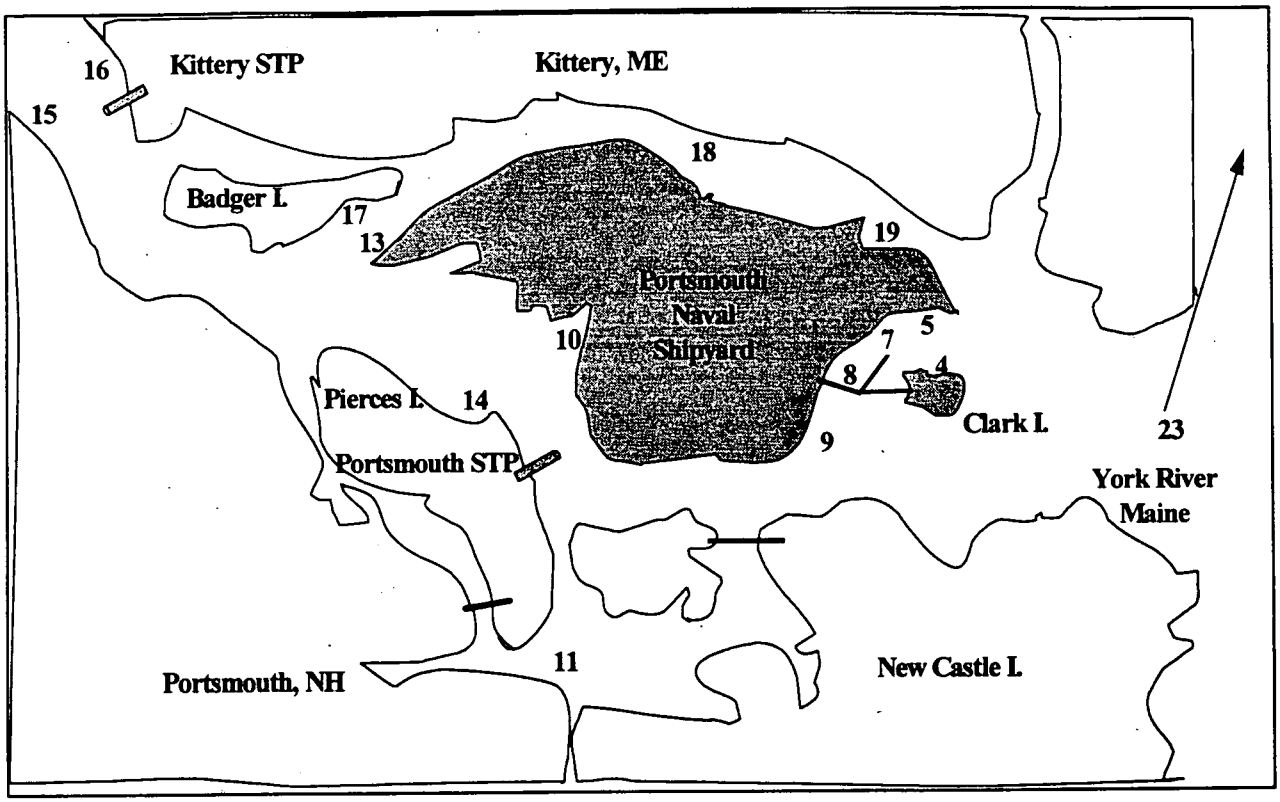
These data indicate that these sediments have not retained a good record of historical inputs to this region. As such, it is not practical to use these sediment cores to construct an accurate record of the onset and suspension of various contaminant sources to this estuary as a function of time. Other cores, collected as part of this study, showed inconsistancies in the down core trend in the radiochemicals ^{210}Pb and ^{137}Cs and were not further analyzed for chemical markers because this data suggested the temporal record was disturbed by bioturbation.

D. Surface Sediments

1. Introduction

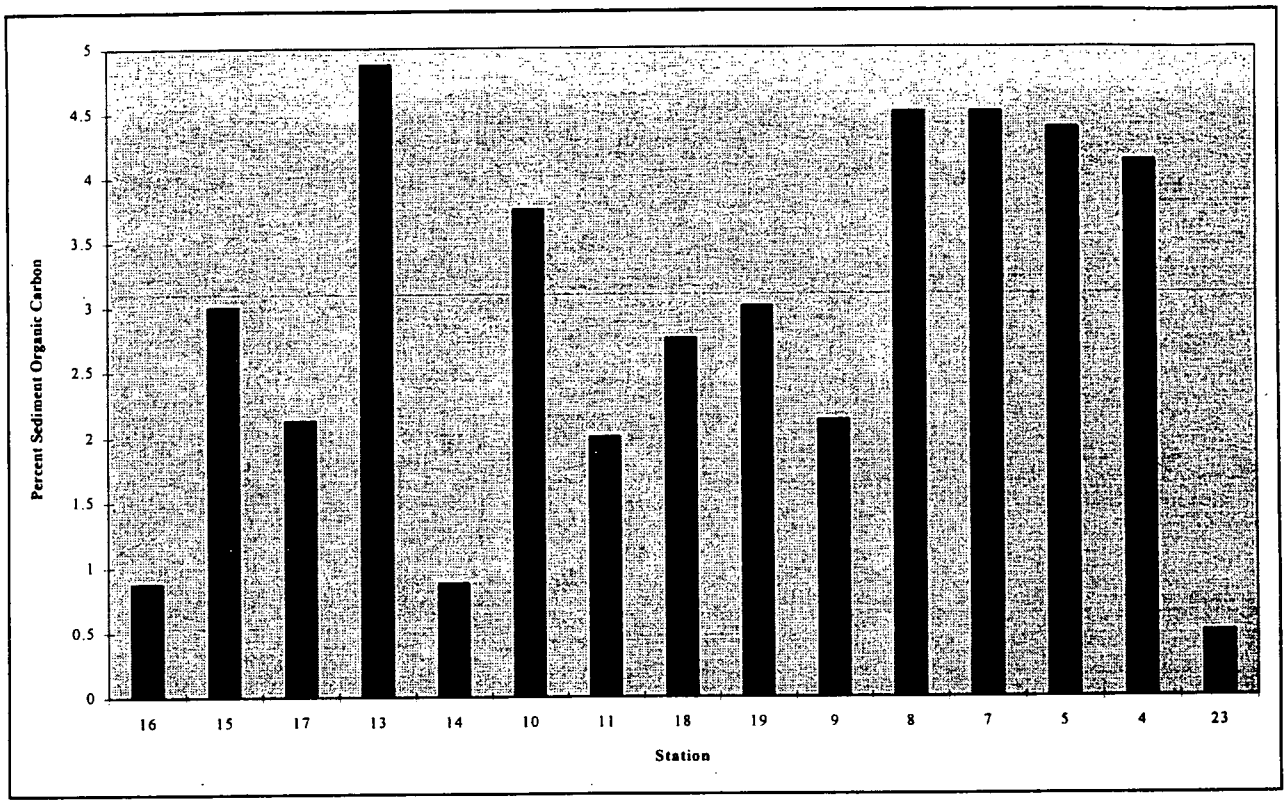
Sediment samples collected during Phase I of the risk assessment were used in this second phase of the chemical markers analysis. The locations of the surface sediment stations used are shown in Figure 11. Samples were chosen from stations adjacent to Seavey Island, upriver from the shipyard, across the channel from the shipyard, and from a reference site in the York River, Maine (Station 23).

Figure 11. Location of Surface Sediment Stations in the Lower Piscataqua River Estuary.



The compounds used as chemical markers in this study are all hydrophobic and are closely associated with the organic carbon portion of the sediments. The organic carbon content of the sediments analyzed varied widely throughout the estuary (Figure 12) tending to be higher in the low energy depositional areas which are represented by some of the samples in this study. In an attempt to normalize the sediment chemical concentrations to remove the influence of these different sediment types, the concentrations of the the chemical markers are reported in nanograms per gram of organic carbon (ng/g C). It can be seen from Figure 12 that sediments from Stations 16, 14 and 23 all have very low organic carbon content. This normalization technique will therefore amplify the measured concentrations at these stations relative to stations such as Stations 13, 8, 7, and 5.

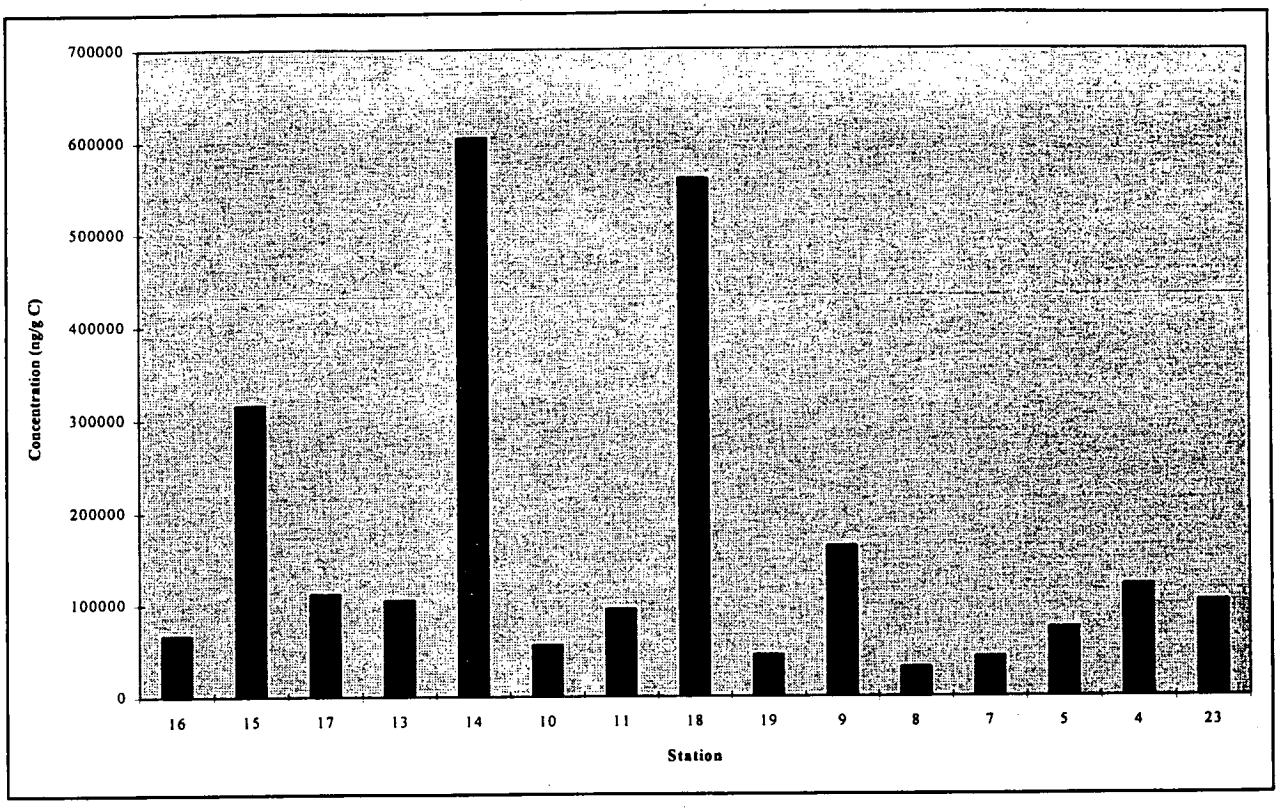
Figure 12. Concentration of Organic Carbon in Surface Sediments (%C).



