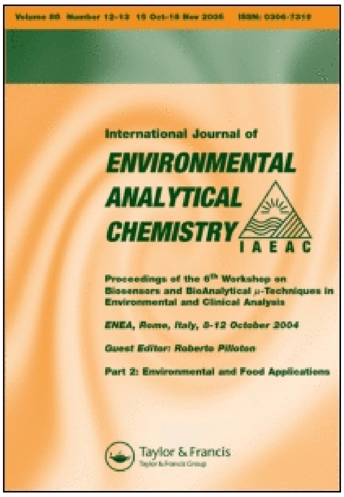

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Polycyclic Aromatic Hydrocarbons in Surface Sediments from the Elizabeth River Subestuary¶

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The concentration and nature of mainly aromatic and polar organic compounds in surface sediments from the Elizabeth River was assessed in 28 samples, using methodology combining simplicity and reliability so that it could be applied in a *quasi routine fashion*. The analyses reveal unsubstituted polynuclear aromatic hydrocarbons (PAHs) as major components of these sediments, indicating an origin from high temperature processes. The conspicuous absence of cyclopenta(c,d)pyrene in these samples is characteristic of an origin from coal. Concentrations of PAHs were highest in the Southern Branch of the Elizabeth River, where the sum of 14 generally abundant pyrogenic PAHs in one sample was 170 ppm and could be traced to two massive spills of wood preservatives. This maximum concentration decreases exponentially towards the mouth of the river with a correlation coefficient of -0.92 and fits a diffusion-advection model for $-k/w = 3.5\,\text{km}$. The physical details of the processes dispersing these PAHs are not understood.

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KEY WORDS: Organic compounds, surface sediment, polynuclear aromatic hydrocarbons (PAHs), Elizabeth River, wood preservative, diffusion-advection model.

INTRODUCTION

The Elizabeth River is a subestuary of the James River, which is the southernmost tributary to the Chesapeake Bay. It is surrounded by the cities of Norfolk, Portsmouth and Chesapeake in the Commonwealth of Virginia (Figure 1). It has been a center of human activity for approximately three centuries and serves as an important waterway for commercial and military purposes. Shipbuilding and repair facilities abound along its shores, but many other industries are also present. Most of the heavy industries are situated on the Southern and Eastern Branches. The Western Branch is surrounded by low density suburban housing.

In a study of organic pollutants in Elizabeth River surface sediments, unsubstituted polynuclear aromatic hydrocarbons (PAHs) of probable high temperature origin[1-7] were found to be dominating. This is not uncommon as the generation of these pyrogenic compounds is widespread and their distribution over large distances has been observed.[8-11] A locally distinct maximum and very high concentrations found in the Southern Branch, however, indicate that the unsubstituted PAHs in this case must be attributed to a point source.

The purpose of this study is multifaceted. It provides data on the concentration and the distribution of toxic organic chemicals in surface sediments. It discusses the presence and characteristics of these compounds with respect to their origin. It looks at possible modes of transport and addresses the question of their geochemical stability.

MATERIALS AND METHODS

Twenty-eight (28) surface sediments were collected with a stainless steel Smith–MacIntyre grab (0.1 m^2) between April 23 and 27, 1981 at locations indicated in Figure 1. The top 3 cm of sediment were removed from the grab with a clean stainless steel scoop and

