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POLYNUCLEAR AROMATIC HYDROCARBONS AND TOXICITY OF SEDIMENTS FROM THE ELIZABETH RIVER, HAMPTON ROADS, VIRGINIA

By

Raymond W. Alden III, Principal Investigator
Guy J. Hall, Co-Principal Investigator

Supplemental Contract Report
For the period ending September 1984

Prepared for the
Department of the Army
Norfolk District, Corps of Engineers
Fort Norfolk, 803 Front Street
Norfolk, Virginia 23510

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Targets lower Southern Branch of Elizabeth River as toxin sink not suitable for ocean disposal, intermediate stations in Southern Branch may not be suitable for ocean disposal. Dredging may actually improve environmental quality by removing toxic sediments.

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POLYNUCLEAR AROMATIC HYDROCARBONS AND TOXICITY OF SEDIMENTS FROM THE ELIZABETH RIVER, HAMPTON ROADS, VIRGINIA

By
Dr. Raymond W. Alden III*
Guy J. Hall**

INTRODUCTION

A series of environmental studies in the Port of Hampton Roads, Virginia indicate that sediments from certain areas of the Southern Branch of the Elizabeth River are quite toxic (Alden *et al*., 1981; Alden and Young, 1982; Alden *et al*., 1984) and are believed to be contaminated by a variety of pollutants (EPA, 1976; Alden *et al*., 1981; Alden *et al*., 1982; VSWCB, 1984). One group of pollutants that is of particular concern is a class of compounds known as polynuclear aromatic hydrocarbons (PNAH's). The potential sources of these compounds are numerous: petroleum products, coal, creosote, and the incomplete combustion of fossil fuels (e.g. automobile exhausts, industrial smoke stacks, home heating, incinerators, etc.), among others (EPA, 1979). Preliminary surveys of the sediments in the most toxic regions of the Elizabeth River revealed that high concentrations of PNAH's (i.e. high ppm range) are found in the sediments. The high levels of these contaminants are of particular environmental concern because they are long-lived toxins and many are mutagenic and/or carcinogenic.

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**Research Associate, Applied Marine Research Laboratory, Old Dominion University, Norfolk, Virginia.

The present study was designed to map and characterize the distribution of PNAH's in the sediments of the major navigation channels of the Elizabeth River. Data from extensive biological chemical investigations of stations located throughout the main stem and Southern Branch of the Elizabeth River were analyzed by multivariate statistical techniques to characterize the major patterns of the sediment quality in the Port. The results of the geographic characterization of chemical and biological effects patterns should provide valuable information to managers and regulators who must make policy decisions concerning issues such as which sediments are acceptable for ocean disposal.

METHODS AND MATERIALS

Study Area

The Elizabeth River (nearly 35 km) includes a main stem extending from Sewell's Point to Town Point, the Lafayette River, and the Western, Eastern and Southern Branches. Water motion within the system contributing to the circulation of the Elizabeth River are: (1) fresh water inflows; (2) tidal and wind action; and, (3) verticial mixing induced by a two layered salinity gradient. Three processes control the hydrographic structure of the river system. Fresh water may enter the Elizabeth River either from local runoff, the James River or from the Dismal Swamp. The latter flow varies seasonally and is controlled by the locks and spillway at Deep Creek. When fresh water input is insignificant, the Elizabeth River tends to become homogenous both horizontally and vertically. There is a net seaward motion of low salinity surface water and an upward intrusion of more dense, higher saline bottom waters. Tidal currents in the Elizabeth River are relatively slow; however, this appears to be the major driving force, particularly along the main stem of the river. Wind is the second most dominating component to circulation within the system.

The overall study area has been described in detail in accompanying reports describing the lethal (Alden and Young, 1984) and sublethal (Alden _et al_., 1984) bioassay studies. The stations considered in the present study were from the Hampton Roads Harbor (Stations D and E) and the Elizabeth River (Stations F-S)

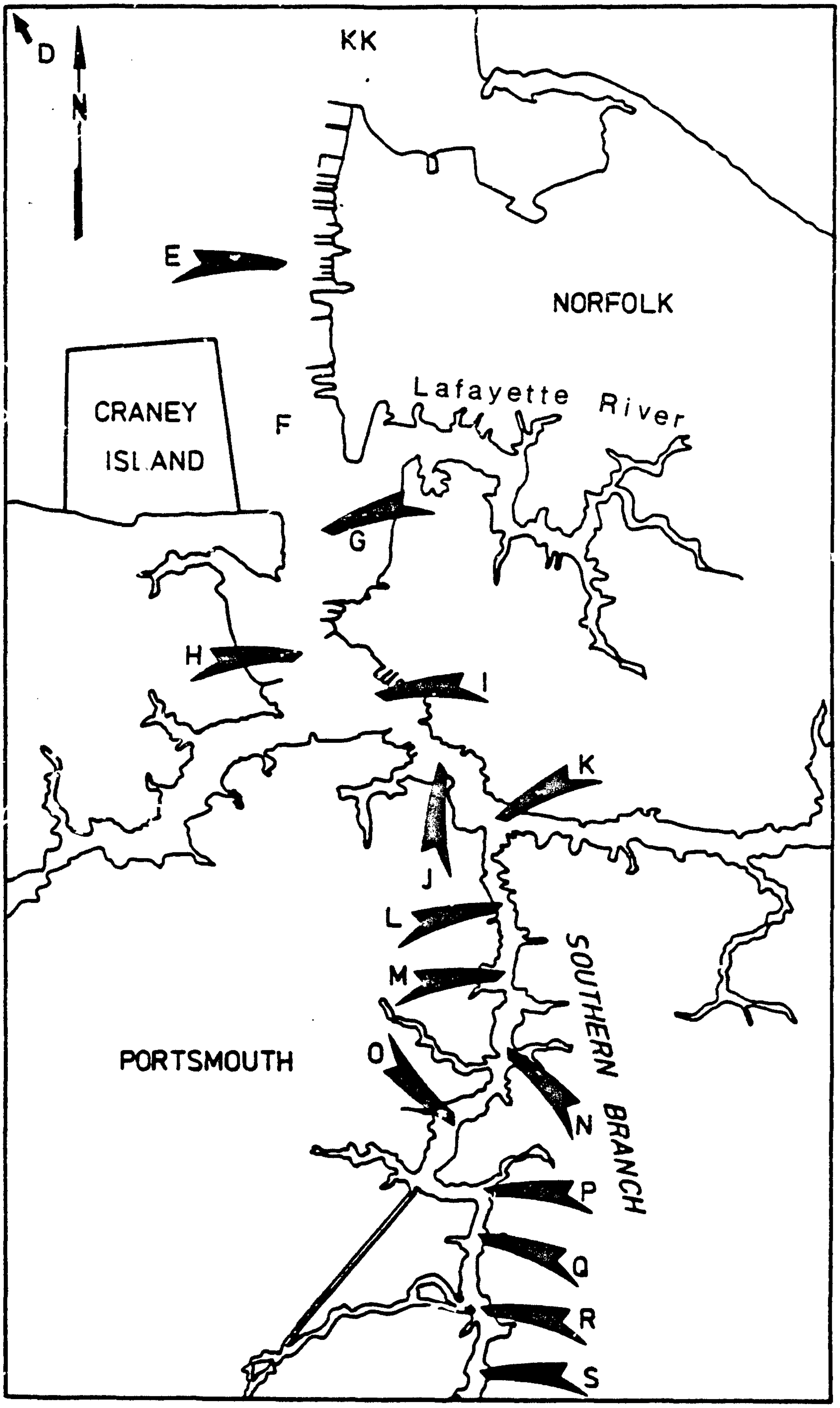
(Fig. 1). The stations were selected to correspond to the river miles of the main navigation channel.

The data from the 10-day solid phase lethal bioassays were collected for Stations E,F,G,H,I,J,K,L,M,N,O,P,Q,R and S. The data from the 96 hour suspended solid phase lethal and sublethal experiments were taken for Stations D,E,F,H,I,J,J/K (located between Stations J and K), K,M,N,N/O (located between Stations N and O), O,O/P (located between Stations O and P), P,Q, and R.

The PNAH's in elutriates investigation was conducted on suspended solid fractions taken from the aquaria at the beginning of the 96 hour bioassays. The PNAH's in sediments survey consisted of transects across the navigational channel at Stations E,F,G,H,I,J,K,L,M,N,O,P,Q,R,and S. Samples from each transect were taken from the center of the channel and mid-way up each side of the channel (at approximately 6m depth).

Sediments were collected at each of the stations with a 20 L stainless steel Pearce bucket dredge. The sediments in the central portion of the bucket were scooped into 18 l snap-top polyethylene containers (biological experiments) or solvent rinsed, teflon capped borosilicate glass jars (PNAH in sediment survey). Sediment samples for biological testing were stored at 4°C until tested (within 2 weeks) and those for chemical analysis were frozen until analyzed.

Figure 1: Map of study area. Stations D-G in open waters are located at 2 river mile intervals while Stations H-S in the Elizabeth River are at 1 river mile intervals.


D
N
KK
D
E
NORFOLK
CRANEY ISLAND
F
Lafayette River
G
H
I
K
J
L
M
SOUTHERN BRANCH
PORTSMOUTH
O
N
P
Q
R
S

Bioassay Methods

Details of lethal and sublethal bioassay methods have been described in accompanying reports (Alden and Young, 1984; Alden et al., 1984, respectively). The solid and suspended solid phase lethal bioassay experiments followed the guidelines established by the Implementation Manual (EPA/COE, 1978). The grass shrimp, Palaemonetes pugio was employed as the test species in all of the bioassays providing data for the present study.

Flow-through respiration chambers were utilized to determine the respiration rates of shrimp exposed to the dredged material elutriates (Alden et al., 1984). Following each suspended solid phase experiment, the shrimp were exposed to high (35 ppt) or low (10 ppt) salinities for 24 hours to test osmoregulation capacities. The osmolality of each shrimp was then determined with a vapor pressure osmometer to test hyporegulation or hyperregulation capacity (Alden et al., 1984).

Chemical Analysis Methods

Elutriate water samples (3 l) were collected as the aquaria in the suspended solid phase bioassays were being filled. The elutriates were filtered through 0.45 micron pre-extracted glass fiber filters and the filtrates and nonfilterable solid fractions were extracted separately. The liquid fractions were extracted by methods described by EPA (1982). The filter paper and filtered sediments were extracted in a soxhlet apparatus according to the method of Brown et al. (1980). The extracts from the two ractions were combined, cleaned-up by the column chromatography method of Boehm (1980), and analyzed on a capillary gas chromatograph fitted with a flame ionization detector (FID). Prior to clean-up, all extracts were spiked with 1-1-Binaphthyl for use as an internal standard in microprocessor-based data reduction.

For the sediment analyses, the internal standard was pipetted onto the air-dried sediment samples. The samples were soxhlet extracted according to Brown et al. (1980), and the extracts were cleaned-up on silisic acid columns (Boehm, 1980). The sediment sample extracts were also analyzed on a capillary gas chromatograph equipped with a flame ionization detector (FID).

Selected elutriate and sediment extracts containing PNAH's identified and quantified by capillary gas chromatography were analyzed by gas chromatograph/mass spectrometry (GC/MS) for confirmation purposes.

Statistical Analysis

The lethal and sublethal toxicity data were previously analyzed (Alden and Young, 1984; and Alden et al., 1984, respectively) to determine which stations contained sediments which produced significant responses in test populations. Histograms of the solid phase mortality data (means and standard errors) were arranged by geographic locations of the stations to provide a visual representation of major toxicity patterns of sediments in the inner harbor. The lethal and sublethal data from suspended solids phase experiments were likewise plotted. However, a discriminant analysis (Klecka, 1975) was employed to reduce the more extensive suspended solids data into a single discriminant function which would summarize the major biological patterns.

The discriminant analysis contrasted the data from two _a. priori_ groups: a group representing noncontaminated conditions (the controls from the various experimental sets); and a group of stations believed to represent the most contaminated region (Stations N, N/O, and O) evaluated by the sublethal tests. Although located in the region of greatest contamination and potential toxicity, Stations K and M were not used in the second group because sediments from this region were so toxic in the lethal bioassays that they were not evaluated in subsequent sublethal experiments. The data from the remaining stations were not grouped for the portion of the analysis which produced the discriminant function. However, discriminant function (D.F.) scores were calculated for all stations in the classification portion of the analysis. The magnitude of the station D.F. scores on geographically sequenced histograms were used to summarize biological trends and the classification analyses provided an objective means of determining whether the data from any given station was statistically more similar to the "clean" or "contaminated" groups in terms of biological effects.