2. Petroleum

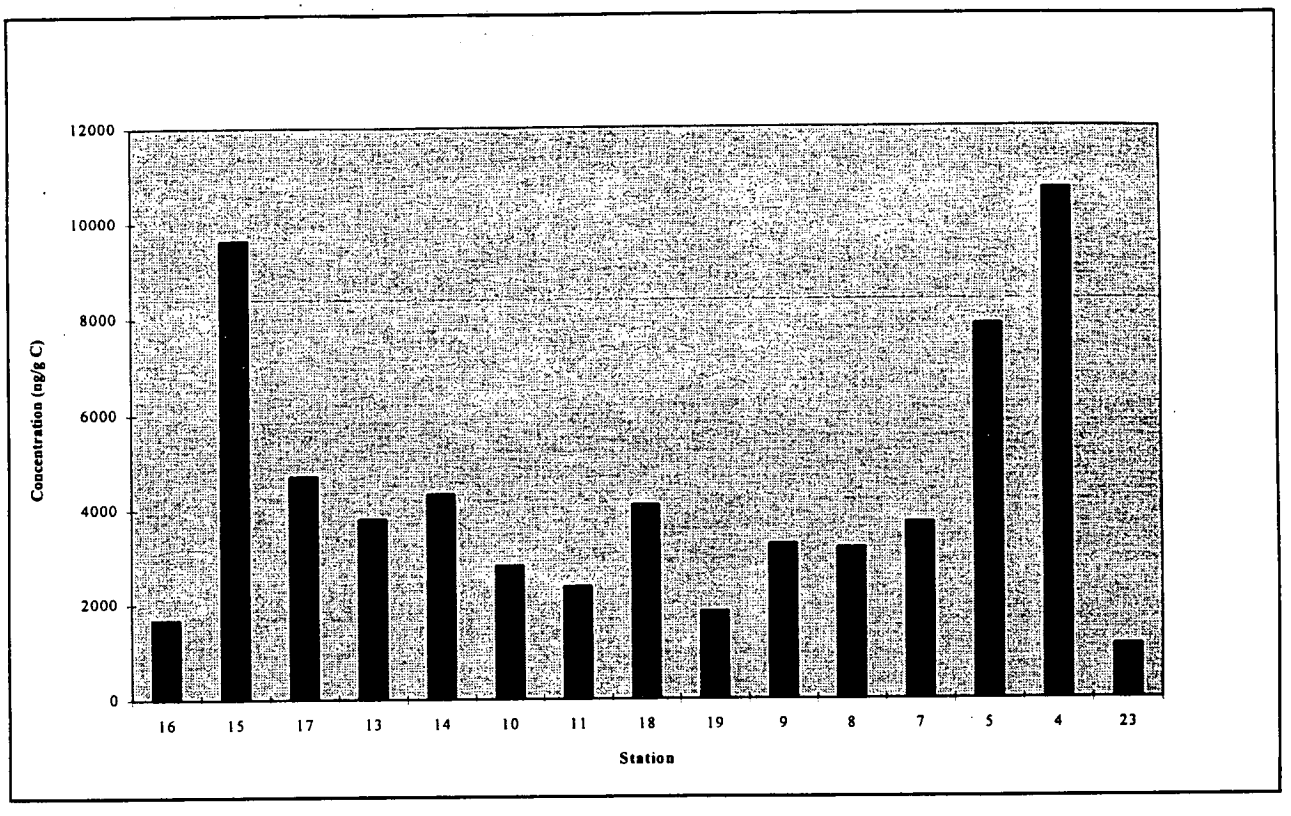
The distribution of PAHs in the surface sediments of the Lower Piscataqua River Estuary is shown in Figure 13. This figure shows very high concentrations of PAHs at Stations 15, 14, and 18. Concentrations at the other stations are much lower with a minimum at Station 8 in the Clark Cove Embayment. The concentrations of PAHs in and around Clark Cove show an interesting pattern. There appears to be a trend of steadily decreasing concentrations entering the cove proceeding from Stations 4, 5, 7, to Station 8. While this does not necessarily implicate a source of PAHs outside of the Clark Cove Embayment it offers no suggestion of a source within the embayment.

Figure 13. Concentrations of the Sum of Measured PAHs in Surface Sediments (ng/g C).



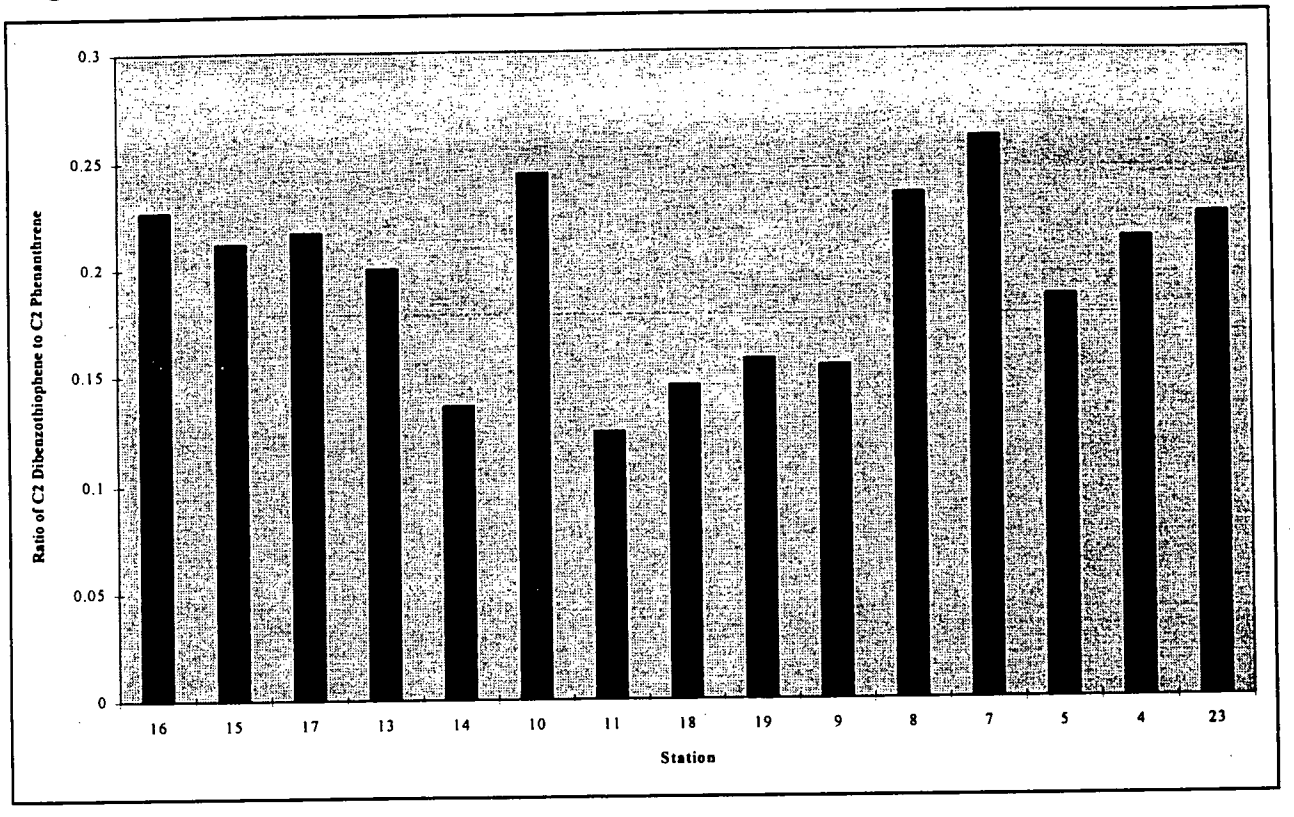
The concentration of the pentacyclic triterpane hopane can be used as an indicator of petroleum inputs to sediments. The distribution of this compound (Figure 14) shows the highest concentrations at Stations 15, 4 and 5. As with the PAH distribution, there is a trend of decreasing concentration entering the Clark Cove Embayment (see Figure 11). This pattern, again, does not suggest a source of this petrogenic compound within Clark Cove. The relatively high concentration at Station 15, located up-river from the Portsmouth Harbor area may indicate a potential up-river source. However, sediment analysis from stations further up-river would be required to do more than speculate on this possibility. This station is also located close by the major roadway crossing the Piscataqua River (Route 95). Runoff of petroleum compounds from this roadway into the estuary may contribute to the high signal seen in the Station 15 sediment.

Figure 14. Concentration of the Petroleum Marker Hopane in Surface Sediments (ng/g C).



The chemical composition of petroleum can vary with different crude oils and distillates of oil. One class of compounds that occurs in varying degrees in oils are the dibenzothiophenes. These compounds occur in higher relative concentrations in oils that have a higher sulfur content. In Figure 15, the ratio of the C_2 alkyl homolgs of dibenzothiophene to the C_2 alkyl homologs of phenanthrene within each sample are shown for the surface sediments. This graph shows the petroleum contamination at Stations 10, 8, and 7 have higher levels of this ratio than the other stations. In addition, Stations 9, 11, 14, 18, and 19 all have lower levels of this ratio and appear to represent a separate grouping from the other stations. These data indicate the petroleum source that contributed to the compounds measured in these sediments is different for these two groups of stations. The stations with values falling in between these two groups may represent a mixture of two, or more, source oils.

Figure 15. Petroleum Source Marker, Ratio of C2 Dibenzothiophene to C2 Phenanthrene



A more detailed look at the distribution of petroleum hydrocarbons within each sediment sample involves the calculation of diagnostic ratios of different alkyl homologs within the sample (Overton, et al , 1981). When two such ratios are examined simultaneously the technique is refered to as a double ratio biplot. In Figure 16 and Figure 17 two double ratio biplots are used to examine the distribution of petroleum types among the surface sediment samples in the Lower Piscataqua River Estuary.

In Figure 16 Stations 10, 8, 7, 13, 16, and 23 appear to cluster of to the right, while Station 11 appears by itself. The other stations fall into two groups in the lower left portion of the graph. The distribution is shown slightly differently in Figure 17 where a different pair of ratios are employed. Stations 10, 8, 7, 13, 16, and 23 again seem to group together while the remaining stations fall into two or more groupings. This analysis does not separate the stations that are located adjacent to the shipyard from those that are located further from the shipyard, however, it does display relationships between Stations 9 and 19, Stations 4 and 17, and Stations 7, 8, and 10 that might not otherwise be suggested.

Figure 16. A Double Ratio Biplot Showing the Ratio of C_2 Phenanthrenes to C_2 Chrysenes vs. C2 Dibenzothiophenes to C2 Chrysenes in Surface Sediments, Station numbers are labelled on the graph.