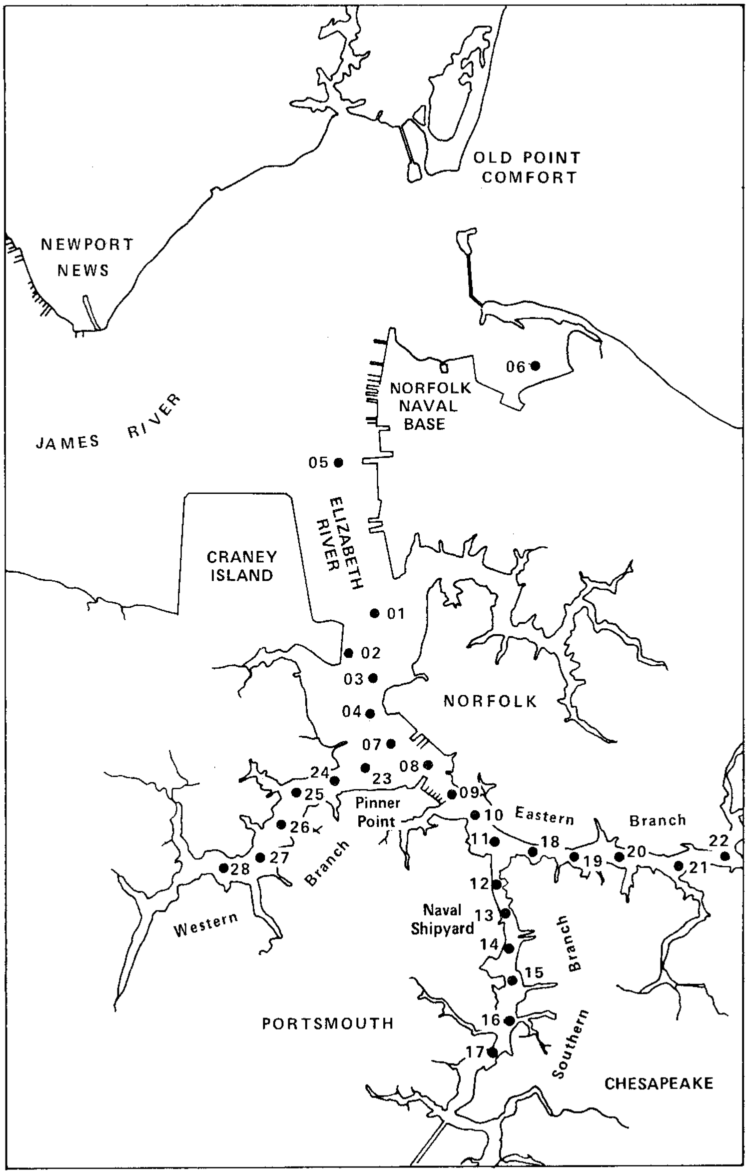
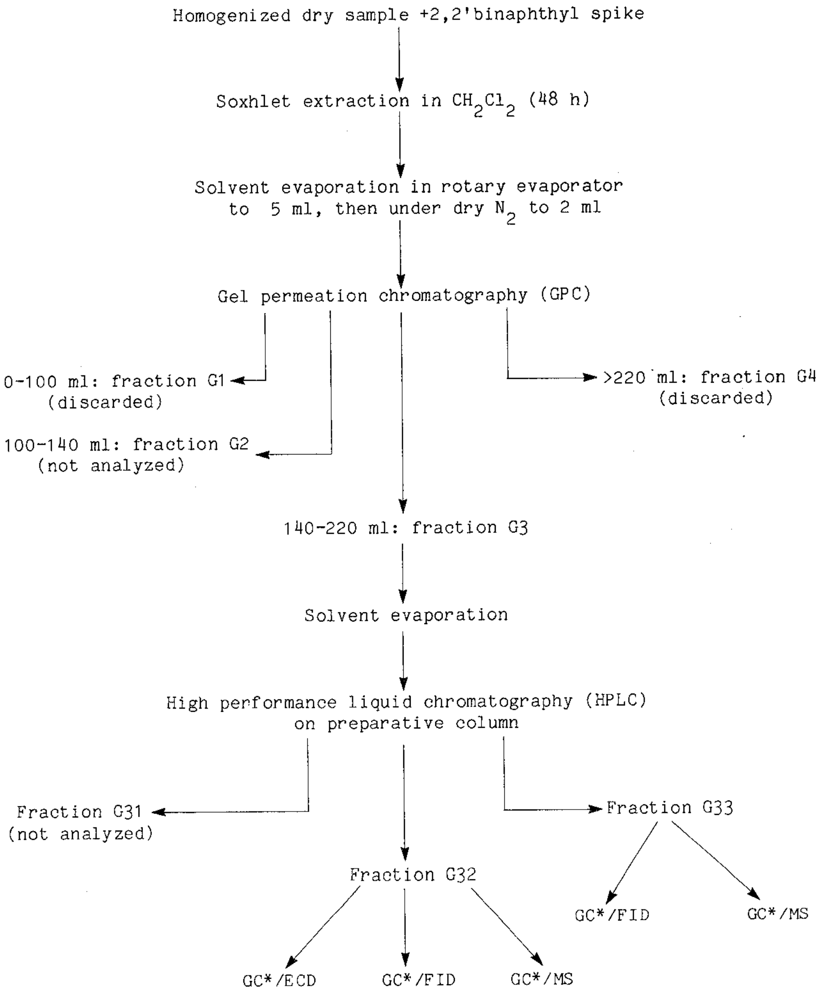


FIGURE 1 Map of the Elizabeth River area. Solid points indicate locations where surface sediment samples were collected. Craney Island is an artificial island built from dredge spoil.

transferred to precleaned one quart glass jars with Teflon®-lined covers. These jars were sealed tightly and placed in a box containing dry ice. In June, the samples were freeze dried and homogenized for extraction. Possible fractionation effects due to the freeze drying were checked by spiked and wetted sand, but were found to be negligible beyond phenanthrene. Comparisons using different methods of water removal such as sodium sulfate drying[12] or dewatering with methanol[13] led to the same conclusion. Details of the analytical methodology are depicted in Figure 2.