The data sets for PNAH's in elutriates and PNAH's in sediments were analyzed in a similar manner. However, the *a priori* groups for the discriminant analyses were determined by the results of the analysis of the biological data sets (i.e. groups of stations producing distinct biological patterns were selected as the new groups for the discriminant analysis of the chemical data). Although no direct evidence of cause and effect relationships can be taken from this statistical protocol, it is felt that if the chemical patterns parallel the toxicity groupings, some qualitative associations may be inferred between the degree of contamination and the biological responses.

RESULTS

The histograms for mortality data, arranged by geographic location (i. e. by river mile) are presented for the solid phase and suspended solid phase experiments (Figures 2 and 3a, respectively). For the maximum control of stations which may have been tested by solid phase bioassays on several occasions, only the mortality values for the experiments producing the greatest effects are shown in Figure 2 (see Alden and Young, 1984 for a discussion of changes in relative toxicity of sediments as related to maintenance dredging). The maximum mortalities were found for experiments involving sediments from Stations K through O, with low to moderate values being found for the remaining tests. Except for the 1980 data from Stations K and M, the mortalities are for a series of suspended solid bioassays which were run concurrently with the sublethal experiments in 1982. As has been previously pointed out (Alden and Young, 1984; and Alden <u>et al</u>., 1984), these experiments were conducted 6-8 months following dredging operations at certain stations in the Southern Branch of the Elizabeth River, possibly explaining the fairly low levels of mortalities observed.

The histograms for the sublethal data are also arranged geographically (Figures 3b, c and d respiration, hyporegulation capacity and hyperregulation capacity, respectively). For presentation purposes, the values for the various sets of controls have been combined into grand means. However, the shading on the

Figure 2: Mortality data from 10-day solid phase bioassays on *Palaemonetes pugio*. Histograms represent mean values (vertical bars are two standard errors; n=5) arranged geographically by river mile (see Figure 1 for station locations). Shading indicates mortalities which were significantly greater (= 0.05) than those controls of the experimental set.

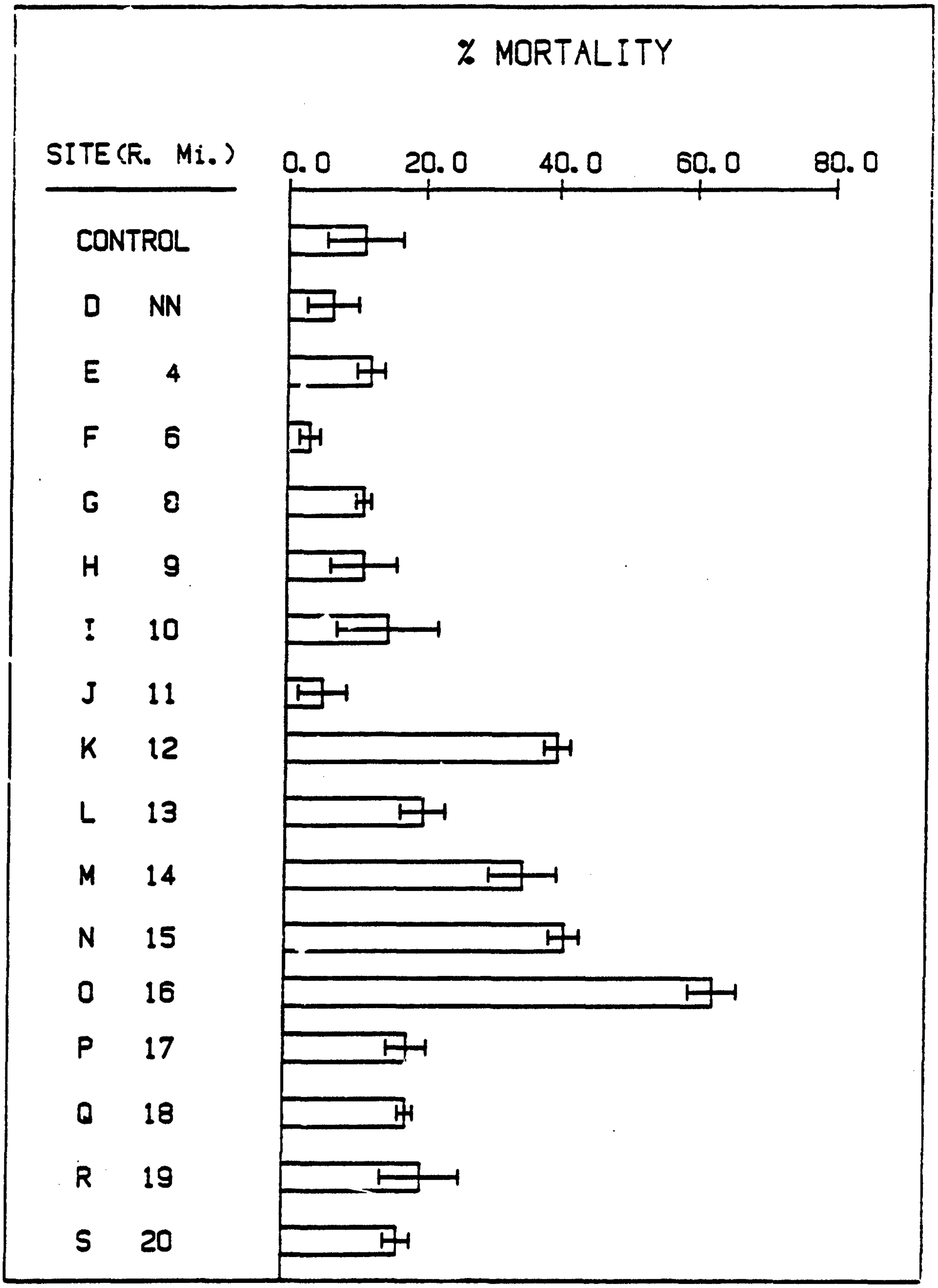
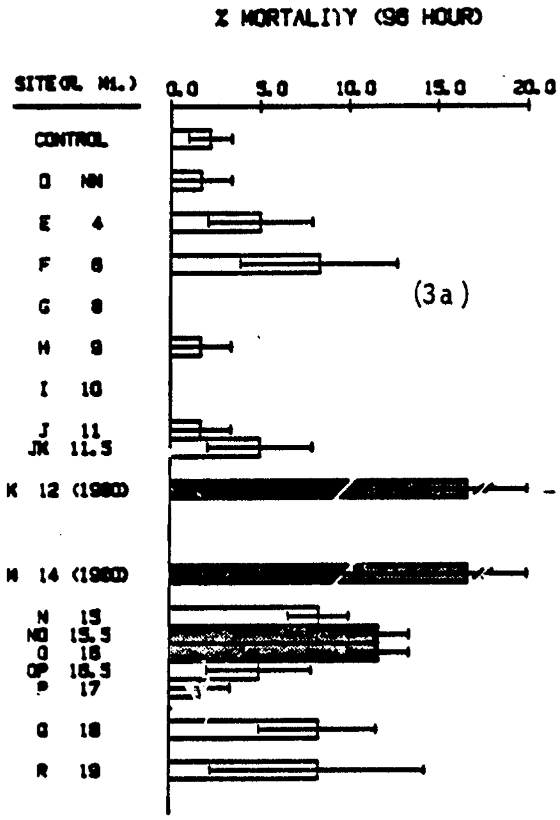
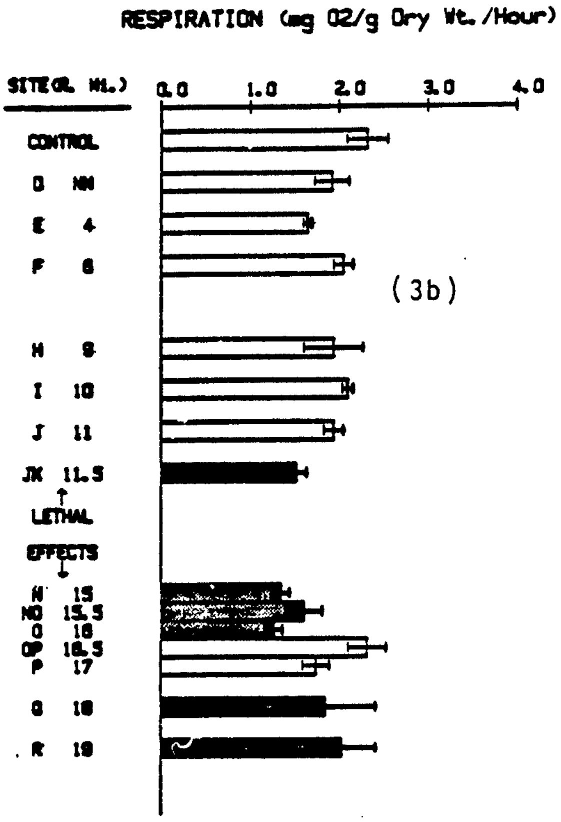
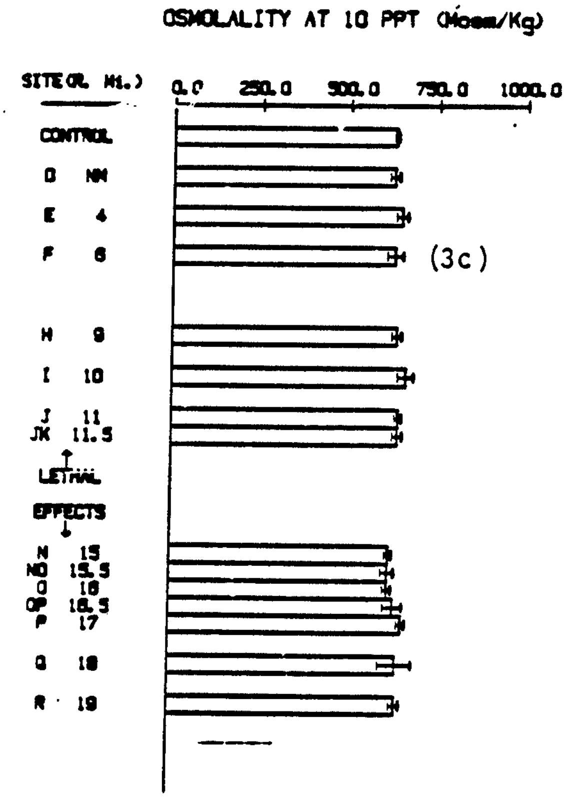

% MORTALITY
SITE (R. Mi.)
0.0
20.0
40.0
60.0
80.0
CONTROL
D NN
E 4
F 6
G 8
H 9
I 10
J 11
K 12
L 13
M 14
N 15
O 16
P 17
Q 18
R 19
S 20

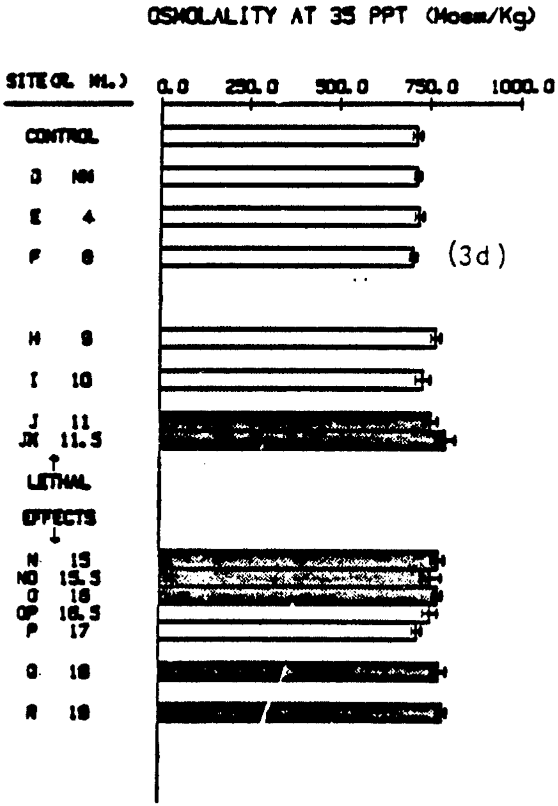
Figure 3: Biological data (means and standard errors arranged geographically as in Figure 2) from suspended solid experiments on <u>Palaemonetes pugio</u>:

a) 96-hour mortalaities (%) (Station K mean 50.00±5.0; Station M mean 90.00±10.00);
b) respiration rates (g/02 g^{-1} dry wt. hr^{-1};
c) internal osmolalities (mOsm kg^{-1}) of shrimp exposed to 10 ppt salinities;
d) osmolalities (mOsm kg^{-1}) of shrimp exposed to 35 ppt salinities.