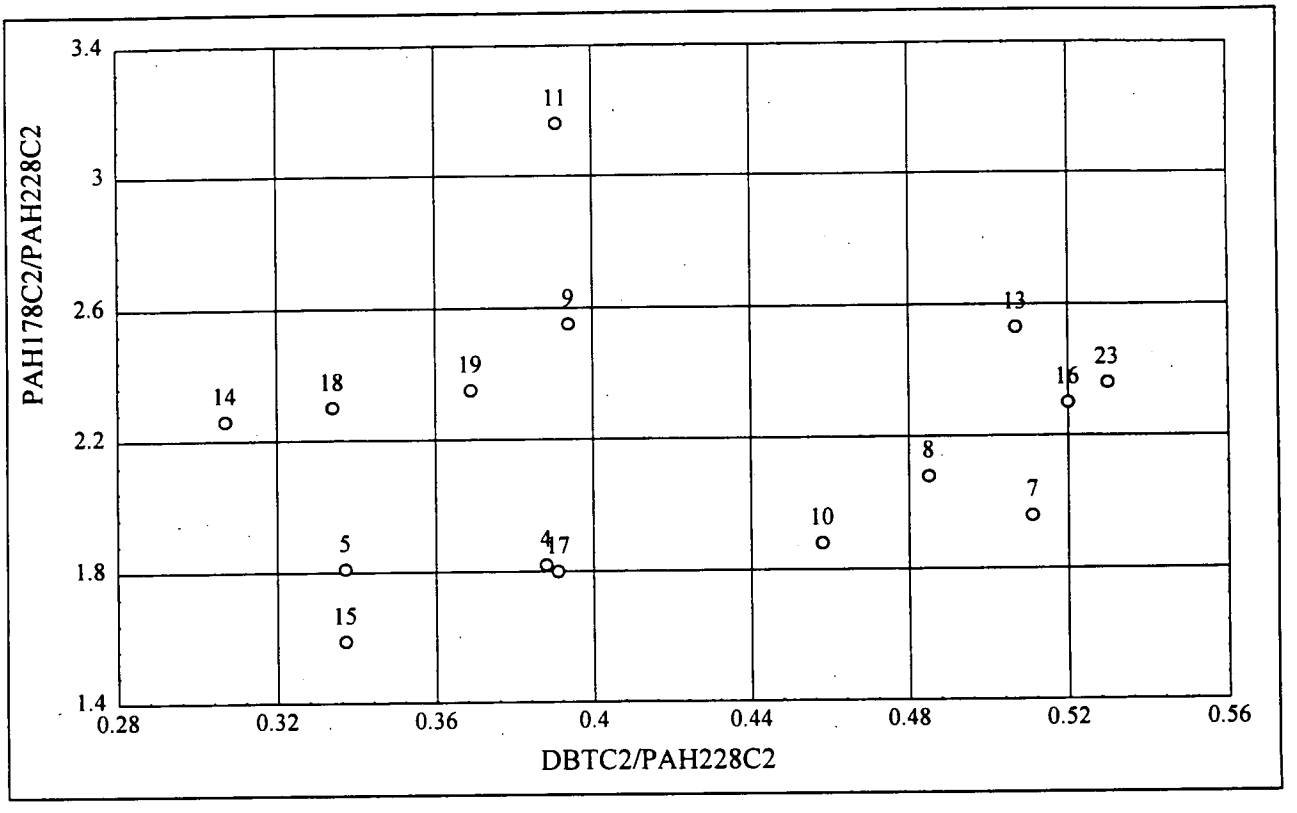
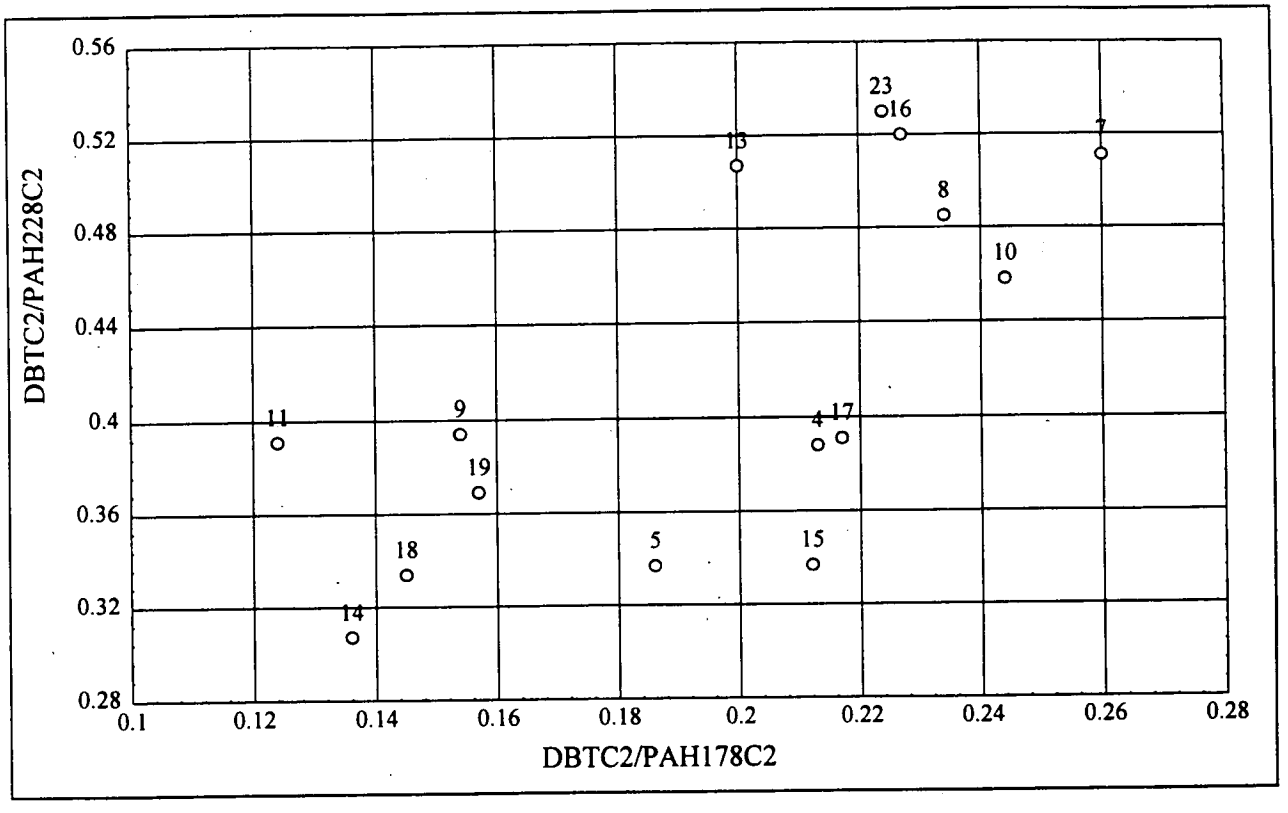


Figure 17. A Double Ratio Biplot Showing the Ratio of C_2 Dibenzothiophenes to C_2 Chrysenes vs. The Ratio of C_2 Dibenzothiophenes to C_2 Phenanthrenes in Surface Sediments, Station numbers are labelled on the graph.



3. Sewage

The concentrations of Linear Alkyl Benzenes (LABs) in surface sediments collected from Portsmouth Harbor are shown in Figure 18. These concentrations are reported in ng/g C so the very high concentration shown for Station 23 is potentially an artifact of the very low organic carbon content in the sediment from that station. With the exception of that station, the concentrations of LABs are relatively high at Stations 16, 10, 11, 9, 8, and 7. Stations 16 and 10 are nearby to the discharge outfalls of the Kittery and Portsmouth sewage treatment plants, respectively. Station 11 is located in a small tributary of the Piscataqua River south of the main harbor area (Figure 11). This location may receive inputs of sewage material from the main harbor via the channel leading back to the area where the station is located.

Concentrations of LABs are not exceptionally high in these sediments. The surface sediment concentrations range from 9 to 141 ng/g dry weight in this estuary, whereas Takada and Ishiwatari (1987) measured concentrations in the Sumidagawa and Tamagawa Rivers averaging 3600 ng/g dry. Eganhouse et al (1983) measured concentrations of 1100 ng/g dry in sediments outside of a major sewage outfall off southern California.

LABs are microbially degraded in an aerobic environment (Eganhouse, 1988; Takada and Ishiwatari, 1990 and 1991) and that degradation follows a pattern that is readily detectable. LAB isomers with the phenyl group substituted on the interior of the chain (carbons 4, 5 and 6 for the C_{12} congeners used for this measurement, herein referred to as internal) are more resistant to microbial degradation than those isomers substituted in the 2 or 3 position (herein referred to as external). Calculating the internal to external ratio (I/E) for a sample then becomes a mechanism of quantitatively describing the degree of aerobic degradation that has occurred in a given sample. If the sediments are collected from anaerobic depositional areas, the I/E ratio may be related to the degree of transport (time exposed to an aerobic environment) sediment particles have undergone prior to settling out of the water column. The I/E ratio calculated for the surface sediments collected from Portsmouth Harbor are shown in Figure 19. The concentration of the C_{12} isomers were too low at Station 23 to perform this calculation.

The distribution of this marker ratio in Portsmouth Harbor is consistent with the location of the sources of sewage material entering the harbor. The low values for this ratio at Stations 16 and 10 reflect the location of the station relative to the sewage outfalls of the Kittery and Portsmouth STPs respectively. The higher ratios suggest a greater degree of degradation and are found at stations located at some distance from the source of the LABs. Station 19 is an anomaly in this analysis as there is no indication of another source of LABs near this station.

Figure 18. Concentration of Total LABs in Surface Sediments. (ng/g C)

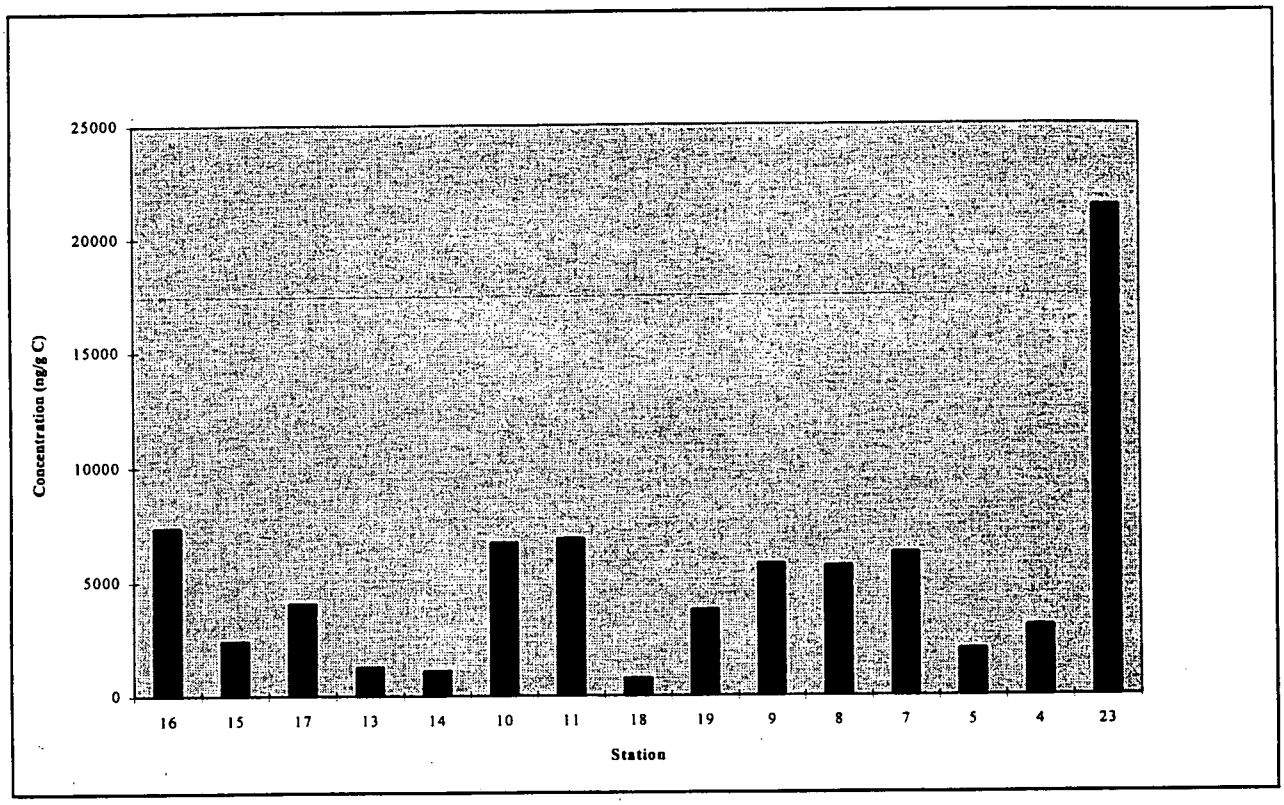
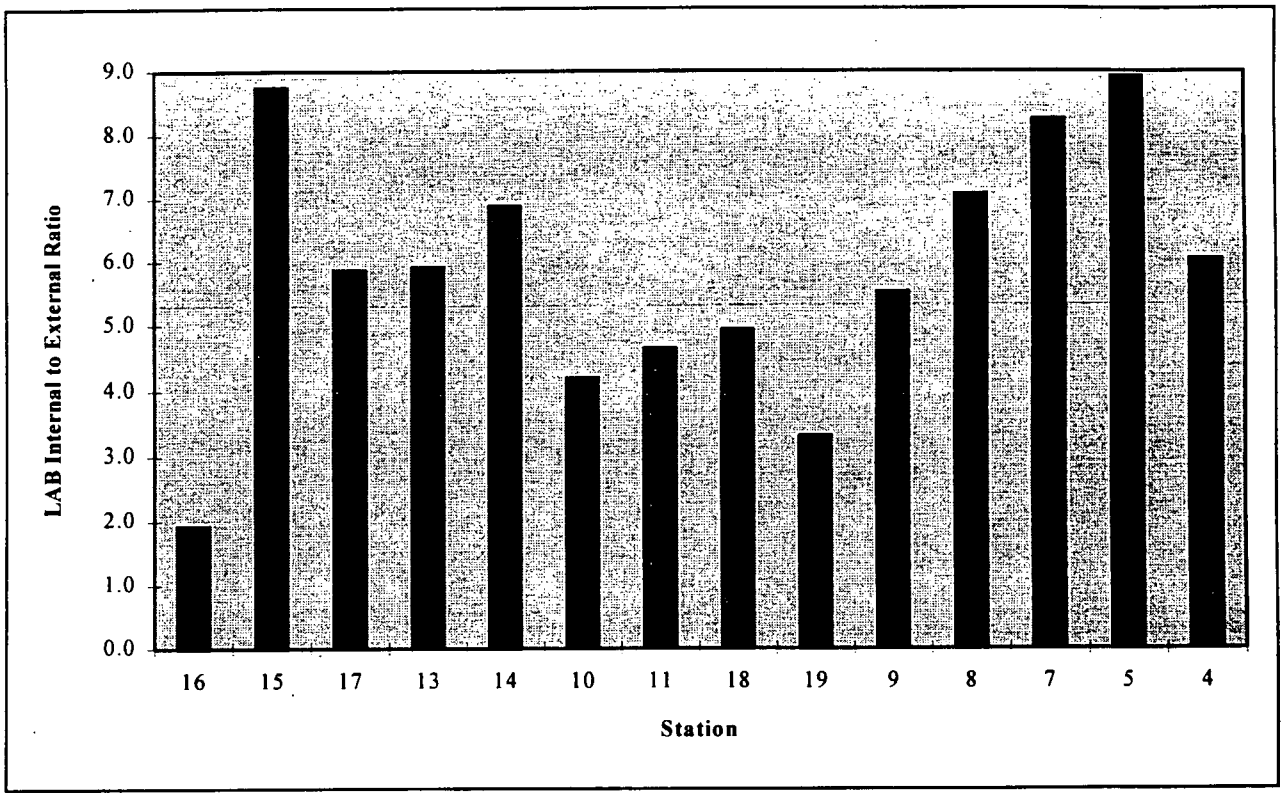