Crude extracts were initially subjected to gel permeation chromatography (GPC) on a 2.5 × 60 cm Bio-Bead S-X8 column to remove heavy biogenic molecules interfering with the analysis.[14,15] Using CH_2Cl_2 as a solvent at a flow rate of 7 ml/min and a pressure gradient of 0.34 atm, most of these molecules eluted in the first 100 ml. The fraction eluted between 140–220 ml (fraction G3) contained most of the compounds of interest to this study and was further processed according to the analysis scheme (Figure 2). The recovery of compounds eluting in this fraction was evaluated with 83 standard compounds (alkanes, aromatics, phenols, phthalate esters, ethers, hydrazine, chlorinated hydrocarbons, PCBs, carbamates, phosphate esters and triazines). For aromatic and chlorinated hydrocarbons, recoveries were typically $>99\%$.

The G3 fraction was further separated by high performance liquid chromatography (HPLC) on a preparative 0.94 × 25 cm Partisil PAC M9 column (Whatman, Inc.), using gradient and flow rate programming. A flow rate of 1.5 ml/min was maintained for the first 11 min, increased to 4 ml/min during 2 min and then kept constant. Hexane was the solvent for the first 17 min, followed by a linear increase of 2-propanol to 100% between 17 and 27 min. Of three fractions derived, only the fraction collected between 10 sec past the onset of a UV response and 23 min (G32 fraction), consisting of slightly polar or polarizable, mainly aromatic compounds is described in this paper. The HPLC separation performance again was tested with a large number of different compounds which included alkanes, polycyclic aliphatics, chlorinated hydrocarbons, polynuclear aromatic hydrocarbons, phthalates, carbamates and thiocarbamates, hydrazine, ethers, fatty esters, triazines, phenols, amines, ketones, phosphate esters, heterocyclics, quinone, benzidine and nitrates to assure all compounds of interest are in the G32 fraction.



*on 30 m silylated borosilicate glass capillaries, 0.3 mm i.d., coated with SE-52 and programmed at 6°C/min from 75-280°C. He at 3 ml/min as carrier.

FIGURE 2 Sample analysis scheme.

Gas chromatography of the G32 fractions was carried out on Varian Model 2740 instruments fitted with Grob injectors[16] and 0.3 mm × 30 m tested[15] glass capillary columns coated with SE-52. Injections were spitless at 75°C. This temperature was maintained until the onset of solvent elution and was followed by linear programming to 280°C at 6°C/min. Helium was used as carrier and makeup gas for the flame ionization detectors. Chromatographic data were processed by a Hewlett–Packard 3354B Laboratory Automation System operating under combined vendor and custom software programs. Individual peak data were quantitated by response relative to a 2,2′-binaphthyl internal standard, and unresolved complex matrix (UCM) response was approximated relative to the same internal standard and a computer program which drew and integrated a UCM contour curve. Since the chemical composition of the UCM is not known, this concentration and the concentration sum in column 4 of Table I can only be an estimate. An analytical precision of 37% average relative standard deviation for the entire procedure was achieved for PAH concentrations in a set of 10 replicate samples.

About 30% of all samples were analyzed by both gas chromatography (GC) and gas chromatography-mass spectrometry (GC-MS). The GS-MS system consisted of a Varian 2740 GC and capillary column as previously described, coupled to a DuPont 492-B mass spectrometer operating with an enhanced 094B data system. Enhancements included development of a program RRI to determine relative retention index and other peak characteristics from GC-MS data.

The identification of all compounds was based on Aromatic Retention Indices (ARI)[18,19] and mass spectral information. The unsubstituted PAHs naphthalene, biphenyl, phenanthrene, pyrene, chrysene, perylene and benzo(ghi)perylene were used as retention index standards. Since all of these PAHs are normally ubiquitous and abundant in sediment extracts and form a distinct, easily recognizable elution pattern in the chromatogram, it is in general not necessary to coinject these retention markers with every sample. Compounds were considered identified if their ARIs and mass spectra coincided with the ARI and mass spectrum of a reference compound. With few exceptions, ARI were found to be reproducible within $\leqq 1\%$. Standards and marker compounds were purchased from Aldrich Chemical Co., Pfalz & Bauer, and Baker.