% MORTALITY (98 HOUR)
SITE (R. Mi.)
0.0
5.0
10.0
15.0
20.0
CONTROL
D NM
E 4
F 6
G 8
H 9
I 10
J 11
JK 11.5
K 12 (1980)
M 14 (1980)
N 15
NO 15.5
O 16
OP 16.5
P 17
Q 18
R 19
(3a)


RESPIRATION (mg O2/g Dry Wt./Hour)
SITE (R. Mi.)
0.0
1.0
2.0
3.0
4.0
CONTROL
D NM
E 4
F 6
H 9
I 10
J 11
JK 11.5
LETHAL
EFFECTS
N 15
NO 15.5
O 16
OP 16.5
P 17
Q 18
R 19
(3b)


OSMOLALITY AT 10 PPT (Mosm/Kg)
SITE (R. Mi.)
0.0
250.0
500.0
750.0
1000.0
CONTROL
D NM
E 4
F 6
H 9
I 10
J 11
JK 11.5
LETHAL
EFFECTS
N 15
NO 15.5
O 16
OP 16.5
P 17
Q 18
R 19
(3c)


OSMOLALITY AT 35 PPT (Mosm/Kg)
SITE (R. Mi.)
0.0
250.0
500.0
750.0
1000.0
CONTROL
D NM
E 4
F 6
H 9
I 10
J 11
JK 11.5
LETHAL
EFFECTS
N 15
NO 15.5
O 16
OP 16.5
P 17
Q 18
R 19
(3d)

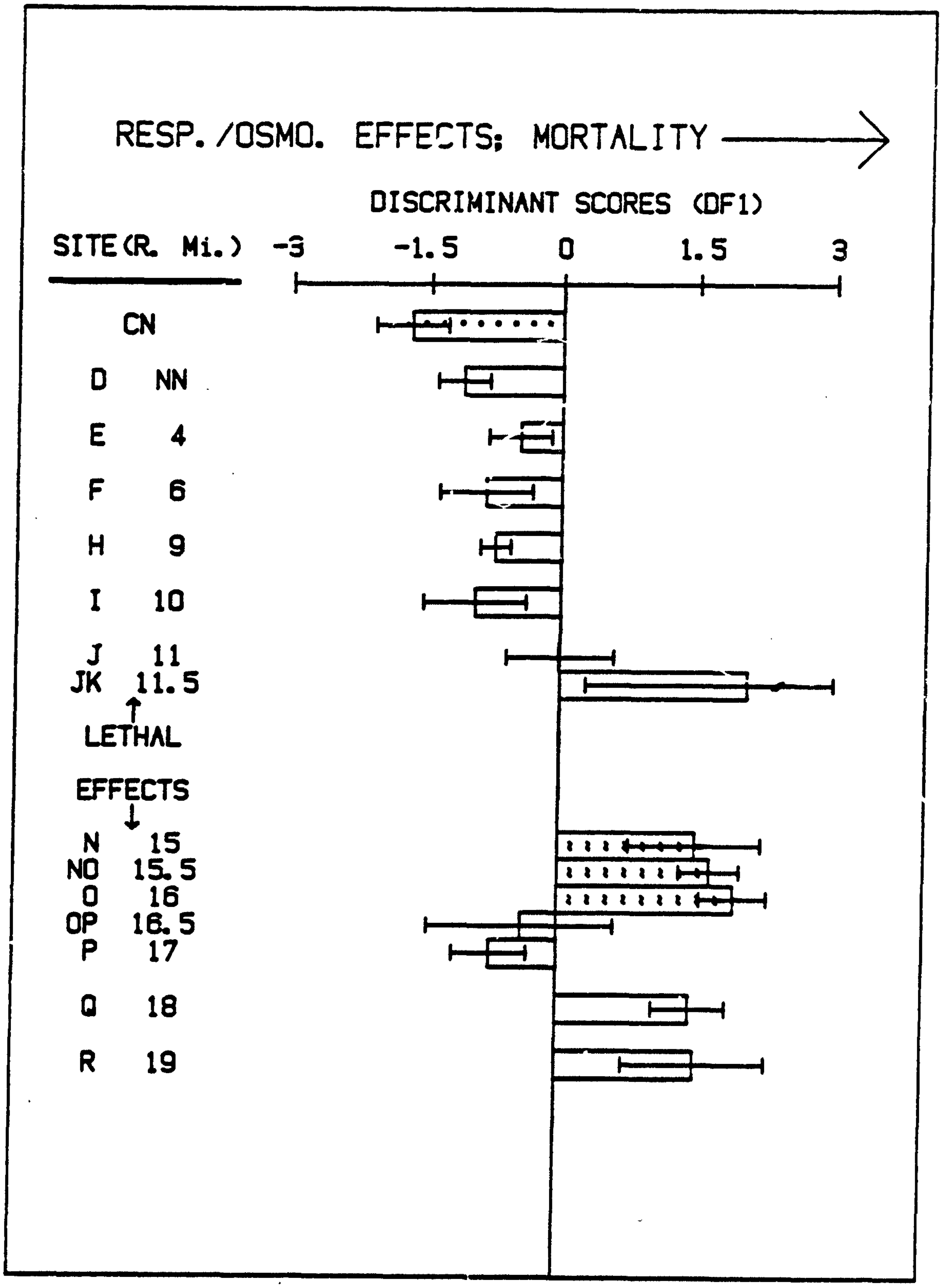
histograms represents those values which were shown to be significantly different from those of the controls which were run in the same test series. Significant sublethal effects were observed for shrimp populations taken from stations surrounding the region producing high mortalities in the 1980 suspended solid bioassays (Stations K and M; Alden _et al_., 1981; Alden and Young, 1982). Sediment elutriates from Stations N,N/O, and O upstream and Stations J/K and J downstream of this region of lethal effects generally produced significantly reduced hyporegulation capacity and depressed respiration rates in the test shrimp (Alden _et al_., 1984). In addition, elutriates from Stations Q and R produced significant effects on respiration and hyporegulatory capacity. Hyperregulation was apparently unaffected by any of the experimental conditions and internal osmolalities of shrimp exposed to low salinity conditions were quite constant (Figure 3c).

A discriminant analysis was conducted on data from the suspended solids experiments, using two _a. priori_ groupings for "clean" (three sets of controls) and "contaminated" (sediments from Stations N,N/O, and O) conditions. The discriminant function produced by the analysis was highly significant ($p<0.001$; Wilk's Lambda = 0.234 and $X^2=21.00$ with 3 d.f.) and a fairly high portion of the variance was explained by the _a. priori_ group effect (canonical correlation = 0.88). Thus, the discrimination portion of the analysis was considered successful and the discriminant function scores were used to classify all of the data.

The mean discriminant scores for all tests are presented in Figure 4. A Pearson's Correlation Analysis was employed to relate the discriminant function scores to the original variables. Internal osmolality at 35 ppt and mortality were directly correlated with D.F. scores, while respiration rates (on every day of the experiments) were inversely correlated. Since there were only two a. priori groups, both with equal numbers of replicates (n=9), the negative scores were statistically classified as "clean" while the positive scores were classified as "contaminated," with the magnitude of the score representing the degree of effect. Stations for which the standard error bars crossed the zero value line were intermediate, with some of the replicates being classified into each of the groups. Correct classification of cases belonging to the a. priori groups was high (95%), emphasizing the strong discrimination between the extreme conditions.

The basic geographic pattern of biological effects is apparent (Figures 2 and 4). The stations from Hampton Roads Harbor and along the main stem of the Elizabeth River produce few, if any, effects, so they have been grouped with the "clean" control conditions. On the other hand, the stations approaching the region previously identified as producing lethal effects contain sediments which produce significant biological responses Figures 2 and 4). In the bioassays of sediments taken from the vicinity of Station P, the biological effects diminish, but significant responses were again observed during the tests of

Figure 4: Discriminant function scores for biological data presented in Figure 3. Histograms represent mean values (vertical bars are two standard errors; n=3) arranged geographically by river mile. The relative correlations of the D.F. scores with the original variables are indicated. The different symbols in the histograms indicate the data included in the *a. priori* groups of the discriminant analysis.


RESP./OSMO. EFFECTS; MORTALITY
DISCRIMINANT SCORES (DF1)
SITE (R. Mi.)
-3
-1.5
0
1.5
3
CN
D NN
E 4
F 6
H 9
I 10
J 11
JK 11.5
LETHAL
EFFECTS
N 15
NO 15.5
O 16
OP 16.5
P 17
Q 18
R 19

dredged materials from the two upstream Stations, Q and R (Figures 2 and 4). Considering these patterns, three contiguous stations groups of roughly equal size were selected for the a. *priori* groupings in the discriminant models for the PNAH analyses: Stations D,E, and F representing clean, nontoxic sediments; Stations N,N/O and O as a group containing contaminated sediments which produce significant biological effects; and Stations Q,R, and S as an intermediate condition.

The elutriates from the suspended solid bioassays were analyzed for the 16 "priority pollutants" PNAH's. The results of these analyses and the abbreviations of the individual PNAH's are presented in Table 1. The geographic distribution of several commonly calculated composite PNAH categories are as follows (Figure 5): total PNAH's; carcinogenic PNAH's consisting of some of the stronger cancer-causing agents such as: Benzo(a)pyrene (BaP), Benzo-Fluoranthenes (BbFL, BkFL) and Indenopyrene (IP); and pyrosynthetic PNAH's consisting of Phenanthrene (Ph), Fluoranthene (FL), Pyrene (P), Benzo(a)Anthracene (BaA), Chrysene (Ch), (BbFL, BkFL), IP and Benzo(ghi)Perylene (BPR). Total PNAH's, carcinogenic PNAH's and pyrosynthetic PNAH's in elutriates were highest for Stations O,O/P,Q and R.

The elutriate data were analyzed by discriminant analysis, using the three a. *priori* groups selected as a result of the biological findings. The analysis produced two highly significant fractions ($p < 0.001$; Wilk's Lamba = 0.005 and $x^2=99.13$ with 22 d.f. for D.F. 1; Wilk's Lambda = 0.107 and $^2=42.52$ with

TABLE 1

Mean PNAH values (standard errors in parentheses; n=3) for elutriates used in 1982 suspended solid phase lethal and sublethal bioassays. Values are in µg/l. The indicated abbreviations are those used in text.