Figure 19. LAB Internal to External Ratio in Surface Sediments.



The distribution of the Nonylphenol sewage marker (Figure 20) is somewhat different from that of the LABs. The concentrations are quite high at Stations 15, 14, 5, and 4. Station 23 also shows a high value for the Nonylphenol concentration on a ng/g C basis, which may be a function of the very low level of organic carbon in that sediment. Stations 15 and 14 are located across from the Kittery, Maine sewage treatement and nearby the Portsmouth sewage treatment plant. Proximity to these two outfalls may be the major factor contributing to the high concentration of this marker in these sediments. The high concentrations at Stations 4 and 5 are not as easily explained. The distribution of the sewage markers in Portsmouth Harbor do not show the same pattern for the different markers used. In Figure 21 the distribution of the compound Coprostanone is shown. Like the LAB distribution, its concentration is quite high at Station 23. Station 16 also has a very high level relative to the other stations in the harbor.

Figure 20. Concentration of Nonylphenol in Surface Sediments (ng/g C).

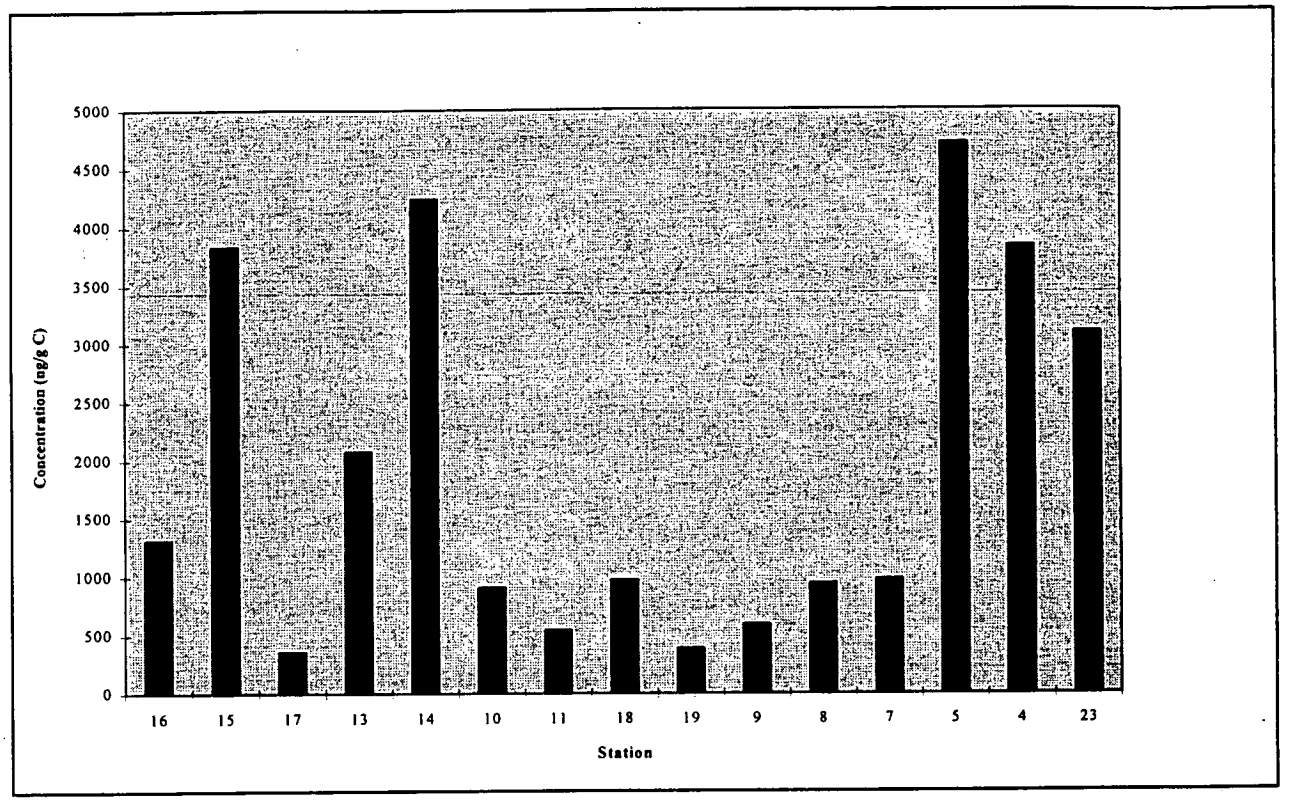
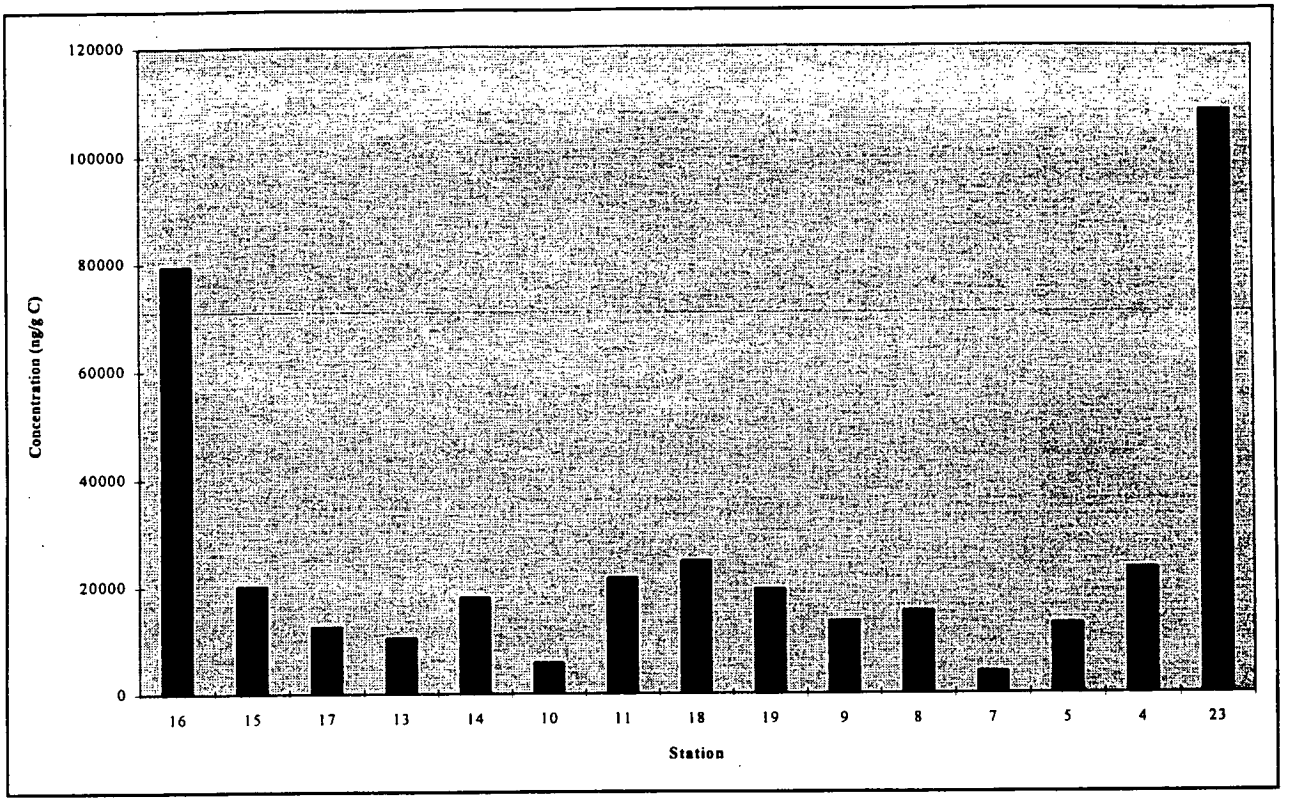


Figure 21. Concentration of Coprostanone in Surface Sediments (ng/g C).