TABLE I

Concentration sums of organic compounds in Elizabeth River sediments (in ng/g dry wt)

Station	Total resolved[a]	Pyrogenic	Total (resolved + UCM)
01	3,000	1,400	4,000
03	2,000	1,200	3,100
04	7,400	3,100	13,000
07	14,000	6,100	31,000
08	7,700	3,800	20,000
09	13,000	6,100	25,000
10	20,000	9,400	44,000
11	31,000	12,000	50,000
12	35,000	15,000	95,000
13	43,000	16,000	110,000
14	67,000	30,000	160,000
15	59,000	30,000	140,000
16	26,000	14,000	45,000
17	360,000	170,000	440,000
18	45,000	16,000	91,000
19	21,000	9,400	41,000
20	34,000	14,000	90,000
21	22,000	11,000	52,000
22	22,000	11,000	48,000
23	3,700	2,500	6,100
24	8,900	5,600	16,000
25	5,100	3,100	9,800
26	3,200	2,100	6,600
27	7,100	4,400	12,000
28	3,600	2,300	5,700
02	7,000	2,700	12,000
05	3,400	2,000	5,300
06	3,900	1,600	7,500

[a] Including resolved pyrogenic PAHs.

RESULTS AND DISCUSSION

Organic concentrations in the G32 fraction of surface sediment extracts from the Elizabeth River are presented in Table I and Figure 3. Due to the complexity of these fractions (Figure 4), an average of only 56% of the total concentration was resolved into

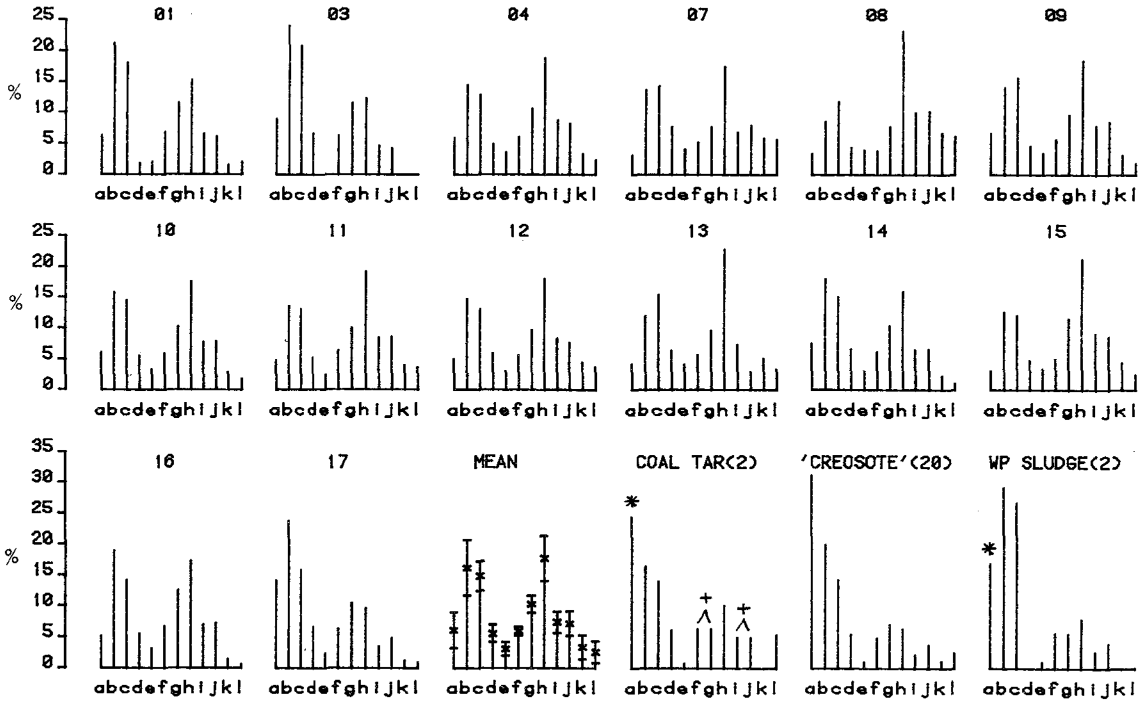


FIGURE 3 Histograms of relative PAH concentrations $C_v/\sum_a^1 C_v$ in individual surface sediment samples from the main branch of the Elizabeth River. Also shown are mean relative concentrations ± standard deviation and PAH concentrations in coal tar, "creosote" and wood preservative sludge, a = phenanthrene; b = fluoroanthene: c = pyrene; d = benzo(b)fluorene; e = benzo(ghi)fluoranthene/benzo(c)phenanthrene; f = benz(a)anthracene; g = chrysene; h = benzofluoranthenes(b, k & j); i = benzo(e)pyrene; j = benzo(a)pyrene; k = indeno(1, 2, 3-cd)pyrene; l = benzo(ghi)perylene.
*Phenanthrene and anthracene were not separated; the bar represents the sum of both concentrations.
+Both isomeric pairs f, g and i, j were not separated; in this plot it was assumed that f/g = i/j = 1.