PNAH (Abbreviation)	Station (River Mile)													
	D (NN)	E (4)	F (6)	H (9)	I (10)	J (11)	J/K (11.5)	N (15)	N/O (15.5)	O (16)	O/P (16.5)	P (17)	Q (18)	R (19)
Naphthacene (N)	0.53 (0.27)	0	0	0	0	0	1.63 (1.63)	4.56 (0.76)	0	2.43 (2.43)	3.57 (1.84)	0.52 (0.45)	0.70 (0.70)	13.44 (4.32)
Acenaphthylene (Acy)	0	0	0	0	0	0	0	0.91 (0.91)	0	0	1.84 (0.27)	0.20 (0.20)	0.80 (0.42)	6.75 (1.67)
Acenaphthene (Acn)	0.34 (0.22)	0	0	0	0	0	2.12 (1.08)	0.78 (0.78)	0	0	2.17 (0.74)	0.25 (0.14)	0.57 (0.29)	1.53 (2.61)
Fluorene (F)	0	0	0	0	2.90 (2.90)	7.72 (1.51)	20.40 (10.41)	8.40 (3.16)	26.65 (6.19)	0	3.58 (1.31)	0	0	37.02 (14.33)
Phenanthrene (Ph)	0	0	0	0	0	0	6.54 (1.20)	4.33 (1.10)	0	3.99 (1.20)	9.84 (2.96)	0.16 (0.16)	3.51 (1.17)	28.48 (6.39)
Anthracene (A)	0.16 (0.16)	0	0	0	0	1.23 (1.23)	8.41 (2.44)	8.78 (3.19)	0	6.68 (0.85)	26.19 (6.72)	0.80 (0.49)	4.32 (2.21)	27.57 (0.81)
Pyrene (P)	0.14 (6.14)	0	0	0	0	0	9.08 (2.46)	6.95 (0.48)	0	52.68 (25.53)	164.47 (35.62)	3.84 (2.18)	16.52 (5.31)	29.79 (6.23)
Fluoranthene (Fl)	0.13 (0.13)	15.49 (2.14)	0	0	0	0	8.45 (1.69)	14.76 (5.99)	14.30 (6.17)	43.11 (19.63)	90.68 (20.21)	0.20 (0.20)	22.43 (7.63)	81.34 (26.78)
BenzoAnthracene (BaA)	3.00 (0.18)	0	0	0	0	0	8.20 (8.20)	11.44 (2.59)	3.96 (3.96)	24.29 (10.11)	74.70 (17.64)	5.31 (0.71)	13.19 (4.46)	38.80 (10.31)
Chrysene (Ch)	3.24 (2.55)	0	5.09 (5.09)	0	0	0	37.84 (10.61)	13.77 (2.16)	10.55 (5.33)	26.46 (16.10)	42.48 (8.41)	0	10.93 (3.75)	163.79 (16.49)
DiBenzoAnthracene (DBa)	0	0	0	0	0	0	7.18 (7.18)	0	0	20.18 (10.18)	31.80 (7.30)	0	16.32 (3.16)	9.27 (5.41)

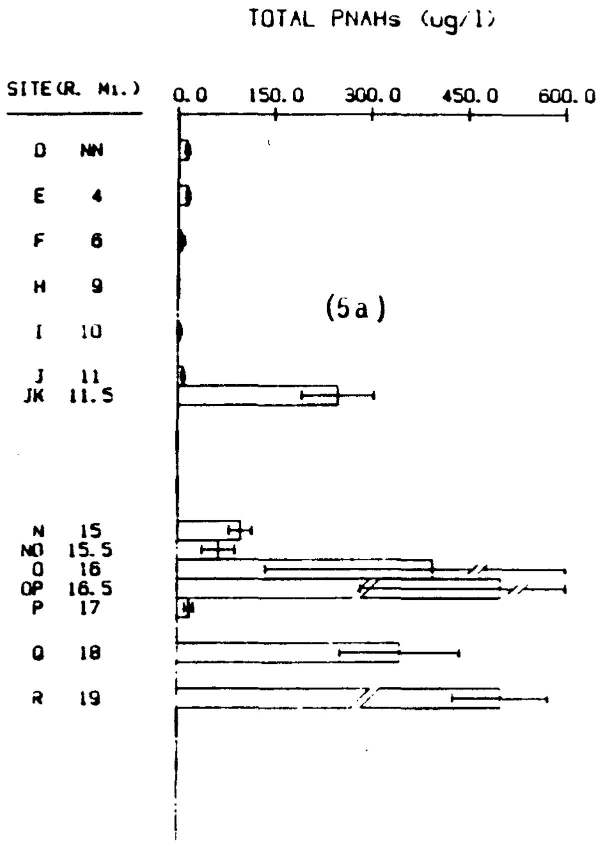
TABLE 1 (Continued)

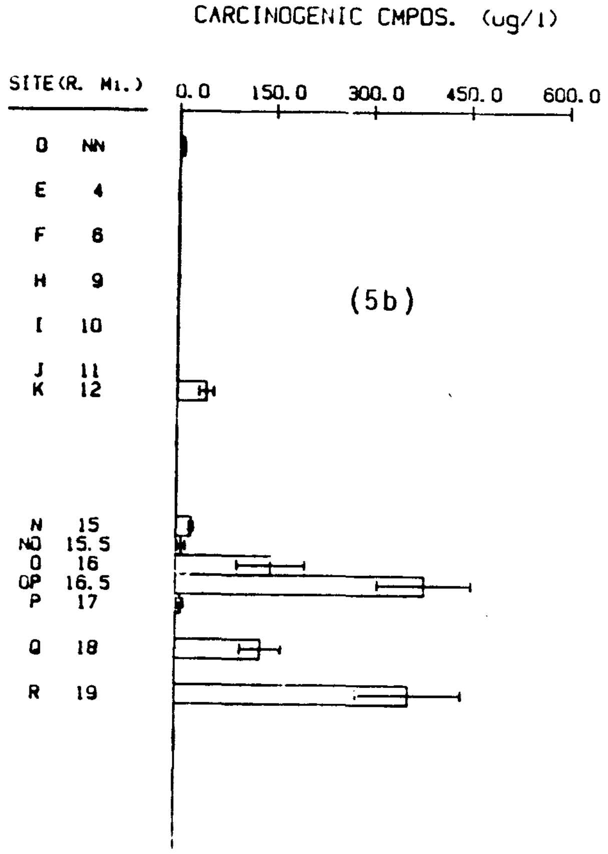
PNAH (Abbreviation)	Station (River Mile)													
	D (NN)	E (4)	F (6)	H (9)	I (10)	J (11)	J/K (11.5)	N (15)	N/O (15.5)	O (16)	O/P (16.5)	P (17)	Q (18)	R (19)
Benzo(ghi)Perylene (BPR)	0	0	0	0	0	0	93.83 (21.55)	0	0	69.38 (25.66)	256.88 (45.11)	0	123.78 (38.53)	376.90 (121.96)
Benzo(a)Pyrene (BaP)	0.77 (0.21)	0	0	0	0	0	19.82 (4.87)	8.29 (2.12)	0	22.97 (3.74)	73.30 (15.96)	4.55 (4.35)	21.26 (7.16)	54.86 (5.29)
Benzo(b)Fluoranthene (BbFl)	4.36 (0.71)	0	0	0	0	0	15.55 (4.42)	7.45 (0.21)	5.72 (3.18)	63.24 (25.79)	144.79 (28.54)	1.16 (0.96)	51.54 (10.29)	144.12 (41.79)
Benzo(k)Fluoranthene (BkFl)	1.32 (0.83)	0	0	0	0	0	1.41 (1.41)	7.06 (1.35)	2.95 (2.95)	46.00 (18.74)	112.88 (20.92)	0.48 (0.33)	39.43 (8.19)	67.00 (6.88)
Indenopyrene (IP)	0	0	0	0	0	0	8.14 (4.99)	0	0	14.33 (4.82)	51.37 (6.77)	0.90 (0.90)	19.07 (6.29)	93.04 (39.94)

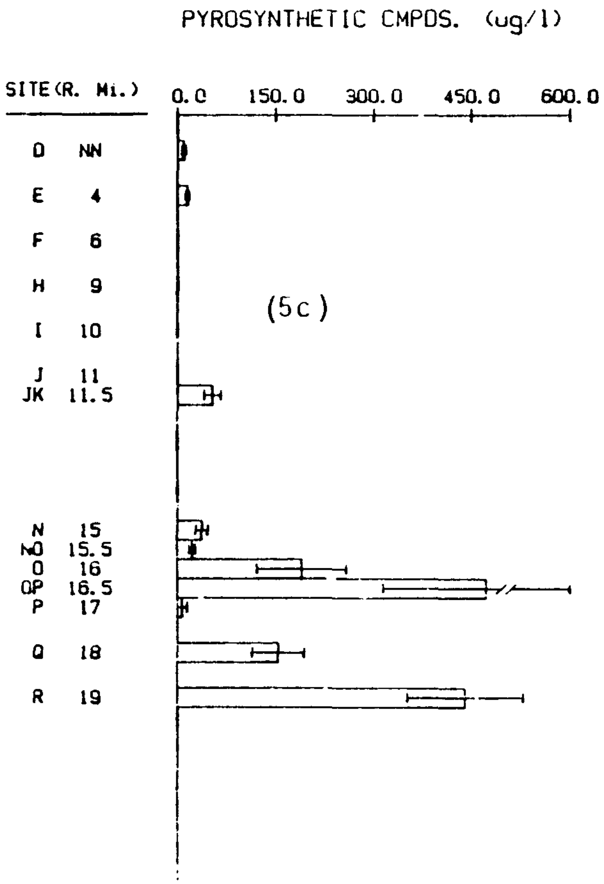
Note: 0 represents mean values below detection limits; see Appendix for detection limits of each compound.

Figure 5: Composite PNAH variables for sediments elutriates (means and standard errors arranged geographically; n=3):

a) total PNAH's (Station O standard error 258.60; Station O/P mean 1090.34±216.25; Station R mean 1183.18±73.25);
b) carcinogenic PNAH's;
c) pyrosynthetic PNAH's (Station O/P standard error 158.68).


TOTAL PNAHs (ug/l)
SITE (R. Mi.)
D NN
E 4
F 6
H 9
I 10
J 11
JK 11.5
N 15
NO 15.5
O 16
OP 16.5
P 17
Q 18
R 19
0.0
150.0
300.0
450.0
600.0
(5a)

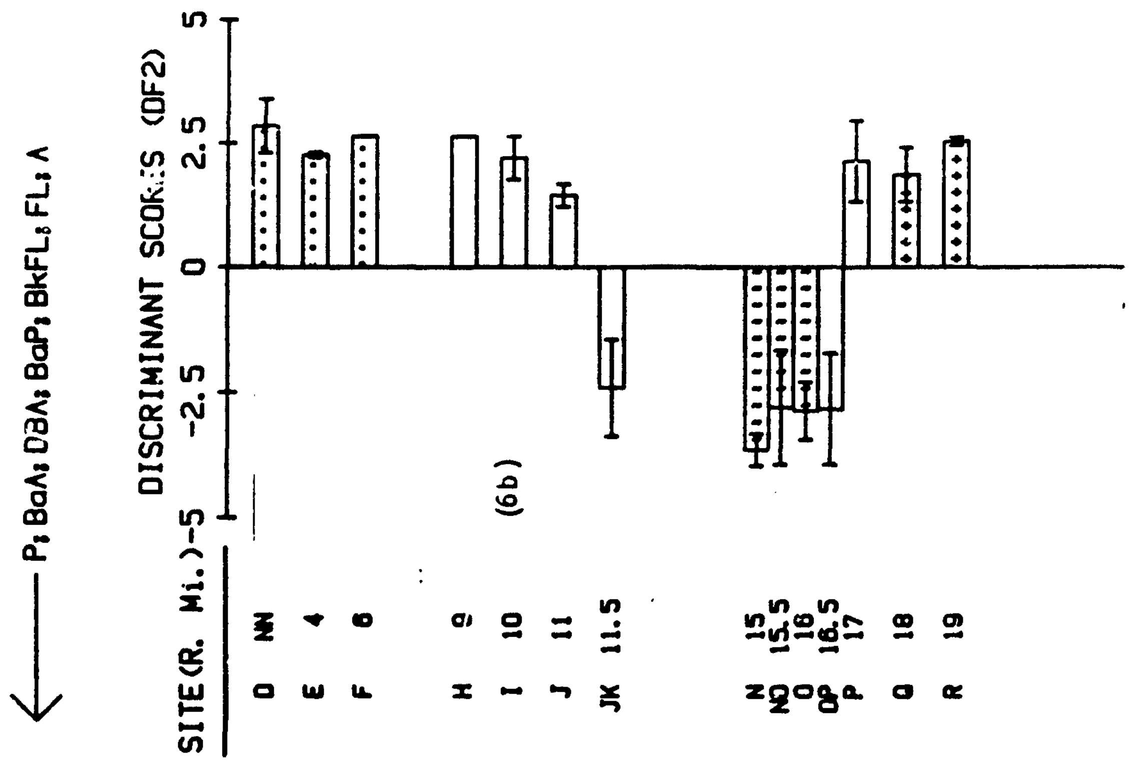

CARCINOGENIC CMPDS. (ug/l)
SITE (R. Mi.)
D NN
E 4
F 6
H 9
I 10
J 11
K 12
N 15
NO 15.5
O 16
OP 16.5
P 17
Q 18
R 19
0.0
150.0
300.0
450.0
600.0
(5b)