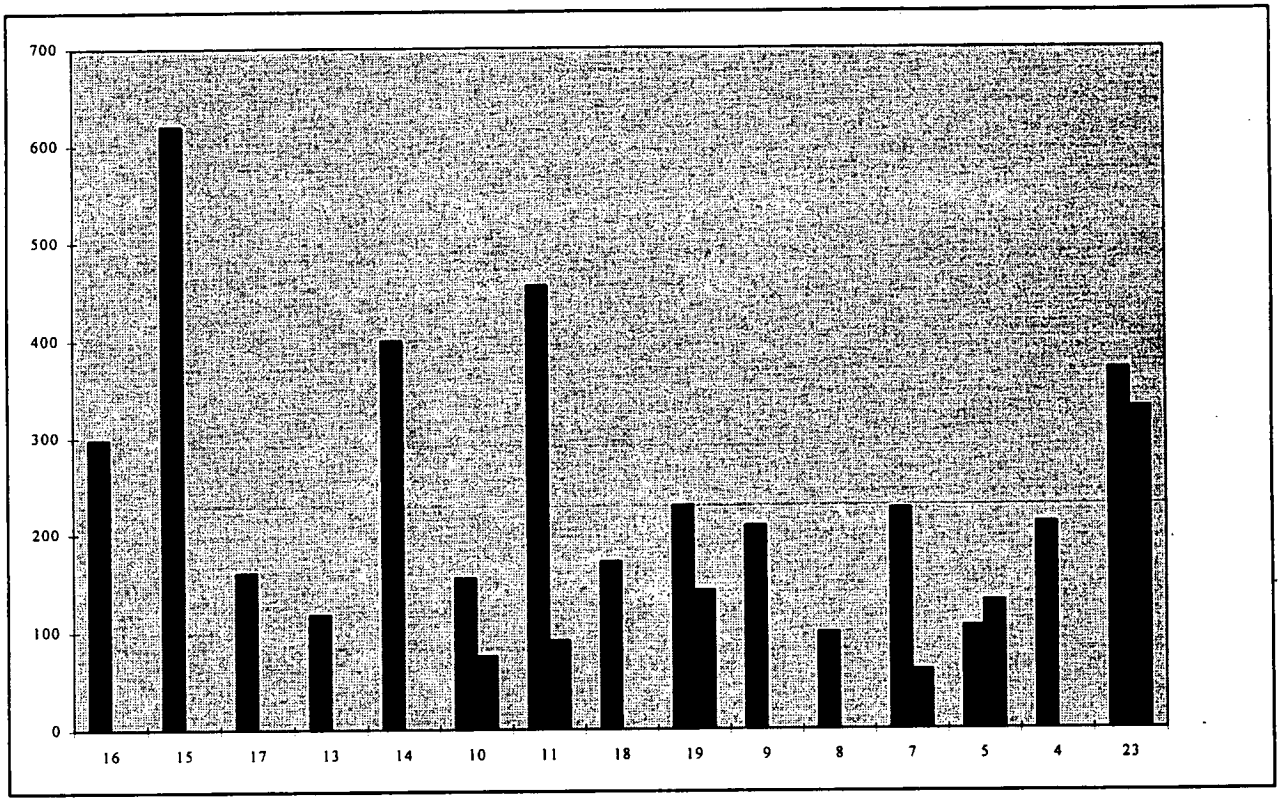


4. Runoff

Two compounds were used as markers of road runoff inputs to this estuary. They are benzothiazole (BZT) and methylthiobenzothiazole (MTBT). The distribution of these analytes in the surface sediment samples is shown in Figure 22. This graph shows high concentrations of BZT at Stations 15, 14, 11, and 23. These concentrations are shown in ng/g C and reflect the normalization for the sediment organic carbon content. This may again be the reason Station 23 shows an anomolously high value for both of these markers due to the very low organic carbon content of this sediment (Figure 12). The MTBT runoff marker shows relatively high concentrations at Stations 10, 11, 5, and 19. This marker may not be as strong an indicator of runoff inputs as its precursor compound BZT, therefore, Stations 15, 14, 11, and 23 may be considered more likely to have received inputs of road runoff derived material. As stated earlier in the petroleum section, Station 15 is located particularly close by a major roadway crossing the

Piscataqua River (Rt. 95). The relatively high concentration of the runoff marker, BZT, and the petroleum marker hopane, are consistant with an input of material from a roadway to this station. Stations 14 and 11 also show a relatively high concentration of the BZT compound. However, the hopane concentrations are not particularly noteable in sediments from these two stations.

Figure 22. Concentration of Road Runoff Markers in Surface Sediments (ng/g C). The lighter bars represent Benzothiazole, darker bars represent Methylthiobenzothiazole.

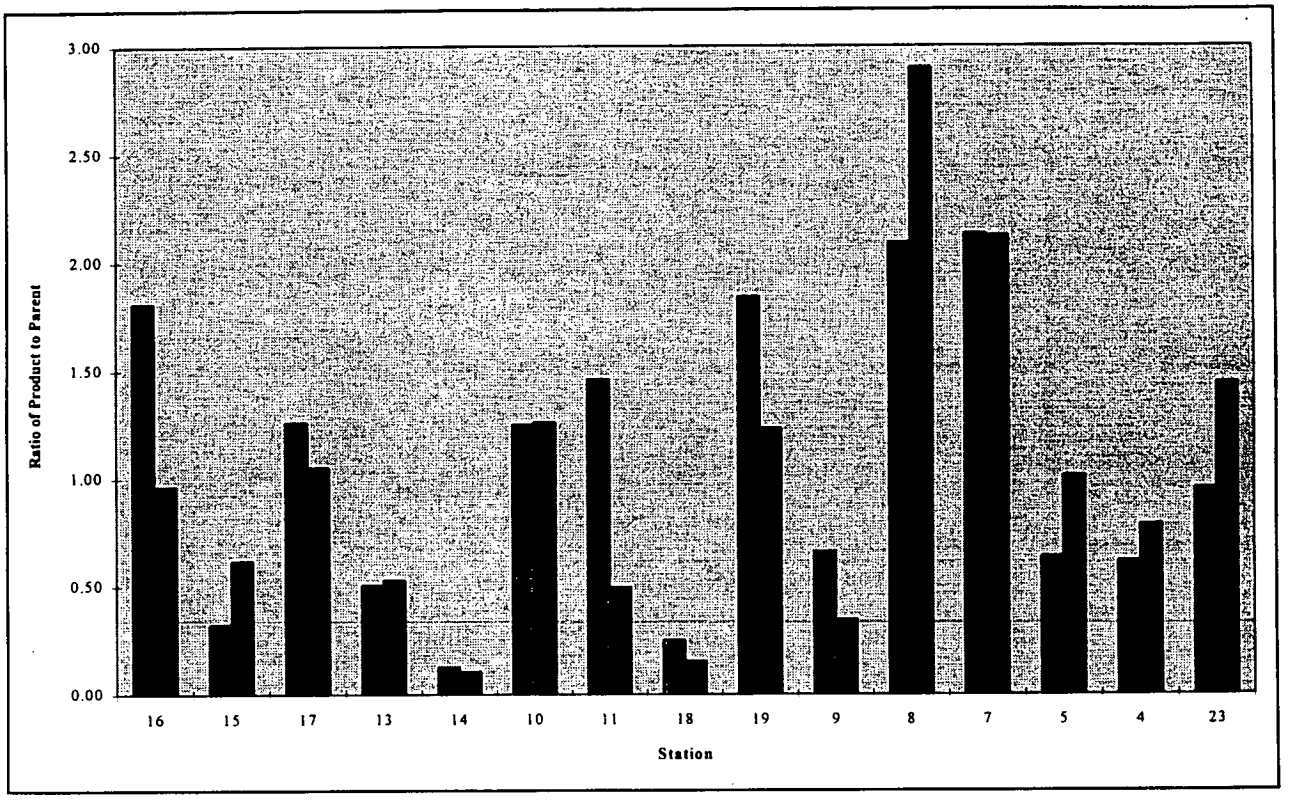


5. Atmospheric Deposition

The distribution of the markers of Atmospheric Deposition in the Portsmouth Harbor sediments is shown in Figure 23. The values of both of the marker ratios are relatively high at Stations 16, 17, 10, 19, 8, and 7. The values are quite low at Stations 14 and 18. This may be a result of the exceptionally high concentrations of PAHs at these two Stations (Figure 13). These markers are ratios of the atmospherically derived oxidation products 9-FLU and ANQ, to the

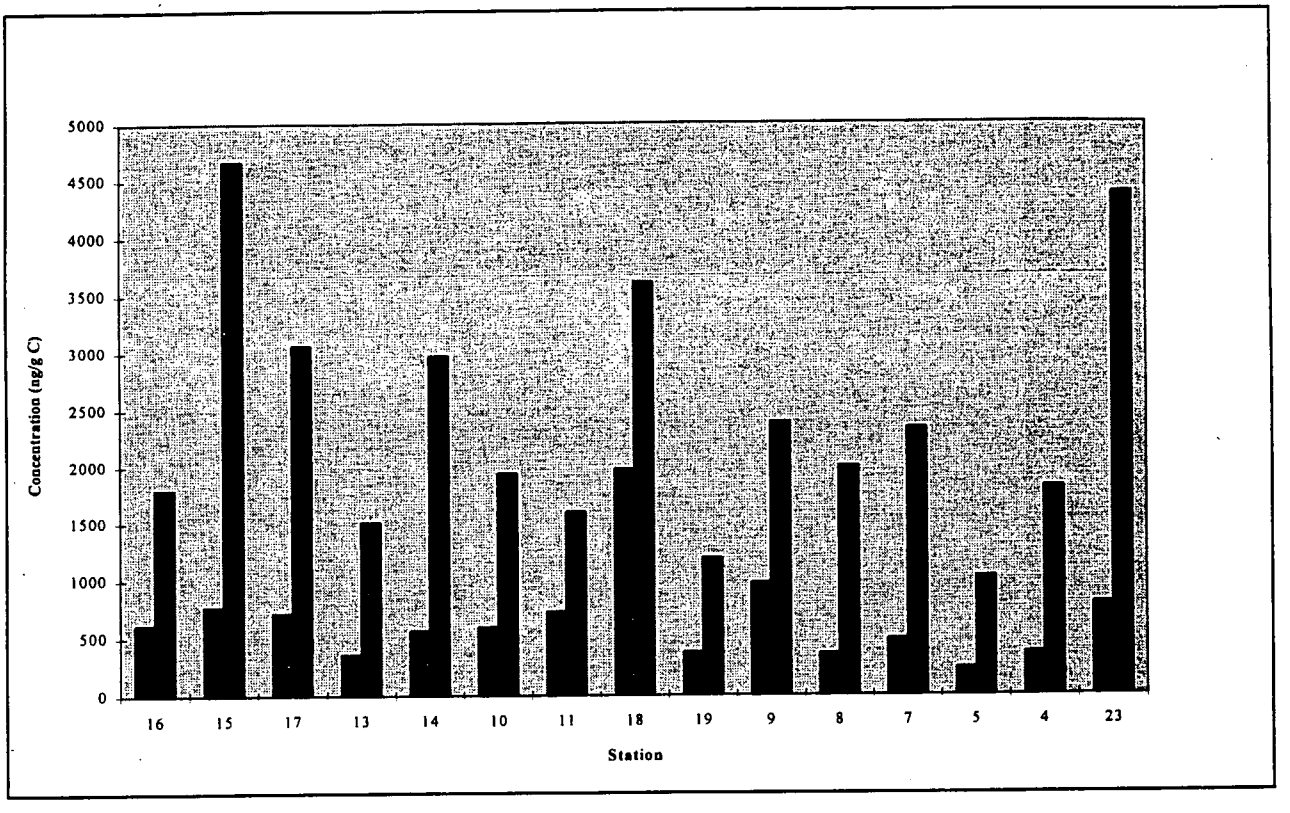
parent PAHs PAH166 and PAH178a (Table 1). Therefore, at Stations 14 and 18, the increased contribution of the lower molecular weight PAHs (PAH166 and PAH178a) will result in a low value for these ratios being used as atmospheric depostion markers.

Figure 23. Atmospheric Marker Ratios in Surface Sediments. Ratio of Oxidation Product to Parent PAH. Lighter bars are 9-Fluorenone to Fluorene; darker bars are Anthraquinone to Anthracene.