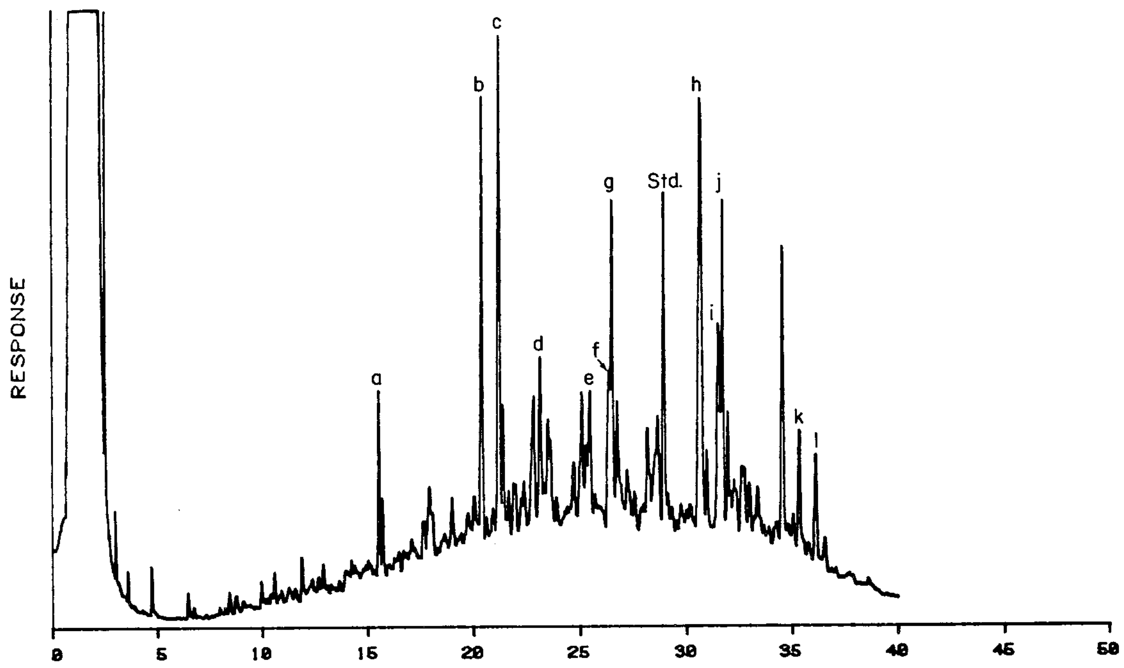


FIGURE 4 Computer reconstructed chromatogram typical of sediment extracts from the Elizabeth River (G32 fraction). Of a total of 197 identified compounds in this particular sample, only a few abundant PAHs are pointed out using the same code as in Figure 3. Std is 2,2′-binaphthyl. GC operation parameters are described in the text.

quantifiable and identifiable peaks by high resolution GC. About half of the resolved concentration sum was accounted for by 14 unsubstituted polynuclear aromatic hydrocarbons (PAHs). These 14 compounds were: phenanthrene, fluoranthene, pyrene, benzo(b)fluorene, benzo(c)phenanthrene, benz(a)anthracene, chrysene, benzo fluoranthenes (j, b, k isomers), benzo(e)pyrene, benzo(a)pyrene, indeno(1, 2, 3-cd)pyrene and benzo(ghi)perylene. All of these PAHs are characteristic of a pyrosynthetic origin.[1-6] It is, however, noteworthy that cyclopenta(c, d)pyrene is absent.

Additional major compounds that were positively indentified by their mass spectra and ARI on SE-52 in the Elizabeth River samples are presented in Table II. Although only 11 of the 28 samples were analyzed by GC-MS, compositional details of samples analyzed by GC can be inferred from ARIs if the qualitative composition of these samples is sufficiently similar to those analyzed by GC-MS, thus permitting location of the ARI standards.

It is evident that most resolved compounds are hydrocarbons, although a few heterocyclic compounds, such as condensed furans and thiophenes, and chlorinated hydrocarbons were also found. Aside from these compounds and the pyrogenic PAHs, many substituted naphthalenes and phenanthrenes are present at relatively low concentration in most samples. These indicate a small but noticeable contribution from petroleum.[20] The presence of a pronounced UCM and of numerous substituted sulfur compounds such as dibenzothiophenes and naphthobenzothiophenes[21] support this contention. A recent study,[5] however, found dibenzothiophenes in oils and from pyrogenic sources to have similar distributions. Since the degree of substitution depends on temperature, this observation may be coincidental. With the exception of dibenzothiophene and naphthobenzothiophene listed in Table II, most of the sulfur compounds are minor components of the extracts. Strong evidence for the presence of oil was also found in aliphatic fractions.[7]

The absence of cyclopenta(c, d)pyrene, found to be a charactistic product in the combustion of oil and to a lesser degree wood,[3,22] the high PAH concentration, and the location of the maximum near an abandoned and an operational wood treatment plant suggest that one or both of these plants are linked to the high pollution level encountered in many of the Elizabeth River sediment samples,

TABLE II

Regularly encountered compounds in aromatic fractions from Elizabeth River surface sediment extracts.