PYROSYNTHETIC CMPDS. (ug/l)
SITE (R. Mi.)
D NN
E 4
F 6
H 9
I 10
J 11
JK 11.5
N 15
NO 15.5
O 16
OP 16.5
P 17
Q 18
R 19
0.0
150.0
300.0
450.0
600.0
(5c)

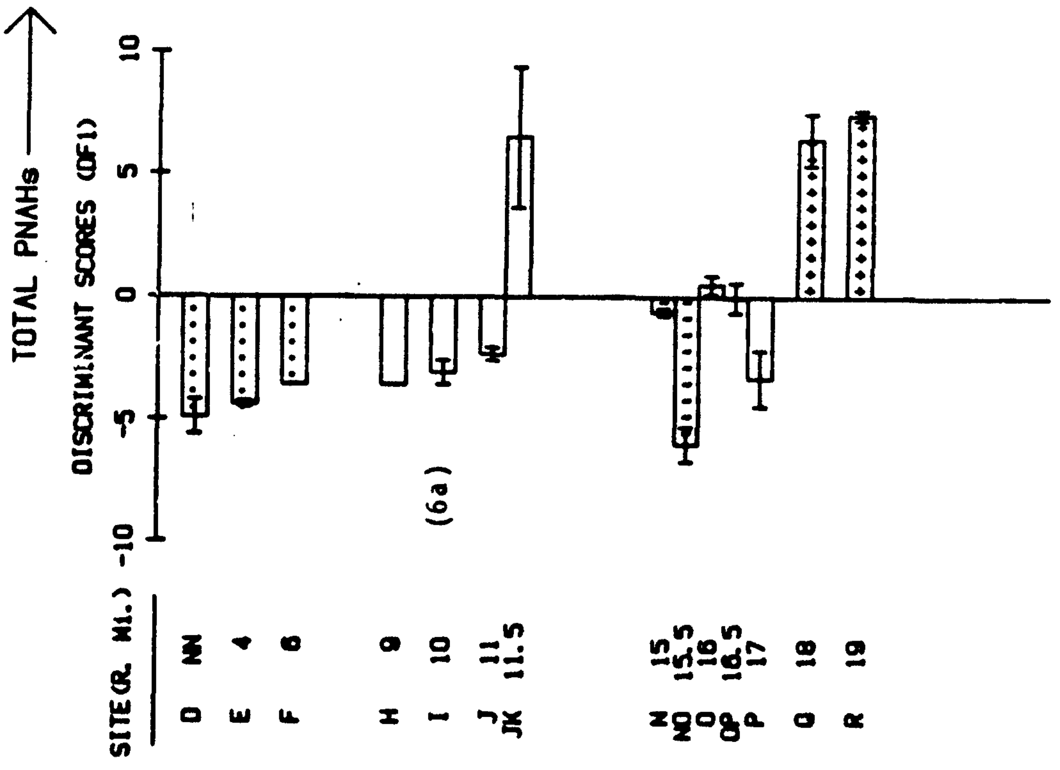
10 d.f. for D.F.2) and a high portion of the variance was explained by the group effects (canonical correlation = 0.97 and 0.95 for D.F. 1 and D.F. 2, respectively). The first discriminant function (D.F. 1) was directly correlated with all of the PNAH's except P, FL and BaA, while the second discriminant function (D.F. 2) was inversely correlated with a certain of the PNAH's there: (P, BaA, DBA, BaP, BkFL, FL and A) (Figure 6). Stations J/K, Q and R had the highest D.F. 1 scores, while Stations J/K, N,N/O, O and O/P exhibited the greatest association with the PNAH's which were significantly correlated (negatively) with the D.F. 2 scores. Thus, there appears to be a difference in the relative composition of PNAH's in elutriates from the mid-Southern Branch reach (Stations N-O/P) and from the upper reach (Q and R). Although total PNAH's are relatively high in the elutriates from both areas, the PNAH's in the suspended solid fractions from the N through O/P region were characterized by compounds which were loaded in the D.F. 2 scores, while the Q-R region had a greater variety of PNAH's in moderate to high concentrations.

In the early fall of 1982, a survey was conducted of the PNAH's of sediments in the Port. The results of the PNAH in sediment analysis are presented in Table 2. Patterns of the composite PNAH groupings for total PNAH's, carcinogenic PNAH's and pyrosynthetic PNAH's are presented in Figure 7. Total PNAH concentrations were greatest for sediments taken from Station M and values generally decreased both upstream and downstream (Figure 7a). However, the sample taken from the center of the

Figure 6: Discriminant function scores for PNAH in elutriates (same format as Figure 4):
a) D.F. 1 scores;
b) D.F. 2 scores.


P; BaA; DBA; BaP; BkFL; FL; A
DISCRIMINANT SCORES (DF2)
5
2.5
0
-2.5
-5
SITE (R. Mi.)
D NN
E 4
F 6
H 9
I 10
J 11
JK 11.5
N 15
NO 15.5
O 16
OP 16.5
P 17
Q 18
R 19

(6b)


TOTAL PNAHs
DISCRIMINANT SCORES (DF1)
10
5
0
-5
-10
SITE (R. Mi.)
D NN
E 4
F 6
H 9
I 10
J 11
JK 11.5
N 15
NO 15.5
O 16
OP 16.5
P 17
Q 18
R 19

(6a)

TABLE 2

Mean PNAH values (standard errors in parentheses; n=3 transect samples) for sediments from 1982 survey. Values are in µg/kg dry wt.

PNAH (Abbreviation)	Station (River Mile)															
	D (NN)	E (4)	F (6)	G (8)	H (9)	I (10)	J (11)	K (12)	L (13)	M (14)	N (15)	O (16)	P (17)	Q (18)	R (19)	S (20)
Napthalene (N)	0	0	0	0	821 (473)	0	1,564 (1,564)	0	309 (309)	588 (294)	466 (308)	953 (953)	417 (212)	0	0	0
Acenaphthylene (Acy)	0	0	0	0	0	0	0	0	230 (230)	2,700 (2,700)	0	0	0	0	0	0
Acenaphthene (Acn)	0	0	0	0	2,509 (2,074)	0	425 (425)	0	438 (438)	591 (297)	255 (255)	1,186 (896)	115 (115)	0	0	0
Fluorene (F)	0	0	0	0	220 (220)	0	596 (596)	0	326 (42)	24,530 (24,205)	234 (234)	866 (866)	115 (115)	465 (465)	0	0
Phenanthrene (Ph)	0	0	32 (32)	0	798 (644)	73 (73)	1,358 (1,168)	0	674 (16)	688 (355)	731 (270)	5,001 (2,145)	527 (77)	0	0	0
Anthracene (A)	0	0	0	0	341 (183)	0	3,413 (3,413)	0	244 (244)	27,200 (26,284)	680 (526)	2,171 (410)	307 (207)	0	171 (171)	189 (189)
Pyrene (P)	0	0	0	495 (87)	2,577 (1,497)	340 (34)	5,179 (3,639)	660 (274)	1,330 (455)	1,075 (565)	2,098 (402)	1,470 (1,470)	1,972 (220)	846 (142)	733 (80)	714 (640)
Fluoranthene (Fl)	0	2,021 (2,021)	65 (65)	0	671 (525)	81 (81)	2,156 (1,218)	804 (654)	1,286 (52)	1,267 (687)	1,809 (331)	1,884 (1,984)	1,747 (576)	345 (345)	753 (227)	1,061 (729)
BenzoAnthracene (BaA)	0	0	0	0	423 (423)	0	1,991 (1,799)	1,406 (1,406)	737 (136)	1,553 (937)	735 (382)	620 (620)	1,292 (237)	505 (257)	283 (143)	1,313 (724)
Chrysene (Ch)	0	789 (202)	81 (81)	0	1,362 (798)	409 (210)	13,900 (8,617)	413 (291)	1,729 (31)	1,515 (1,515)	3,160 (1,256)	1,120 (1,120)	2,090 (1,160)	1,731 (551)	1,745 (271)	1,574 (1,574)
Benzo(ghi) Perylene (BPR)	0	0	0	0	0	0	1,079 (1,079)	0	0	0	0	0	548 (548)	0	0	0

TABLE 2 (Continued)

PNAH (Abbreviation)	Station (River Mile) D (NN)	E (4)	F (6)	G (8)	H (9)	I (10)	J (11)	K (12)	L (13)	M (14)	N (15)	O (16)	P (17)	Q (18)	R (19)	S (20)
Benzo(a)Pyrene (BaP)	0	277 (277)	0	0	1,312 (305)	366 (366)	16,486 (9,898)	628 (628)	731 (731)	2,291 (1,396)	362 (362)	872 (872)	3,324 (1,887)	2,783 (933)	2,674 (1,337)	1,652 (1,652)
Benzo(b)Fluoranthene (BbFl)	0	302 (302)	0	0	0	0	2,974 (2,974)	1,962 (1,962)	1,220 (446)	1,274 (655)	11,340 (10,860) (16,455)	1,010 (512)	2,570 (847)	2,075 (1,206)	1,839 (327)	121 (121)
Benzo(k)Fluoranthene (BkFl)	0	0	0	0	0	0	1,430 (1,430)	0	352 (352)	252 (252)	7,698 (7,698)	570 (570)	962 (580)	263 (263)	211 (211)	0
Indenopyrene (IP)	0	0	0	0	0	0	372 (372)	0	0	0	0	0	0	0	0	0

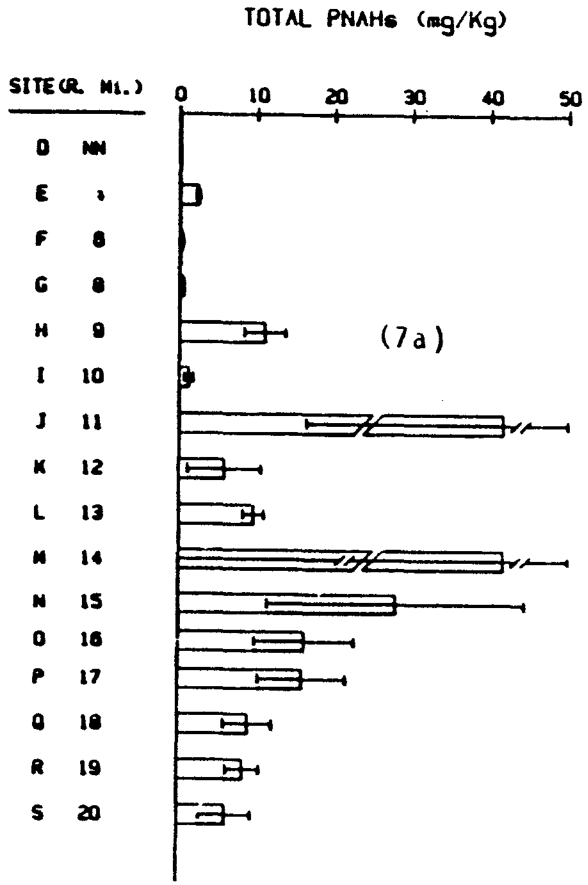
Note: 0 represents mean values below detection limits; see Appendix for detection limits of each compound.