The concentrations of the oxidated PAHs used in these ratios are shown in Figure 24. Station 18 shows a very high level of the compound fluorenone, which, while high in concentration at this station is far outweighed by the concentration of the parent PAH fluorene (the concentration of 9-fluorenone is 1970 ng/g C and the concentration of fluorene is 7860 ng/g C at this station).

Figure 24. Concentrations of Oxidated PAHs Fluorenone (lighter bars) and Anthraquinone (darker bars) in Surface Sediments (ng/g C).



E. Source Materials

Samples of sewage sludge were collected from the Portsmouth and Kittery sewage treatment plants. Three replicates of each of these samples were analyzed for chemical markers using the methods applied to the surface sediments. A sample of sediment was collected and analyzed from each of three sediment traps in the stormwater runoff drains located along the waterfront area of northwestern Portsmouth, New Hampshire and separated into < 63 μm fraction and whole. Atmospheric particulate material was collected on glass fiber filters using a high volume pumping system by the Air Resources Division of the New Hampshire Department of Environmental Services located in Portsmouth, NH. Four samples were collected, one every six days, during August of 1993. A soil sample was collected in Maine from a heath located to the northwest of Portsmouth Harbor. This sample was collected because the source of contaminants

to this location may only have come from the depostion of atmospheric material. These source material samples were analyzed for chemical markers and the results are shown in Table 11.

Table 11. Concentrations of Chemical Markers in Source Materials (mean concentration in ng/g dry).

	Atmospheric Particulate	Portsmouth Sludge	Kittery Sludge	Runoff	Runoff <63 mm	Heath
Petroleum Markers						
PAH128	5650	173	417	47.1	213	27.6
MW128 homologs	15200	1570	10300	487	546	74.1
DBTH	20800	3.80	129	93.8	84.6	5.88
DBTH homologs	3490	1940	2250	698	655	61.7
PAH178p	6880	154	1150	1960	1810	111
PAH178a	790	52.0	144	225	148	9.80
MW178 homologs	8910	3120	4580	2050	1870	204
PAH202f	20400	703	1240	3400	4980	247
PAH202p	16100	1010	993	2670	3870	204
PAH228b	3530	281	471	874	1510	45.3
PAH228c	4970	276	477	940	1830	76.6
MW228 homologs	4980	556	475	1060	1590	58.8
PAH252p	1160	262	166	217	460	21.1
Sum MW252 PAHs	26200	1680	2610	3790	9410	524
Hopane	3520	2180	1300	994	2480	69.6
Sewage Markers						
Octylphenol	1140	6850	3380	20.6	43.6	ND
Nonylphenol	24100	77600	78400	164	306	12.7
Total LABs	7120	27500	37900	22.5	144	31.2
Coprostanone	4150	130000	111000	61.9	733	686
Runoff and Atmospheric Markers						
BZT	20800	248	60.2	94.3	984	12.8
MTBT	731	538	216	66.1	148	ND
9-FLU	900	35.9	59.2	66.2	247	13.0
ANQ	7660	494	929	338	818	42.5
9-FLU/PAH166	4.54	6.27	0.37	0.489	26.6	5.40
ANQ/ANTH	9.70	9.50	6.45	1.50	5.53	4.34

F. Statistics

The surface sediment data has been combined with the data generated from the analysis of the source materials to compare the chemical distributions among these different samples.

The goal of this portion of the project is to determine how the sediments at each of the stations sampled compare chemically with the potential sources of contaminants to the estuary. For this analysis an extended group of compounds were used. This extended group comprises those from Table 1 along with additional compounds and compound ratios. The full group is listed in Table 12.

Table 12. Compounds used for the Principal Components Analysis of the Surface Sediments and Source Materials.

Abbreviation	Compound Name	Abbreviation	Compound Name
FLUONE	9-Fluorenone	PAH252BB	Benzo[b]fluoranthene
ANQ	Anthraquinone	PAH252BK	Benzo[k]fluoranthene
OCTYLPHE	Octylphenol	PAH252E	Benzo[e]pyrene
NONYLPHE	Nonylphenol	PAH252A	Benzo[a]pyrene
BAQ	Benzanthraquinone	PAH252P	Perylene
COPRONE	Coprostanone	PAH276I	Indeno[1,2,3-cd]pyrene
STANONE	Cholestanone	PAH278	Dibenzanthracene
STENONE	Cholestenone	PAH276GH	Benzo[ghi]perylene
BZT	Benzothiazole	HOPANE	Hopane
MTBT	Methylthiobenzothiazole	C10_LABS	C10 Linear Alkylbenzenes
PAH166	Fluorene	C11_LABS	C11 Linear Alkylbenzenes
DBT	Dibenzothiophene	C12_LABS	C12 Linear Alkylbenzenes
DBT1	C1-Dibenzothiophene	C13_LABS	C13 Linear Alkylbenzenes
DBT2	C2-Dibenzothiophene	C14_LABS	C14 Linear Alkylbenzenes
DBT3	C3-Dibenzothiophene	TOTAL_LA	Total Linear Alkylbenzenes
PAH178P	Phenanthrene	F1802FLU	Ratio of 9-Fluorenone to Fluorene
PAH178A	Anthracene	ANQ2ANT	Ratio of Anthraquinone to Anthracene
PAH178C1	C1-Phenanthrenes	BAQ2BAA	Ratio of Benzanthraquinone to Benzanthracene
PAH178C2	C2-Phenanthrenes	PHE2ANT	Ratio of Phenanthrene to Anthracene
PAH178C3	C3-Phenanthrenes	BAP2BEP	Ratio of Benzo[a]pyrene to Benzo[e]pyrene
PAH178C4	C4-Phenanthrenes	DBT2PHE	Ratio of C2 Dibenzothiophenes to C2 Phenanthrenes
PAH202F	Fluoranthene	DBT2CHR	Ratio of C2 Dibenzothiophenes to C2 Chrysenes
PAH202P	Pyrene	PHE2CHR	Ratio of C2 Phenanthrenes to C2 Chrysenes
PAH228B	Benz[a]anthracene	TOTPAH	Total Measured PAHs
PAH228C	Chrysene		
CHRYC1	C1-Chrysene		
CHRYC2	C2-Chrysene		
CHRYC3	C3-Chrysene		

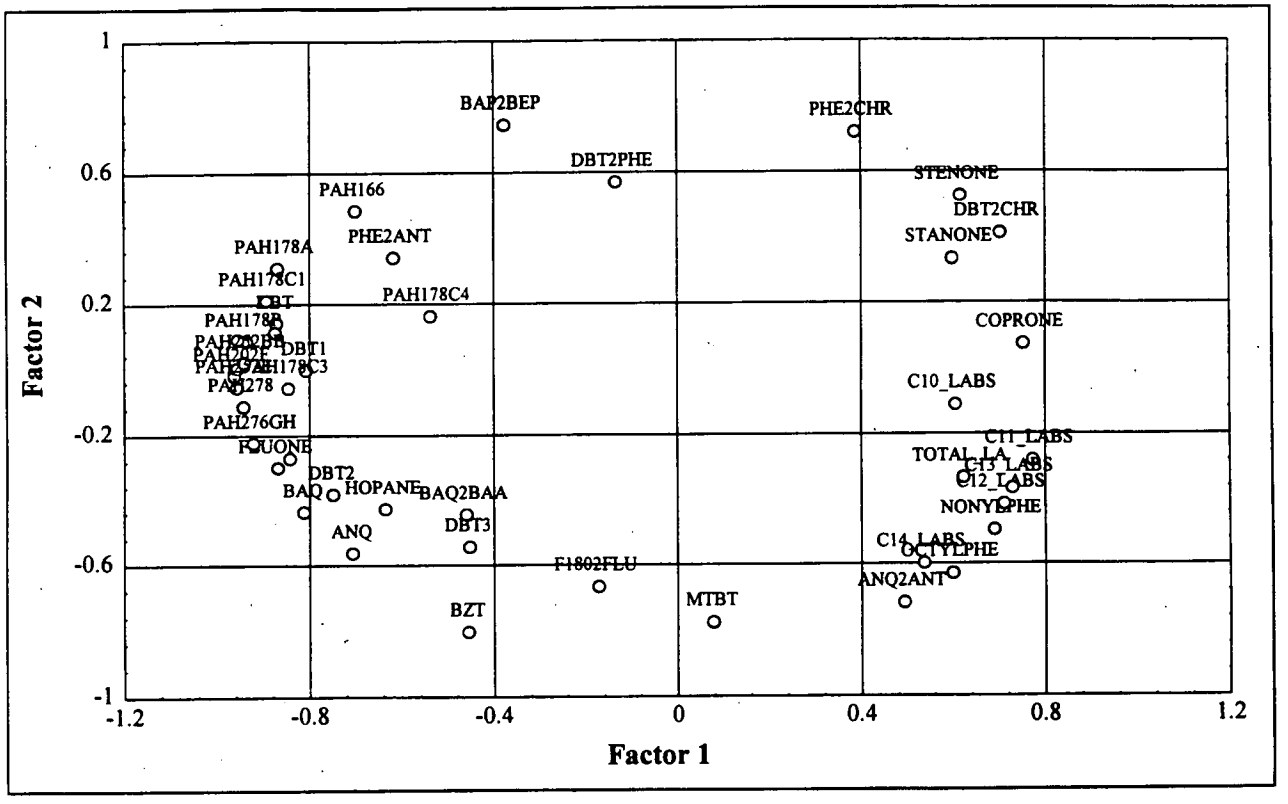
Data from the analysis of these samples was processed in two ways prior to performing the multivariate statistical analysis. In cases where a sample analyte was not detected the value of the method detection limit (MDL) was substitued for the missing value. The data were then block normalized, by sample, in two blocks. The first block were all of the individual compounds and sums of compounds (such as C10_LABs and TOTPAH, Table 12). The second

block were all of the compound ratios (such as ANQ2ANT and BAP2BEP Table 12). The resulting data were then transformed according to the equation $x' = \log(x) + 6.0$. The transformation of the sample data in this fashion allows all samples to be compared without their relative concentrations among samples strongly influencing the analysis.

A Principal Components Analysis (PCA) was done using the Statistica/W software package (Statsoft, Tulsa, Oklahoma). This technique has been extensively reviewed (Wold, et. al., 1987) and won't be described in detail here. The purpose of PCA is to decompose the sample matrix of n samples by m variables into two smaller matrices of n samples by j scores and m variables by j loadings and a third matrix of the residuals. The construction of the latent variables, or components, is accomplished in a fashion to successively account for as much variance as possible within the constraint of orthagonal score and loading vectors.