Compound name	Molecular weight	Aromatic retention index (ARI)[a]	I.D. code[b]
Naphthalene	128	0.0	A
2-methylnaphthalene	142	53.8	A
1-methylnaphthalene	142	62.4	A
Biphenyl	154	100.00	A
Ethylnaphthalene	156	103.6	B
Dimethylnaphthalene	156	106.3	B
Dimethylnaphthalene	156	110.2	B
Dimethylnaphthalene	156	115.4	B
Acenaphthene	154	126.3	A
Dibenzofuran	168	134.6	A
Fluorene	166	151.7	A
2-Methylfluorene	180	181.0	B
1-Methylfluorene	180	182.7	B
Dibenzothiophene	184	193.5	A
Anthracene	178	203.1	A
3-Methylphenanthrene	192	236.7	B
2-Methylphenanthrene	192	238.2	B
4H-Cyclopenta(def)phenanthrene	190	242.6	A
Methylphenanthrene	192	245.2	B
2-Phenylnaphthalene	204	260.9	A
Methyl-4H-cyclopentaphenanthrene	204	278.7	A
Methylfluoranthene	216	321.7	A
Benzo(a)fluorene and/or Methylfluoranthene	216	330.1	A
Retene	234	332.7	A
Benzo(b)naphtho(2,1-d)thiophene	234	377.3	B
Benzo(ghi)fluoranthene	226	380.4	B
Benzo(c)phenanthrene	228	380.4	B

[a] Based on naphthalene, biphenyl, phenanthrene, pyrene, chrysene, perylene and benzo(ghi)perylene as retention markers for 0, 100, 200, 300, 400, 500 and 600, respectively.

[b] A indicates mass spectrum and chromatographic retention index agree with standard compound injected into GC-MS under identical condition as sample. B indicates mass spectrum and chromatographic retention index agree with data available in the literature.

especially in the highly industrialized Southern Branch. This suspicion was confirmed by the discovery that thousands of gallons of creosote, either pure or mixed with coal tar, had been spilled into the river through two accidents at the now abandoned plant in 1960 and again in 1963.[23] In absence of reliable information about the spilled product the term "wood preservative" will be used.

These spills present an opportunity to seek information on the transport and the chemical fate of unsubstituted PAHs. If the logarithms of individual PAH concentrations or of the PAH concentration sum in the Southern Branch and the main stem are plotted versus distance from station 17, a linear decrease is observed. For the concentration sum, the slope is -0.123 with a correlation coefficient R of -0.92. Individual PAHs from phenanthrene to the benzofluoranthenes have slopes between -0.119 and -0.130 and R's between -0.85 and -0.93. These regression data were calculated by using concentrations from samples 17, 16, 15, 14, 13 and 12 in the Southern Branch and from samples 11, 10, 09, 08, 07, 04, 03 and 01 in the main stem. Sample 02 was excluded because it was collected outside the channel and could have received runoff from Craney Island (Figure 1) which was created from dredge spoils. Samples 05 and 06 were excluded because they are outside the river environment.

An exponential decrease of the PAH concentrations, indicated by the linear regression of log concentration versus distance, can be interpreted in several ways. For example, the differential equation (1) for advective and diffusive transport describing a linear situation and steady state conditions:[24]

$$k\frac{d^2c}{dx^2} - w\frac{dc}{dx} = 0 \tag{1}$$

(where k = eddy diffusion coefficient, c = concentration, x = distance from the source, positive in the direction from source to mouth, and w = advection velocity) has solutions that, for $k/w = -3.5\,\mathrm{km}$, fit the experimental data points well and indicates a negative advection term. Assuming a sediment associated near-bottom transport of PAHs, this is not unusual for a tidal estuary.[25]

An exponential-like decrease also results from solutions of a differential equation (2) describing the disperion from an instantaneous point source.[26]

$$\frac{d^2c}{dx^2} - \frac{1}{k}\frac{dc}{dt} = 0 \tag{2}$$

(c, k and x as defined before, and t = time). Thus, while (1) assumes quasi fixed boundary conditions (time to reach equilibrium < time constant for changes in boundary concentrations) but allows for the continuous reformation of polluted particles, (2) demands that the PAH carriers diffusing at the present are essentially the same as those generated shortly after the spill. In view of the considerable changes the river bottom has undergone since the spills, partially by the turbulence created by ships and documented by side scanning sonar records[27] and partially by dredging (both contributing to the re-formation of polluted particles), the requirements for the instantaneous point source model seem impossible to fulfill.