Figure 7: Composite PNAH variables for sediments (means and standard errors arranged geographically; n=3 samples per transect):

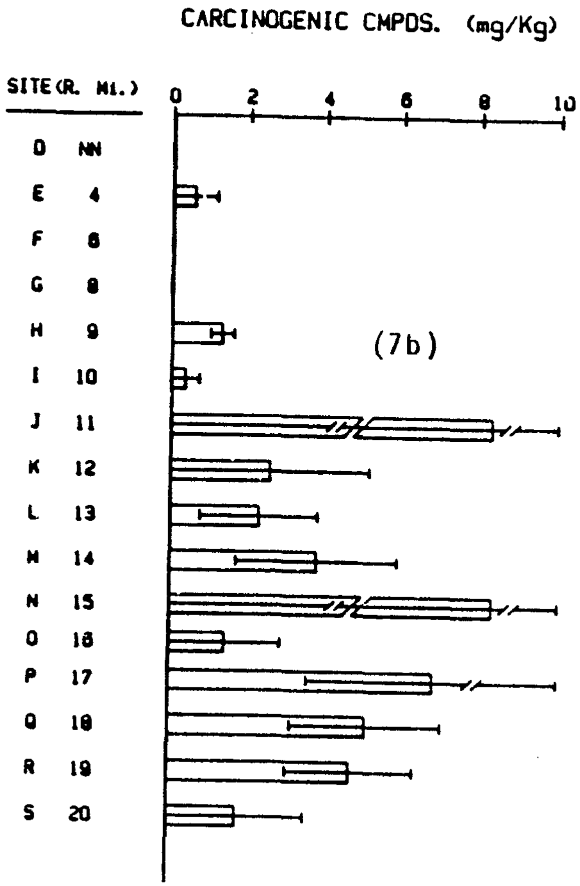
a) total PNAH's (Station J mean 52.93±25.26; Station M mean 65.53±43.77);

b) carcinogenic PNAH's (Station J mean 21.26±10.37; Station N mean 17.76±16.18; Station P standard error 3.26);

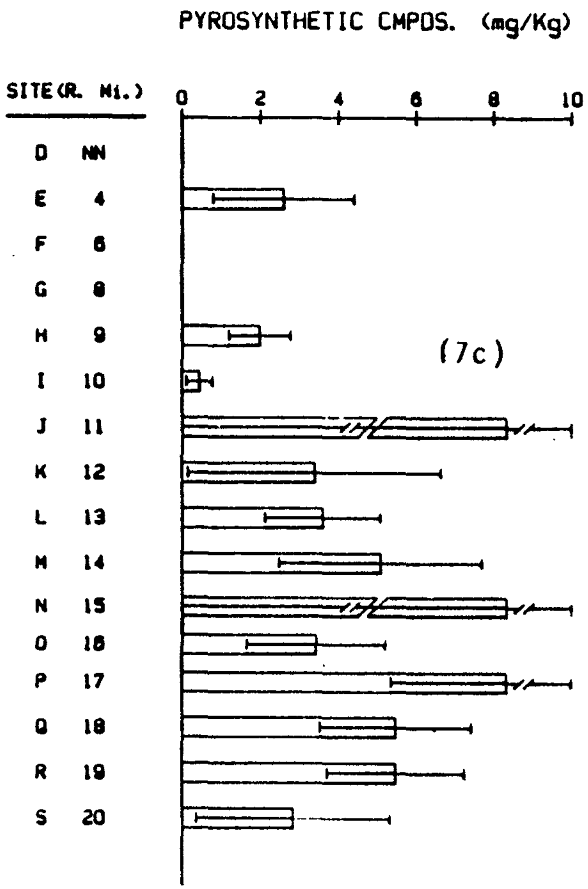
c) pyrosynthetic PNAH's (Standard J mean 23.42±11.10; Station N mean 19.57±16.12; Station P standard error 2.98).


TOTAL PNAHs (mg/Kg)
SITE (R. Mi.)
0
10
20
30
40
50
D NN
E 4
F 6
G 8
H 9
I 10
J 11
K 12
L 13
M 14
N 15
O 16
P 17
Q 18
R 19
S 20

(7a)


CARCINOGENIC CMPDS. (mg/Kg)
SITE (R. Mi.)
0
2
4
6
8
10
D NN
E 4
F 6
G 8
H 9
I 10
J 11
K 12
L 13
M 14
N 15
O 16
P 17
Q 18
R 19
S 20

(7b)

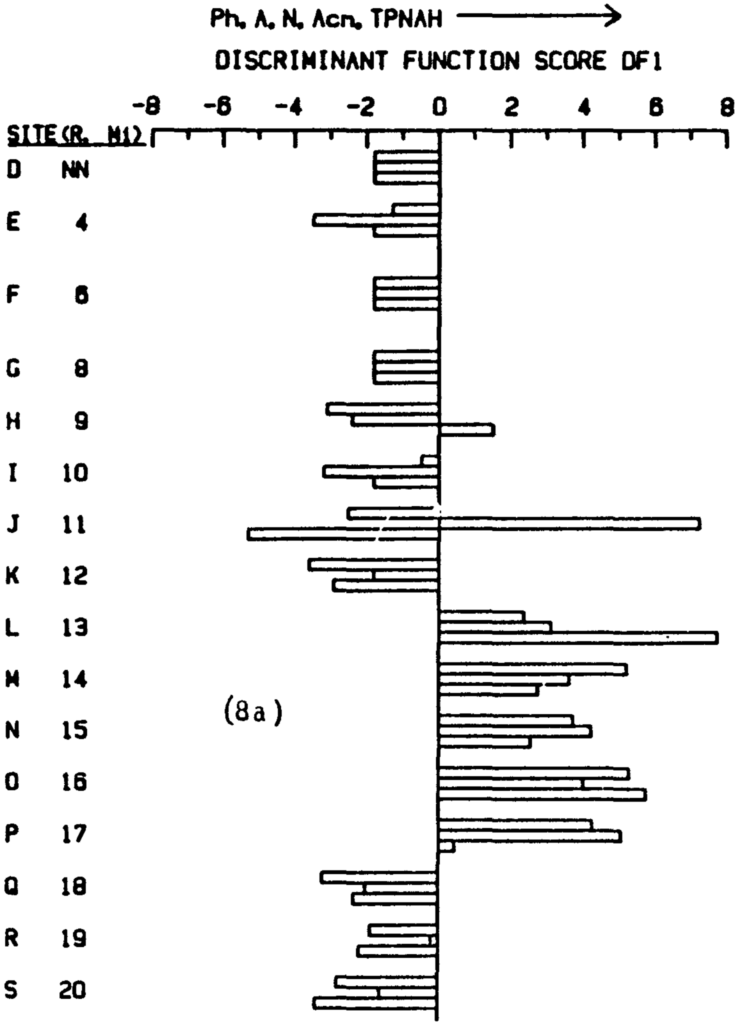

PYROSYNTHETIC CMPDS. (mg/Kg)
SITE (R. Mi.)
0
2
4
6
8
10
D NN
E 4
F 6
G 8
H 9
I 10
J 11
K 12
L 13
M 14
N 15
O 16
P 17
Q 18
R 19
S 20

(7c)

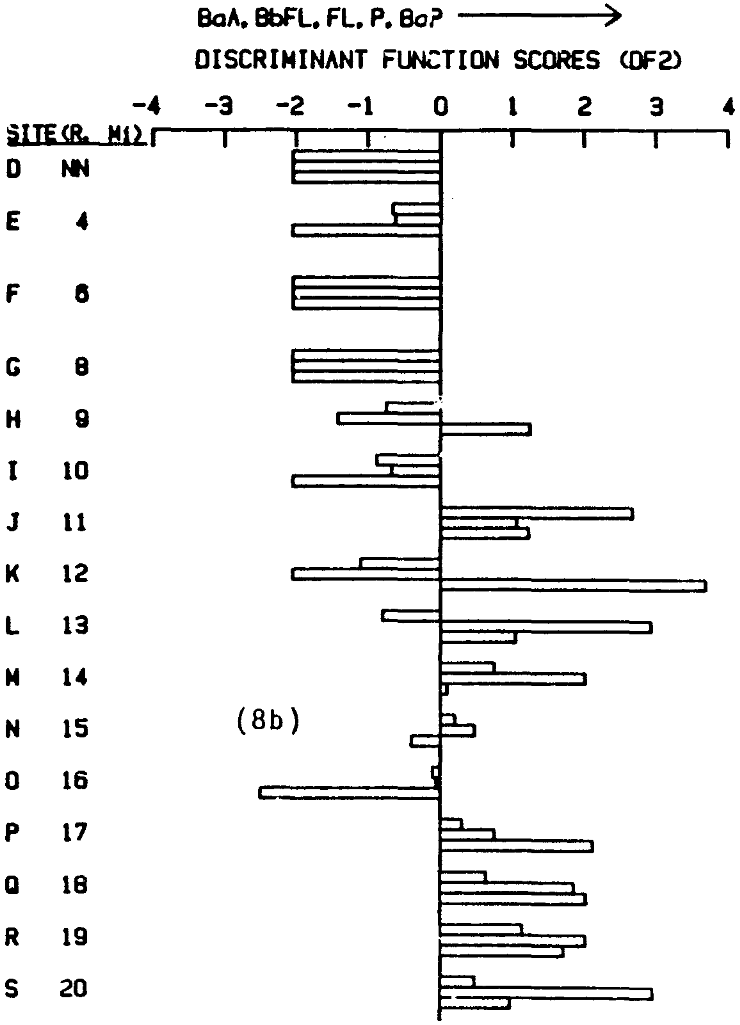
channel at Station J had high PNAH concentrations. The carcinogenic and pyrosynthetic compounds exhibited the same basic pattern, except that the high values were for Stations J and N (Figure 7b,c).

The sediment PNAH data were analyzed with a discriminant analysis employing the same a. priori groups as were employed in the elutriate data analysis. The discriminant functions were highly significant ($p < 0.001$; Wilk's Lambda = 0.038 and $x^2=67.28$ with 16 d.f. for D.F. 1; and Wilk's Lambda = 0.30 $x^2=20.93$ with 7 d.f. for D.F. 2). Although there was a considerable degree of intrastation variance among samples across the transects, a fairly high portion of the total variance was correlated with the group effects (canonical correlations = 0.95 and 0.88). The D.F. 1 scores were correlated with concentrations of 2- and 3- ring compounds such as Ph, A, N, Acn, and with total PNAH's. The D.F. 2 scores were correlated with 4- and 5- ring compounds: BaA, BbFL, FL, P, BaP. The geographic distribution of the discriminant scores are presented in Figure 8. Since the samples from each station were from a transect (i.e. not true replicates) the scores were plotted as triplets: data from the western side of the channel appears on top; the mid-channel sample data is plotted in the middle; and the eastern side of the channel is found on the bottom. Sediments taken from Stations L through P generally had higher concentrations of all PNAH's, particularly those in the lower molecular weight range (Figure 8a). Higher concentrations of PNAH's were noted for two additional samples: that taken in the middle of the channel in the Station J transect; and that taken on

Figure 8: Discriminant function scores for PNAH in sediments. Triplets of histogram bars represent scores for samples from western side, mid-channel, and eastern side of each transect:
a) D.F. 1 scores;
b) D.F. 2 scores.


Ph, A, N, Acn, TPNAH →
DISCRIMINANT FUNCTION SCORE DF1
-8
-6
-4
-2
0
2
4
6
8
SITE (R. Mi)
D NN
E 4
F 6
G 8
H 9
I 10
J 11
K 12
L 13
M 14
N 15
O 16
P 17
Q 18
R 19
S 20

(8a)


BaA, BbFL, FL, P, BaP →
DISCRIMINANT FUNCTION SCORES (DF2)
-4
-3
-2
-1
0
1
2
3
4
SITE (R. Mi)
D NN
E 4
F 6
G 8
H 9
I 10
J 11
K 12
L 13
M 14
N 15
O 16
P 17
Q 18
R 19
S 20

(8b)

the eastern side of the Station H transect. It should be noted that the latter sample location is directly off one of the largest coal piers in the world, so coal dust in the sediments is strongly suspected as the source for the elevated concentrations of PNAH in this sample.

The D.F. 2 scores exhibit a different geographic pattern (Figure 8b). The 4- and 5- ring compounds associated with D.F. 2 are observed most consistently for the region from Stations P through S and, more sporadically, for certain of the samples (particularly the mid-channel samples) from Stations J through M. The sample from the eastern side of the Station H transect also had a higher D.F. 2 score than the other samples from the main stem of the Elizabeth River.

DISCUSSION

PNAH's in Elutriates and Sediments

In reviewing the literature for previous elutriate chemistry studies of organic compounds, it becomes obvious that little work has been done on organic chemicals other than chlorinated hydrocarbons (e.g. PCB's and pesticides) or "generic" organics (e.g. "grease and oil," and "total hydrocarbons") (Fulk *et al.*, 1975; DiSalvo *et al.*, 1977; Hirsch *et al.*, 1978; Engler, 1980). No laboratory studies were found which specifically examined the concentrations of PNAH's in elutriates, but Boehm and Fiest (1982) evaluated the concentrations of PNAH's in the water column following open ocean dredged material disposal operations.