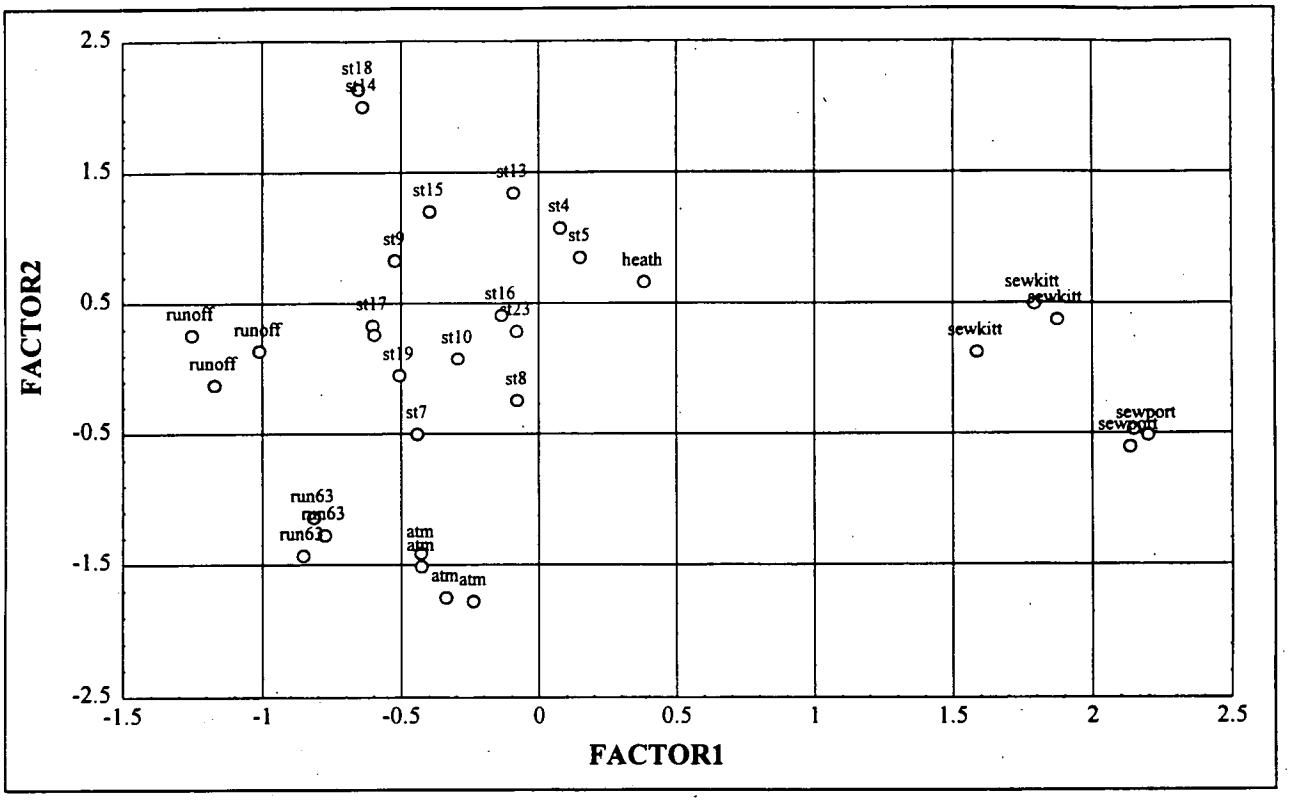
The PCA was performed on the variables listed in Table 12 for 15 surface sediments, 4 atmospheric particulate samples, 3 samples of sewage sludge each from the Portsmouth, NH and Kittery, ME STPs, 3 samples of road runoff material, 3 samples of the < 63 mm fraction of those 3 road runoff material samples, and a sample of the top 1cm of soil from a heath in Maine located northwest of Portsmouth Harbor. A total of five components were extracted which accounted for approximately 88% of the total variance in the data matrix. The component loadings for the first two components are shown in Figure 25. Loadings for the first component (Factor 1) are weighted positively for the compounds used as markers of sewage inputs, such as, LABs, octylphenol and nonylphenol, and coprostanone. The loadings for this factor are weighted negatively for bulk of the PAHs (shown overlaping in this figure).

Figure 25. Principal Component Loadings for the First Two Components in the Surface Sediment and Source Material Distributions.



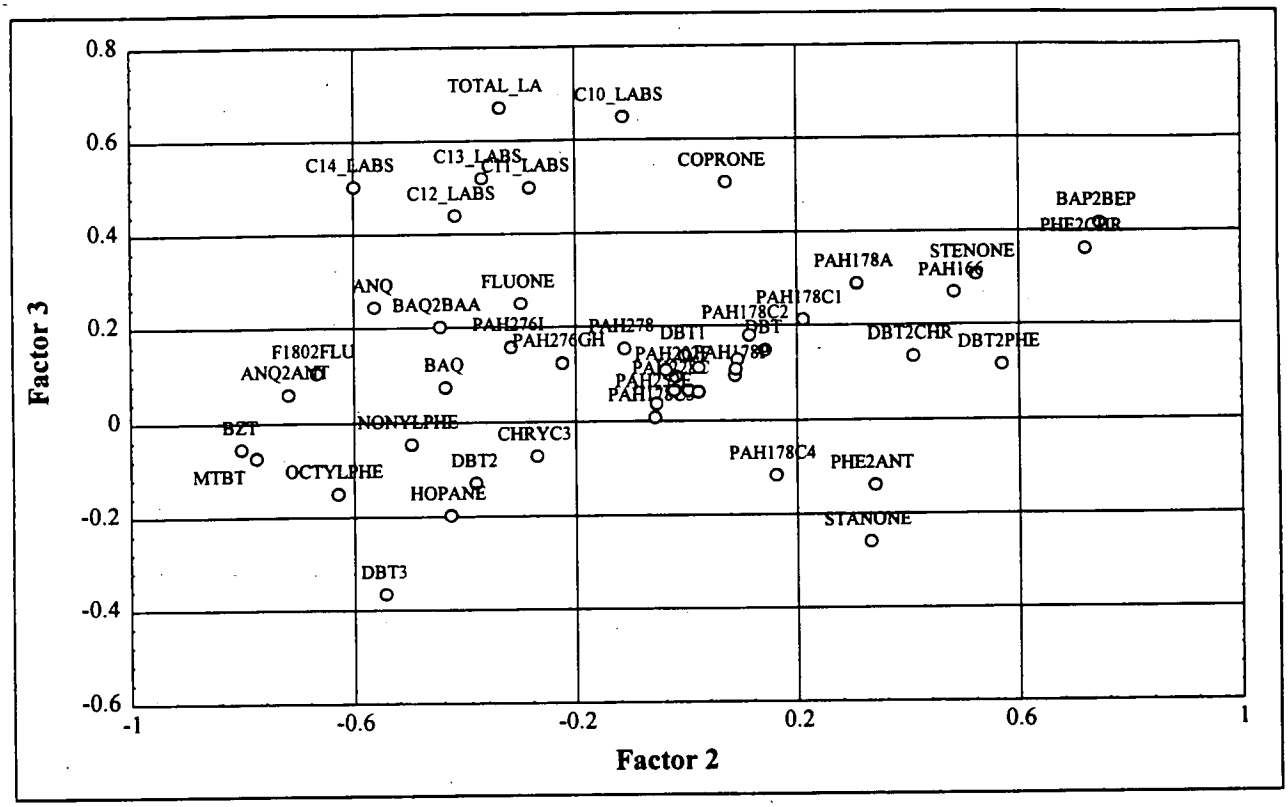
This means that samples with high concentrations of the sewage markers will have a high, positive score for Factor 1 and those with high PAH concentrations will have a high, negative score for Factor 1. The factor scores for the first two principal components are shown in Figure 26. High scores for Factor 1 place the sewage treatment plant sludge samples (sewkitt is Kittery Sewage Treatment Plant material, sewport is the Portsmouth Sewage Treatment Plant material) far to the right on the Factor 1 axis, which, given the sewage markers are loaded positively for this factor is to be expected. The road runoff samples (run63 is the < 63 μm fraction and runoff is the whole fraction) and atmospheric particulate samples (atm) are scored negatively for Factor 1. The surface sediment samples (labelled by Station st4, st5, st7, etc.) appear to fall between the sewage samples and the runoff samples along the Factor 1 axis.

Figure 26. Principal Component Scores for the First Two Components in the Surface Sediment and Source Material Distributions.



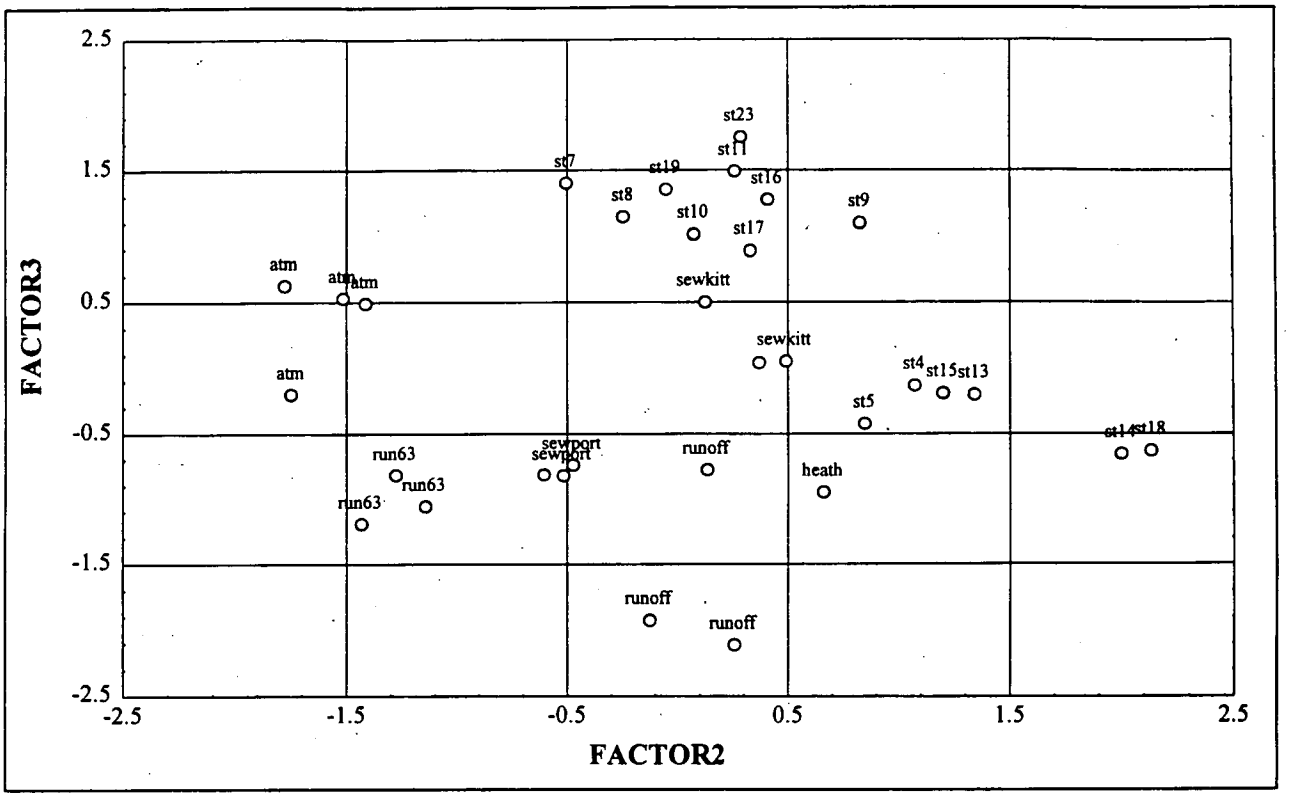
Loadings for the second and third principal components are shown in Figure 27. Factors 2 and 3 comprise 15% and 7% of the total variance respectively. Factor 2 appears to be loaded negatively for the compounds BZT, MTBT and the marker ratios F1802FLU and ANQ2ANT (Table 12). These compounds represent the influence of road runoff material and the deposition of atmospheric particulates. Factor 3, while it only represents 7% of the variability in the dataset, is loaded positively by all of the LABs and the coprostanone (COPRONE). The other sewage input markers are the octylphenol and nonylphenol, yet these two compounds do not appear to strongly influence this factor.

Figure 27. Principal Component Loadings for the Second and Third Components in the Surface Sediment and Source Material Distributions.