Finally, an exponential concentration decrease with distance can also result in a purely advective environment ($k = 0$) as described by Eq. (3).

$$\frac{dc}{dx} + ac = 0 \tag{3}$$

(c, x as defined before; a = constant) if the substances under observation are non-conservative and their transformation obeys a first order reaction. But the absence of an eddy diffusion term is unlikely to fit the dispersive pattern of a tidal estuary.

A diffusion-advection model therefore comes closest to describing the dispersion of the spilled material in the Elizabeth River, but quantitative understanding of the various factors will require more research of physical details.

The spilled wood preservative offers an opportunity to look at the geochemical stability of PAH in the Elizabeth River environment. Figure 3 contains relative concentration plots for PAH in sediments and three source materials: coal tar,[2] "creosote"[23] and wood preservative sludge.[2] It is evident that these source materials cannot be expected to characterize the spilled wood preservative exactly due to compositional variability of coal and coal tar. In addition, "wood preservative sludge" is a poorly defined term that can mean a number of things. The "creosote", picked from a cohesive, tarry globule from a sediment core collected near station 17,[23] may be suspected to be a remnant of the spilled material and therefore show closest agreement with sediment data, but one really does not know whether this globule is representative of the PAH found in sediments elsewhere in the river.

Considering such uncertainties, one notes that relatively few modifications are needed to bring relative source concentrations into agreement with the sediment extracts. Depletion of more soluble lower M.W. compounds, e.g. phenanthrene, from source pollutants would be expected. Such losses would mainly affect finely divided material but not so much large cohesive masses like the sediment inclusion from which the "creosote" data were derived. Some losses would also be expected for fluoranthene and pyrene, although they would be smaller, as the solubility of fluoranthene is approximately 1/5 and the solubility of pyrene approxmately 1/10 of the solubility of phenanthrene.[28] A decrease of these 3 PAHs then would raise the relative concentrations of heavier PAHs, as is observed in the sediment data. The relatively high concentration sum of the benzofluoranthenes is an exception. But we have shown this compound mixture to be easily underestimated if electronic integrators are used.[29]

Therefore, there is no evidence that the observed PAH distributions in sediments have been influenced by geochemical reactions. This is in agreement with analyses of sediment cores, which contain a record of PAH input and stability over a period of approximately 80 years.[30,31]

Although the application of a diffusion-advection model and the assumption of fixed boundary conditions may not withstand closer scrutiny, for the data set presented in this paper it suggests that the PAH concentrations between station 17 and the mouth of the Elizabeth River are essentially dominated by the wood preservative spills near station 17. There is little doubt that other sources also exist, but it is difficult to detect their presence with the high background near the site of the spills. Such additions would therefore be expected to become more visible farther away from the spill. This may be why PAH concentrations averaging 2.4 times those in samples 03 and 04 were found in sample 02, possibly as a result of runoff from dredge spoil-created Craney Island. In sample 05 collected near the Hampton Roads Naval Piers, concentrations were about 30% higher than those in sample 01, but since the relative standard deviation of a single measurement averaged 37%, the difference is not significant. Polychlorinated biphenyls (PCBs) were identified in two samples, stations 13 and 9, one close to the Naval Shipyard and the other off the Pinner Point Sewage Treatment Plant outfall.

The concentrations of PAHs in the Elizabeth River sediments are among the highest found anywhere in the nation. Table III presents a summary of available data from other polluted areas. Although there are compositional differences in these data sets, there is reason to be concerned about the ecological effects of these high concentrations in the Elizabeth River.

TABLE III

Concentrations (in μg/g dry wt) of select PAHs in sediment from some of the most polluted areas in continental USA

Area	Phe	Fla	Pyr	BaA	Chr	BFls	BeP	BaP	Ref.
Charles River Massachusetts	3	13	12	21		—	33	—	32
Elliot Bay (Pier 54) Washington	7	8	11	7	6	5	4	2	33
Commencement Bay (Hylebo Waterway) Washington	0.4	2	2	2	2	3	1	0.5	33
Newton Creek New York	14	10	7	6	3	—	1	1	34
Elizabeth River Virginia	25	42	28	11	19	17	6	9	this article