The PNAH concentration in the elutriates from most of the stations tested were quite low (low ppb, if detectable). However, the elutriates from Stations J/K,O,O/P,Q and R were quite high (i.e. mean values of total PNAH's from approximately 200-1200 ug/l). It is almost certain that the high levels of PNAH's in the elutriates were directly associated with the fine suspended sediments remaining in the water column following the one hour setting period prescribed by the *Implementation Manual* (EPA/COE, 1978) for the preparation of the suspended solid phase of dredged materials. Most of the heavier compounds which have characteristically low solubilities were found at concentrations greatly exceeding saturation levels (EPA, 1980; May 1980), indicating that they must have been sediment-bound.

Boehm and Fiest (1982) reported that PNAH's associated with fine suspended sediments were readily detectable (i.e. in the ug/l range) in the lower portion of the water column, even 2.5 hours after open ocean disposal of contaminated dredged materials in the New York Bight. Considering the great dilution and dissipation potential of open ocean conditions, the values found for the suspended solid fractions produced by the static, closed conditions of the elutriation procedured employed in the present study do not seem to be unreasonable for PNAH-contaminated sediments. In fact, if a conservative mixing zone dilution factor of 0.06 is employed (see EPA/COE, 1978; and Alden and Young, 1982 for the assumptions of the mixing model from which this factor was derived), the PNAH concentrations in the elutriates all fall within the same order of magnitude as those water column values reported by Boehm and Fiest (1982). Although the mixing zone dilution factor is for a 4 hour time period and the data for Boehm and Fiest (1982) are for a time period of 2.5 hours after disposal, the comparison suggests that the observed values are high, but not improbable.

The overall PNAH concentrations in sediments found during the 1982 survey exhibited the same sort of geographic pattern as seen for the results of the elutriate analyses. Sediments from stations in Hampton Roads Harbor and most of the main stem of the Elizabeth River had quite low concentrations. However, in the Southern Branch, the PNAH concentrations were quite high. A review of the literature indicates that the mean levels observed at the most contaminated stations during the present study are exceeded by only a very small percentage values reported for samples collected world-wide. The mean total PNAH for the most contaminated station in the present study (i.e. >60 ug/g dry wt. was exceeded only by concentrations in a single sample from the Charles River in Boston, MA (Hites et al., 1980), by the maximum values observed in the Severn and Usk estuaries in England (Thompson and Eglinton, 1978), and by two samples of contaminated dredged materials of unspecified origin (Boehm and Fiest, 1982). The concentrations of PNAH's in sediments collected from various marine and estuarine sediments world-wide were often orders of magnitude lower than the values observed in the present study (see LaFlamme and Hites, 1978; Hites et al., 1980; Pancirov et al., 1980; Murray et al., 1981; Poutanen et al., 1981; and Readman et al., 1982, among others). It must be noted that the term "total PNAH's" is not at all standardized and therefore, it generally represents only what the investigators define it to mean. In the present study, total PNAH's represents only the total of the 16 "priority pollutants," whereas many studies include all alkylated and parent PNAH's and their metabolites.

Studies conducted prior to this decade generally employed analytical techniques which could not resolve and isolate PNAH's effectively, so "total PNAH" values often included unconsolidated masses containing interfering compounds as well as the PNAH's. Unless the authors have specified the particular compounds considered in the total (such as Hites et al., 1980), one might assume that most of the values in the literature represent far more compounds than the ones considered in the present study. Therefore, the high concentrations of the PNAH's observed in the present study become more pronounced. Qualitative estimates based upon GC/MS analyses suggest that the PNAH's considered in the present study may represent only 20% of the total amount of all aromatics observed in certain of the more contaminated sediments.

Not only does the magnitude of the PNAH's in sediments make the findings of this study somewhat unique, but the relative abundance of the individual PNAH's was somewhat unusual as well. Hites et al., (1980) report that the relative distribution of PNAH's in sediment samples collected world-wide almost always exhibit the same pattern: fluoranthenes and pyrenes were in the greatest concentrations, followed by benzo-fluoranthenes (BFL) and benzopyrenes (BP), followed by chrysene and benzoanthracenes (BA), while phenanthrenes and anthracenes were in the lowest concentrations. These investigators interpret this pattern to be indicative of a combustion source and atmospheric transport of the PNAH's. Lake et al., (1979) reported nearly the same pattern in numerous samples from Rhode Island except that the relative abundance of the first two groups were reversed (i.e. BFL & BP > FL & P > C & BA > Ph & A). These investigators also attributed the distribution of PNAH's in the sediments to a combustion source. Quite possibly the slight difference in the patterns noted between the two studies can be attributed to the fact that Lake et al., (1979) noted that the dominant fuel source of their study area is petroleum, while LaFlamme and Hites (1978) report that much of the data later reported by Hites et al., (1980) were collected from highly urbanized areas of New England where coal combustion is predominant. Whatever the case, the relative PNAH observed during the present study do not present such a uniform pattern, indicating that there are probably numerous potential sources in the Port.

In the Hampton Roads Harbor and most of the main stem stations, all PNAH's are relatively low. The PNAH's that are sporadically detected tend to be those that have been identified as the principal combustion product parent compounds (FL, P, BFL, BaP). Two exceptions were obvious: the sample taken from the Station H transect in the vicinity of the coal piers; and the mid-channel sample from Station J. It is speculated that the Station H sample was contaminated by coal dust since many of the same PNAH's observed to predominate in this sample have been reported by John _et_ _al_., (1979) as the principal PNAH in sediments from the Severn estuary in a coal mining region (e.g. P/FL, P/A, C, BaP). The Station J sample had many of the same characteristics, except that BaP and C clearly dominated the PNAH's, so the source of this mid-channel accumulation is open to speculation.

In the region of maximum PNAH concentration (Station M), the lower molecular weight (2- and 3- ring) compounds were clearly dominant. This location represents the most heavily industrialized zone on the Southern Branch of the Elizabeth River. Shipbuilding and repair operations and the associated shipping/anchorage activities are the most likely sources of

PNAH's in the area. Oils, fuels, paints and solvents from ship bilges, fueling facilities and dry docks,as well as greases, soot and spent oils cleaned from the ships are potential sources of PNAH's observed in the region. Banks (1978) reported that the waters in this region contained high concentrations of single ring aromatics which he attributed to oils, solvents, and paints from the shipyards.

Stations N and O were located in the vicinity of two creosote plants. The creosote from past spills and runoff from storage yards at these plants are the most likely source of PNAH's in this region. The relative abundance of PNAH's in the sediments of the region were similar to those reported for creosote contaminated estuarine (Lake et al., 1979) and riverine (Black, 1982) sediments: high levels of Ph & A, followed by P & FL, BaP & BFL, and C & BaA.

Proceeding southward from Station P, the composition of PNAH's in the sediments begin to change and the overall levels decline. Higher molecular weight PNAH's such as BaP and BFL were found to be predominate, followed by C, P, FL, and BaA. At Stations Q, R and S, the 2- and 3- ring compounds virtually disappeared. This pattern reflects a high temperature combustion source such as was suggested by the Rhode Island studies of Lake et al., (1979). There is a large power plant in this region, possibly a major source of the PNAH's. EPA, (1979) report that power plants are a major emission source of BaP, P and FL. Of course, two major highways, Military Highway and I-64 cross the

Southern Branch of the Elizabeth River in this region. Bridges and street runoff have been identified as potential sources of many of these same PNAH's (John et al., 1979; Wakeham et al., 1980), so the identity of the prinicipal source of the 4- and 5-ring PNAH's characteristic of the region is open to speculation.

One major point that should be made concerning the distribution of PNAH's in the Port involves the effects of maintenance dredging on the absolute concentrations found in the sediments. Results of lethal bioassays have suggested that maintenance dredging in the region between Stations N and P conducted during the fall of 1981 drastically reduced the toxicity of the sediments (Alden and Young, 1984). Subsidiary chemical analyses associated with these experiments strongly indicate that PNAH contamination in this region may have been reduced by the dredging operations as well.

During the summer of 1981, a series of solid phase bioassays were conducted to determine the potential bioaccumulation of Kepone and other chlorinated hydrocarbons from sediments collected throughout the Port. The test organisms exposed to sediments taken from Station O exhibited high mortalities during the first few days of the experiment. Therefore, the sediments were analyzed by gas chromatography and high pressure liquid chromatography in an attempt to determine the toxin(s) responsible. Subsequent bioassays in 1983 also involved the chemical analysis of sediments composited from each of the aquaria prior to the experiments. The data from these analyses are presented in Table 3, along with the 1982 survey data from the same station. The pre-dredging 1981 concentrations of PNAH's in sediments are phenomenally high, greater than any values that could be found in the published literature for estuarine sediments. The sediments collected at this time had a distinct petroleum odor and lumps of creosote could be found in the sediments prior to homogenization. However, during the 1982 sediments survey which was conducted nearly one year following dredging, PNAH concentrations had decreased to more moderate levels.

The 1983 sediment data were collected nearly 18 months following dredging, and PNAH concentrations appeared to be rising again. It is believed that slumping of contaminated sediments from the sides of the channels and/or new input of contamination from the sources of the region are responsible for this increase. The return to previous concentrations may or may not occur, depending upon the magnitude of the current sources. The rate of increase of most PNAH's would be expected to be somewhat slow since the input and transport of most of the principal compounds found in the region is likely controlled by the movement of suspended particulate loads in the estuary (see Readman et al., 1982 for a detailed examination of the dynamics of PNAH's in estuaries).

Biological Effects

Strong geographic patterns of biological effects were noted in the toxicity data. Stations in Hampton Roads Harbor and the

TABLE 3

Comparison of sediment PNAH values from Station 0 in 1981, 1982 and 1983. Values are means (standard errors in parentheses; n=3 except for composite 1981 samples) in μg/kg dry wt.

PNAH	1981*	1982**	1983***
N	786 (786)	953 (953)	743
Acy	676 (676)	0	432
Acn	39,898 (1,135)	1,186 (896)	1,184
F	29,251 (6,128)	866 (866)	3,602
Ph	83,429 (4,926)	5,001 (2,145)	19,290
A	46,845 (5,592)	2,177 (410)	2,150
P	202,175 (15,570)	1,470 (1,470)	6,120
Fl	271,717 (2,784)	1,984 (1,984)	11,734
BaA	21,983 (15,930)	620 (620)	3,516
Ch	25,668 (6,576)	1,120 (1,120)	4,700
BPR	0	0	884
BaP	21,674 (2,417)	872 (872)	1,834
BbFl	48,325 (10,540)	0	6,190
BkFl	32,035 (12,499)	570 (570)	5,024
IP	0	0	534
<PNAH	818,540 (55,124)	17,721 (6,390)	67,938

NOTES:

* Sediment samples taken from 1981 Kepone bioaccumulation experiments.

** PNAH survey (this study).

*** Composite sediment sample from 1983 solid phase bioassays (Alden *et al*., 1984).

main stem of the Elizabeth River contained sediments which produced little or no biological effects. Elevated mortalities and significant sublethal effects were found for test organisms exposed to fractions taken from Stations J/K-O, despite the fact that the sublethal experiments were conducted only 6 months after the dredging of region between N and P. Thus, residual sublethal toxic effects were observed for sediments taken from Stations N-O, even though a major portion of the contamination may have been removed by the dredging operations. In fact, it was the unexpectedly low levels of mortalities observed in the 1982 bioassays and the subsequent PNAH analyses that lead to an extensive search of the dredging records to confirm the cause of the apparent decrease in toxicity in this region.

It is felt that once the pollutants reach a post-dredging equilibrium, the region between Stations N and O may have a toxic potential equal to, or greater than the area between Stations K and M which has been identified previously as containing contaminated sediments which are unacceptable for ocean disposal (Alden et al., 1981; Alden and Young, 1982). The area between Stations Q and R also contained sediments which appeared to cause moderate, but significant biological responses in test populations.