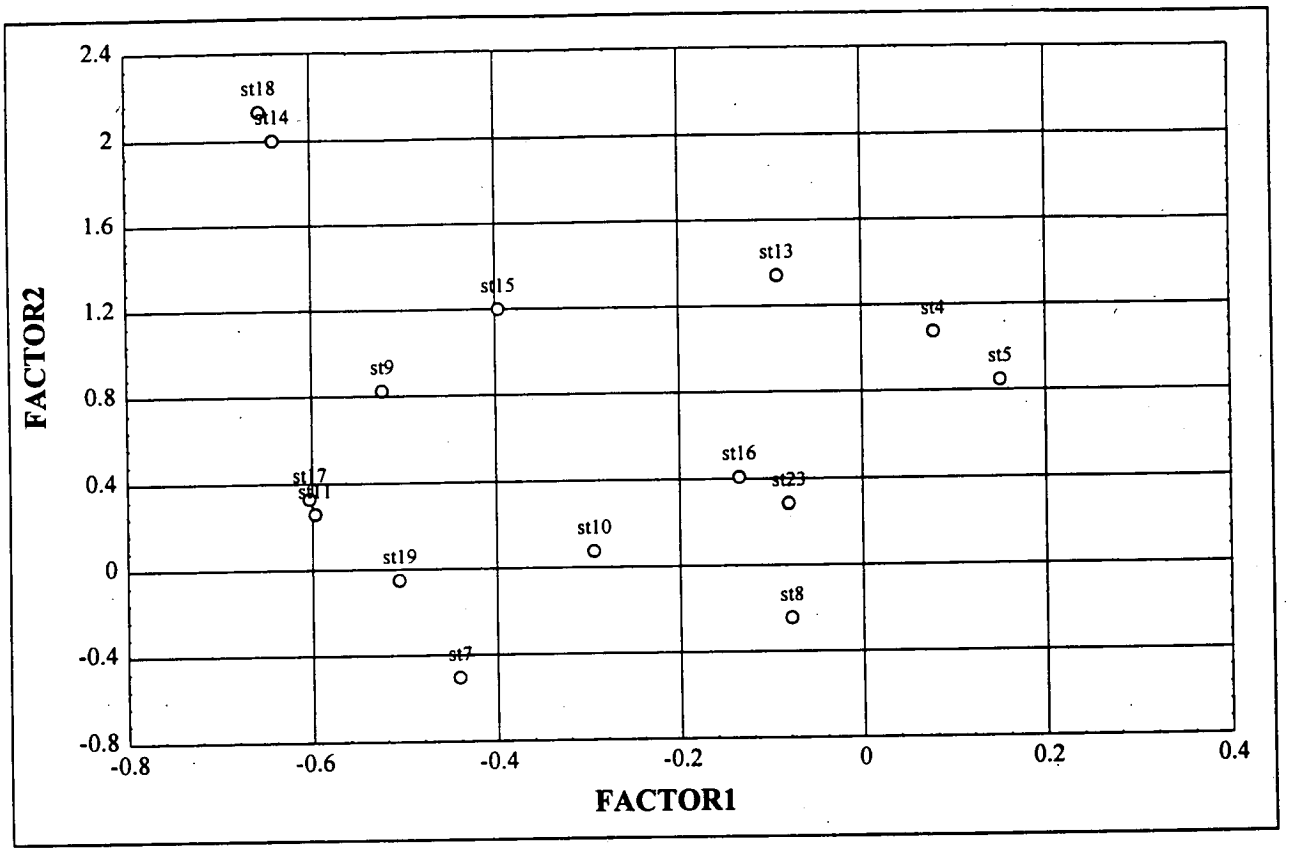
The scores for the second and third components of the PCA analysis are shown in Figure 28. Both the atmospheric particulate material and the < 63 mm fraction of the road runoff material are located to the left on the Factor 2 axis (atm and run63 samples respectively). One grouping of the surface sediment samples (st7, st8, st19, st10, st11, st23, st16, st17, and st9) are located with the Portsmouth STP (sewport), Kittery STP (sewkitt) and runoff source materials along the Factor 2 axis, however this group is separated from these source materials by Factor 3. The other grouping of surface sediments (st5, st4, st15, st13, st14, and st18) isz located to the right of the source materials on the Factor 2 axis and with the source materials on the Factor 3 axis.

Figure 28. Principal Component Scores for the Second and Third Components of the Surface Sediment and Source Material Distributions.



We also looked at how the PCA scores from the surface sediment samples plot without the source materials Figure 29. It is easier to see potential similarities among stations in this figure than in the previous figures. It appears that Stations 14 and 18 have very similar compositions as do Stations 17 and 11. The other Stations are more scattered about this figure. There does not appear to be a grouping of stations from around the shipyard.

Figure 29. Principal Component Scores for the Surface Sediments, First Two Components of the PCA Done on Both Samples and Sources.



IV. Conclusions

In the second phase of our work to investigate the sources of contamination to the Lower Piscataqua River Estuary in the area surrounding the Portsmouth Naval Shipyard, Kittery, Maine, we used several approaches. One area of research was a continuation of our previous work to identify a chemical marker specific to the shipyard. This work focussed on the analysis of cutting oils for chlorinated paraffins. Our attempt at the use of GC/MS analysis with NCI showed that we were unable to detect these compounds in standards of chlorinated paraffins. This result, therefore, precluded any further work on the analysis of cutting oils for traces of chlorinated paraffins by this technique. This concluded our efforts to identify a chemical marker that could be considered specific to the shipyard.

The remainder of the work done during this phase can be broken into two areas. The investigation of historical inputs of contaminants to the estuary, and the investigation of present day contaminant sources. The historical inputs were investigated by analyzing two sediment cores collected from Portsmouth Harbor. One core was collected off Badgers Island at Station 17 (Figure 11). This core showed evidence of atmospheric inputs throughout its depth of 38 cm. Petrogenic hydrocarbon inputs are maximized in the upper (2-4 cm and 10-12 cm) sections of the core and pyrogenic inputs appear to maximize in the lower, 18-20 cm section. Inputs of sewage material to this core show inconsistencies among the four markers of sewage inputs measured. The high concentrations of the road runoff markers found deep in this core (34-36 cm) are not easily explained.

The second core was collected from a marsh on Clark Island and is referred to as the Clark Cove Marsh core. This core had PAH concentrations with surface maximums and a subsurface maxima in the 16-18 cm section indicative of an increased input at some early date. Inputs due to pyrogenic sources appear to have maximized in the 16-18 cm section while those with petrogenic sources maximize in the 32-34 cm section before dropping to non-detectable in the 40-42 cm section. Only one of the sewage markers was detected, coprostanone, and only in the top four sections analyzed. The coprostanone concentration showed a subsurface maximum in the 8-10 cm section. The road runoff marker showed a decreasing down core trend becoming undetectable in the 48-50 cm section. The atmospheric depostion markers are inconclusive, showing little variation in the top four sections and not-detectable in the lower sections. Overall these results indicate that the two cores analyzed did not retain a detailed historical record of the potentially changing sources of contaminants to this estuary.

To investigate the present day status of contaminant inputs to the estuary both surface sediments and water samples were analyzed. Water samples were collected on September 15th, 1993 and analyzed for chemical markers. The results of these analyses showed potential inputs of petroleum to the estuary, evidenced by the concentrations of the alkyl homologs of PAHs, especially at Station 16 located off the Portsmouth sewage treatment plant outfall. Sewage and atmospheric markers were not detected; however, an elevated concentration of the road runoff marker BZT was measured at Station 12, at the mouth of the Clark Cove Embayment.

Surface sediments were collected and analyzed from 15 Stations in the Portsmouth Harbor and a reference site in the York River, Maine. In addition, samples of material representing potential sources of contaminants; sludge from two sewage treatment plants discharging to the harbor (Portsmouth and Kittery), road runoff material from Portsmouth, NH, and atmospheric particulate material from Portsmouth, NH were collected and analyzed.

Measurements of chemical markers from these samples were used to identify the relative impacts of each of these sources at the different sampling stations in Portsmouth Harbor. While the overall concentration of measured PAHs is highest at Stations 14 and 18, petroleum inputs appear to be highest at Stations 15, 5, and 4. The petroleum signatures indicate differing mixtures of petroleum among the stations. Stations 16, 13, 10, 8, 7, and 9 all appear to group near each other (Figure 17) while there appear to be two other groupings. One included Stations 15, 17, 5, and 4, and one included Stations 14, 11, 18, 19, and 9. These groupings may be the result of inputs from different petroleum mixtures or the influence of different weathering regimes at these stations.

The principal components analysis performed on the source materials and the sediment samples showed the sewage markers to strongly load the first principal component (Factor 1) in the positive direction. The principal component scores for the surface sediments show Stations 16, 13, 8, 5, 4, and 23 with more positive scores for Factor 1. Stations 17, 14, 11, and 18 all score fairly low for Factor 1. Principal component Factor 2 appears to be influenced strongly in the negative by the compounds BZT, MTBT and the marker ratios F1802FLU and ANQ2ANT. These markers signify inputs from road runoff and atmospheric deposition, respectively. Stations 10, 8, 7, and 19 have low scores for Factor 2 which may signify a strong component of runoff and atmospheric deposition contributing to these locations.

Overall, the sediments of the Portsmouth Harbor estuary contain a very complex pattern of marker compounds. This probably reflects the influence of many contamination sources as well as complicated water circulation patterns in the estuary.

V. References

Campbell, I. and G. McConnell. 1980. Chlorinated Paraffins and the Environment. 1. Environmental Occurrence. Environmental Science and Technology 14(10): 1209-1214.

Eganhouse, R.P., D.L. Blumfield, and I.R. Kaplan. 1983. Long-Chain Alkylbenzenes as Molecular Tracers of Domestic Wastes in the Marine Environment. Environmental Science and Technology 17(9), 523-530.

Eganhouse, R.P. and I.R. Kaplan. 1988. Depositional history of Recent sediments from San Pedro Shelf, California: Reconstruction using elemental abundance, isotopic composition and molecular markers. Marine Chemistry 24: 163-191.

Gjos, N. and K.O. Gustavsen. 1982. Determination of Chlorinated Paraffins by Negative Ion Chemical Ionization Mass Spectrometry. Anal. Chem. 54: 1316-1318.

Schmid, P.P, and M.D. Muller 1985. Trace Level Detection of Chlorinated Paraffins in Biological and Environmental Samples, Using Gas Chromatography/Mass Spectrometry with Negative-Ion Chemical Ionization. J. Assoc. Off. Anal. Chem. 68(3): 427-430

Muller, M.D and P.P. Schmid. 1984. GC/MS Analysis of Chlorinated Paraffins with negative Ion Chemical Ionization. J. High Resolut. Chromatogr. Chromatogr. Commun. 7: 33-37.

Jansson, B., Andersen, R., Asplund, L., Bergman, A., Litzen, K., Nylund, K., Reuterdardh, L., Sellstrom, U., Uvemo, U., Wahlberg, C., and Widqvest, U. Fresenius J. Anal. Chem. 340, 439-445 (1991).

Overton, E.B., J.A. McFall, S.W. Mascarella, C.F. Steele, S.A. Antoine, I.R. Politzer, and J.L. Laseter. 1981. Identification of Petroleum Residue Sources after a Fire and Oil Spill. In Proceedings, 1981 Oil Spill Conference, API, Washington D.C., pp 541-546.

Takada, H. and R. Ishiwatari. 1990. Biodegradation Experiments of Linear Alkylbenzenes (LABs): Isomeric Composition of C12 LABs as an Indicator of the Degree of LAB Degradation in the Aquatic Environment. Environmental Science and Technology 24(1), 86-91.

Takada, H. and R. Ishiwatari. 1991. Linear alkylbenzenes (LABs) in urban riverine and coastal sediments and their usefulness as a molecular indicator of domestic wastes. Water Science Technology 23: 437-446.

Ward, L.G. 1994. Sedimentology of the Lower Great Bay/Piscataqua River Estuary. Draft Final Report for An Ecological Risk Assessment Case Study, Portsmouth Naval Shipyard, Kittery Maine.

Wold, S., Esbensen, K. and P. Geladi, (1987). Principal Component Analysis - A Tutorial. Chemometrics and Intelligent Laboratory Systems, 2, 37-52.