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References

1. R. C. Lao, R. S. Thomas, H. Oja and L. Dubois, *Anal. Chem.* **45,** 908–915 (1973).
2. R. C. Lao, R. S. Thomas and J. L. Monkman, *J. Chromatogr.* **112,** 681–700 (1975).
3. M. L. Lee, G. P. Prado, J. B. Howard and R. A. Hites, *Biomed. Mass Spectr.* **4,** 182–186 (1977).
4. R. E. Laflamme and R. A. Hites, *Geochim. Cosmochim. Acta* **42,** 289–303 (1978).
5. S. Sporstol, N. Gjos, R. G. Lichtenthaler, K. O. Gustavsen, K. Urdal, F. Oreld and J. Skei, *Environ. Sci. Technol.* **17,** 282–286 (1983).
6. W. W. Youngblood and M. Blumer, *Geochim. Cosmochim. Acta* **39,** 1303–1314 (1975).
7. E. G. Merrill and T. L. Wade, *Environ. Sci. Technol.* **19,** 597–603 (1985).
8. G. Lunde and A. Bjorseth, *Nature* **268,** 518–519 (1977).
9. M. Blumer and W. W. Youngblood, *Science* **188,** 53–55 (1975).
10. G. Lunde, J. Gether, N. Gjos and M. B. Strobet Lande, *Atmospheric Environment* **11,** 1007–1014 (1977).
11. P. M. Gschwend and R. A. Hites, *Geochim. Cosmochim. Acta* **45,** 2359–2367 (1981).
12. P. O. deFur, M. E. Bender, C. W. Su, R. J. Huggett, H. D. Slone and C. L. Smith, Report to A.P.I. (April, 1984).
13. W. D. MacLeod, P. G. Prohaska, D. D. Gennero and D. W. Brown, *Anal. Chem.* **54,** 386–392 (1982).
14. W. Giger and C. Schaffner, *Anal. Chem.* **50,** 243–249 (1978).
15. L. S. Ramos and P. Prohaska, *J. Chromatogr.* **211,** 284–289 (1981).
16. K. Grob and G. Grob, *Chromatographia* **5,** 3–12 (1972).
17. K. Grob, Jr., G. Grob and K. Grob, *J. Chromatogr.* **156,** 1–20 (1978).
18. R. H. Bieri, M. K. Cueman and C. W. Su, Abstracts of Papers, 30th Regional Meeting of the American Chemical Society, Savannah, GA (1978).
19. M. L. Lee, D. L. Vassilaros, C. M. White and M. Novotny, *Anal. Chem.* **51,** 768–774 (1979).
20. M. Blumer, "A Guide to Marine Pollution," Goldberg, E. D., Ed.; Gordon and Breach Science Publ., New York, Chapter 2 (1972).
21. J. S. Warner, "Proceedings, 1975 Conference on Prevention and Control of Oil Pollution"; A.P.I., E.P.A., U.S.C.G., San Francisco, 97–101.
22. G. Grimmer, K. W. Naujack and D. Schneider, "Polynuclear Aromatic Hydrocarbons" Battelle Press, Columbus/Richland, 107–125 (1979).
23. Muzhen Lu, Thesis, College of William and Mary, School of Marine Science, Gloucester Point, VA (1982).
24. H. G. Gade, "Pollutant Transfer and Transport in the Sea," Vol. II, Kullenberg, G., Ed. CRC Press, Inc., Boca Raton, Fl, Chapter 4 (1982).
25. K. R. Dyer, "Estuarine Transport Processes," Kjerfve, B., Ed. Univ. of S. Carolina Press, Columbia, S.C., 135–145 (1978).
26. J. Crank, "The Mathematics of Diffusion," Clarendon Press, Oxford, first edition (1956).
27. M. Nichols, Virginia Institute of Marine Science, Gloucester Point, VA; personal communication (1983).
28. D. Mackay and W. Y. Shiu, *J. Chem. Eng. Data* **22,** 399–402 (1977).

29. R. H. Bieri, P. deFur, R. J. Huggett, W. MacIntyre, P. Shou, C. L. Smith and C. W. Su, “Organic Compounds in Surface Sediments and Oyster Tissues from the Chesapeake Bay”, Vol. I, NTI No. PB83-187443 (1983).
30. R. A. Hites, R. E. LaFlamme, J. G. Windsor, Jr., J. W. Farrington and W. G. Deuser, *Geochim. Cosmochim. Acta* **44,** 873–878 (1980).
31. S. G. Wakeham and J. W. Farrington, “Contaminants and Sediments,” Vol. 1, Baker, R. A., Ed. Ann Arbor Science Publishers, Inc., Ann Arbor, MI (1980).
32. J. G. Windsor and R. A. Hites, *Geochim. Cosmochim. Acta* **43,** 27–33 (1979).
33. D. C. Malins, B. B. McCain, D. W. Brown, A. K. Sparks, H. O. Hudgins and Sin-Lam Chan, NOAA Technical Memorandum OMPA-19 (1982).
34. J. W. Anderson, “Ecological stress and the New York Bight: Science and Management,” Mayer, G. E., Ed., Estuarine Research Federation: Columbia, N.C. (1982).