Although no direct cause and effect relationship can be drawn between the PNAH and the apparent toxicity of sediment fractions, there appears to be strong circumstantial evidence to indicate that there is an association between PNAH's and/or related organic contaminants and the lethal and sublethal effects observed. Geographic groupings shown to be statistically distinct with respect to the biological data proved to be unique in chemical characteristics as well. Regions of the Port which produced few biological effects had low levels of PNAH contamination. Even the toxicological classification of Station H sediments with the "acceptable" group makes sense because the high levels of PNAH's observed for the single sample from this area are throught to be due to coal dust which is believed to be biologically innocuous and fairly chemically inert (John et al., 1979).

The second geographic group included the mid to lower reaches of the Southern Branch of the Elizabeth River (Stations K and O) which contained sediments which produced significant lethal and sublethal effects and were shown to be heavily contaminated with PNAH's. Sediments from Station M exhibited the greatest degree of toxicity in suspended solid bioassays and was characterized by large concentrations of 2- and 3- ring PNAH's. Anderson (1979) reviewed the literature on the biological effects of petroleum products and concluded that the 2- and 3- ring compounds were the most toxic of the PNAH's. These low molecular weight PNAH's are the most soluble in water, a characteristic believed to be directly responsible for their relative toxicity to aquatic organisms, since the heavier PNAH's are more tightly "bound" to the sediments. Alden et al., (1981) and Alden and Young (1982) speculated that the toxins responsible for the lethality of Station M sediments were associated with the elutriates which were, to a degree, flushed out of the solid phase aquarium by the water replacement schedule. The 2- and 3- ring PNAH's would fit these characteristics. Additional evidence is found in the fact that the liquid phase extracts of Station M sediments produced pronounced respiratory depression in test shrimp populations (Alden et al., 1981). Thus, the toxins responsible for the sublethal effects must have had a moderate degree of solubility to appear in the dissolved phase. Anderson (1979) reported an identical depression in the respiration rates of *P. pugio* exposed to the water-soluble fraction of No. 2 fuel oil.

Stations N and O in the "contaminated" geographic grouping also displayed high levels of PNAH's in the sediments. In addition to significant acute toxic effects, the PNAH's characteristic of this region may also create a serious long-term impact on biota, since carcinogens such as BaP and BFL were found in high concentrations. This concern is particularly relevant for future dredging/disposal operations when one considers the high pre-dredging levels of PNAH's. Also, there is an apparent "re-invasion" of these pollutants into the area since the time of the 1982 sediment survey being discussed.

The third geographic group (Stations Q-S) apparently contains sediments of a unique chemical character and producing a different sort of biological response in test populations. The levels of PNAH's in the sediments are more moderate than those found in the second grouping. The relative distribution of the PNAH's favors the 4- and 5- ring compounds characteristic of a high temperature combustion source. However, these higher molecular weight PNAH's are not nearly as toxic as the 2- and 3- ring compounds (Anderson, 1979) so mortalities of test populations exposed to the suspended solid and solid fractions of sediments from these stations are rather low.

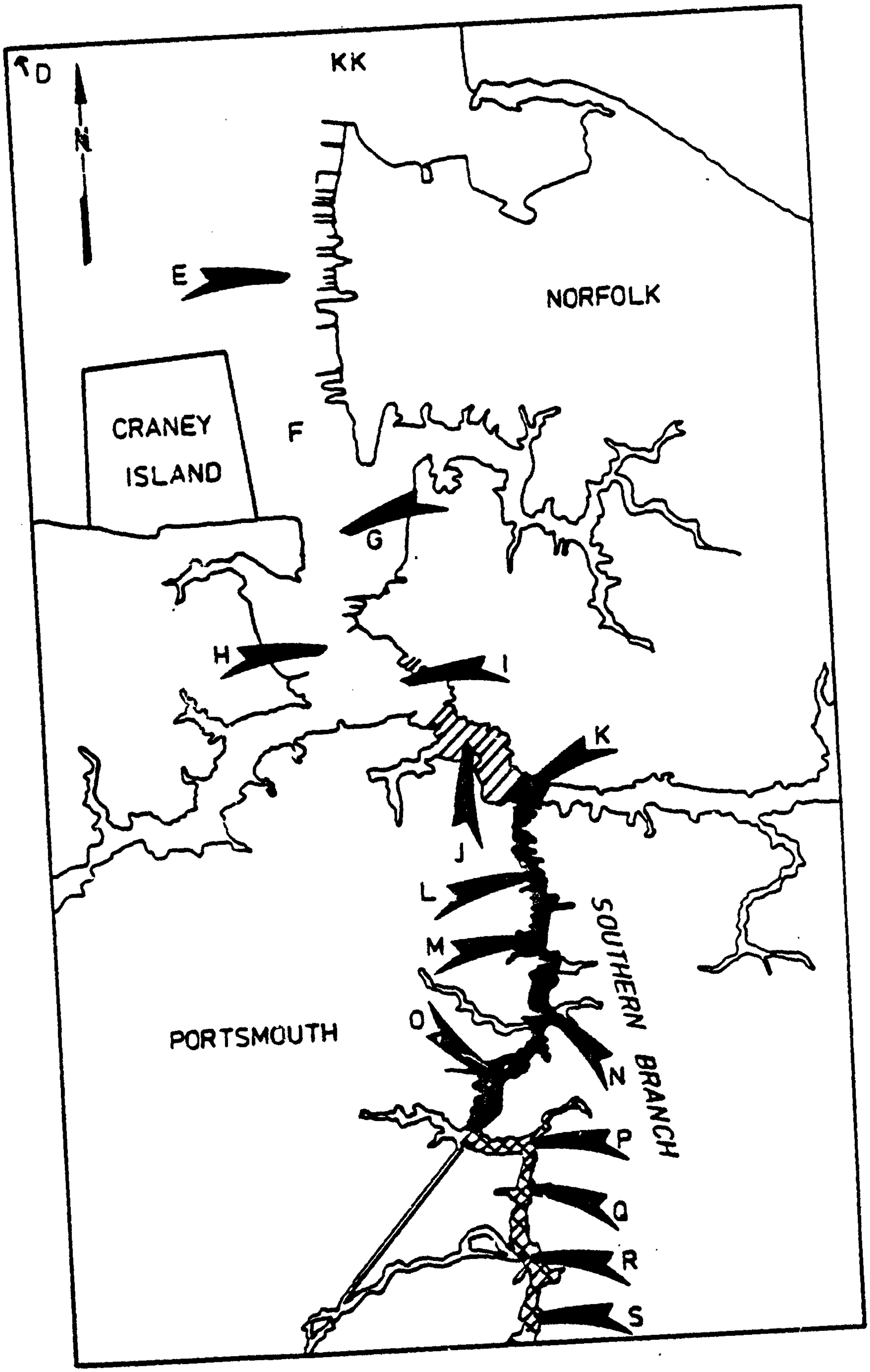
Significant osmoregulation and, to a lesser degree, respiration effects were observed during the tests of the sediments from this region. The moderate PNAH load of the sediments may be responsible for subtle sublethal effects in the test populations. As previously pointed out (Alden et al., 1984), sediments from this "intermediate" group should be biologically and chemically assessed more thoroughly before they can be considered completely "safe" for ocean disposal. Multiple-species microcosms and bioaccumulation/mutagenic experiments should focus upon the biological availability of the predominant, carcinogenic PNAH's of the region.

A schematic map of the study area indicating the consensus findings of the biological and chemical statistical models is presented in Figure 9. The regions without shading are considered acceptable for ocean disposal with respect to biological effects and PNAH contamination. The heavily shaded region represents sediments which should not be considered for ocean disposal. The single cross-hatched region is a transition zone between the acceptable and unacceptable for which biological effects and/or PNAH concentrations are sporadically found. This region may also be seen to be acceptable for ocean disposal, when one considers the dilution effect of mixing the more "contaminated" sediments with "clean" sediments during dredging and the great dissipation potential at the disposal site. Especially relevant to this point is the fact the sediments in this region meet the quality criteria established by the Federal Register (January 11, 1977) for ocean disposal.

The double cross-hatched region is an "intermediate" group in terms of biological effects and PNAH concentrations. It is somewhat questionable whether these sediments should be considered acceptable for ocean disposal. It is believed more intensive biological and chemical investigations should be made into their unique characteristics.

The summary sediment quality map presented in Figure 9 could have been developed from either the biological or the PNAH data sets. The fact that the findings coincide suggests an association. Although other industrial pollutants may be responsible for the sediment toxicity, those which have been examined to date do not exhibit the same distributional pattern (e.g. heavy metals), if they are detectable at all (e.g. chlorinated hydrocarbons) (Alden et al., 1981, 1982).

Figure 9: Consensus map of study area indicating overall geographic patterns of sediment quality. Unshaded areas represent sediments judged acceptable for ocean disposal; heavily shaded areas are believed to be contaminated and unacceptable for ocean disposal; single cross-hatching represents transition areas; the double cross-hatched region is an "intermediate" geographic group which contain sediments of questionable quality.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The multivariate statistical approach to hypothesis-testing and classification of samples (i.e. "mapping") appears to hold great promise for environmental studies in general and dredged material assessment studies in particular. Future studies involving more intensively defined groupings may allow classification of sediments by pollutant source. In other words, once a sediment sample has been chemically "fingerprinted" by analytical techniques, it could be classified according to a source in a statistically based, objective manner. Such a source classification may provide the first step in the effective pollution control and resource management.

SUMMARY AND CONCLUSIONS

The data from a series of lethal and sublethal toxicity tests were analyzed by discriminant analysis to statistically classify stations into "clean" and "contaminated" groupings. A clear geographic pattern of stations resulted from the analysis. Stations containing sediments producing little or no biological effects on test populations were found in Hampton Roads Harbor and the main stem of the Elizabeth River. As the Southern Branch is approached, biological effects increase and the sediments from Stations K-O produce significant impacts. The region of the Southern Branch in the vicinity of Station P represents a transitional area where biological impacts moderate but remain statistically significant. In this third geographic area (Stations P-S), the lethality of the sediment fractions are moderately low, but sublethal effects (particularly hyporegulation capacity) are significant.

The three groupings defined in the analysis of the biological data were employed in the analysis of PNAH data. These _a. priori_ groups were employed to evaluate the hypothesis that geographic patterns defined for sediment toxicity may be reflected in the distribution of PNAH's. The three _a. priori_ geographic groups were shown to contain sediments which had unique PNAH characteristics in both the suspended solid and solid fractions. The "clean" group of stations which produced few biological effects generally contained sediments with low levels of PNAH's.

The "contaminanted" group which produced significant biological effects contained sediments with extremely high levels of PNAH's. The third georgraphic group of stations from the upper reach of the Southern Branch produced moderate biological responses and contained intermediate levels of PNAH's in the sediments.

In addition to differences in overall magnitude of PNAH load, the statistical analysis clearly indicated different characteristic patterns of individual PNAH's in the various geographic regions, probably associated with multiple sources of input. The few samples in the first group which contained elevated levels of PNAH's were shown to have characteristics indicative of contamination from local sources such as coal piers. The innocuous nature of coal dust toxicologically explains why these "contaminated" samples were statistically classified as being "clean" in the biological effects analysis. The "contaminated" stations in the Southern Branch had relatively high concentrations of lower molecular weight PNAH's which exhibit the greatest toxicity. Even within this region, the discriminant function scores indicated that there may be differences in region contaminant sources. The PNAH's in sediments from Stations N and O were indicative of a creosote source, while Station M contained sediments which suggested that oils and solvents from the shipyards may represent a major input. The third "intermediate" geographic region contained sediments with a PNAH distribution which indicated a high temperature combustion source. The PNAH's from this region had a relatively low proportion of the more toxic

2- and 3- ring compounds. The power plant located in this region is the most probable source. However, input from two major highways crossing the Southern Branch in this region represent another possible source.

The consensus "map" of sediment quality suggests that sediments from Hampton Roads Harbor and the main stem of the Elizabeth River would be acceptable for ocean disposal. The sediments from the lower reaches of the Southern Branch (Stations K through O) probably should not be considered for ocean disposal. The acceptability of sediments from the "intermediate" group of Stations from P through S in the upper reach of the Southern Branch is open to debate. Further studies may demonstrate whether the moderately low biological effects and the bioaccumulation potential of PNAH's known to be in the sediments are of ecological significance.

The multivariate statistical approach to the evaluation of geographic patterns of sediment contamination has been shown to provide an effective, objective means of classifying data. The statistical "fingerprinting" of both biological and PNAH data produced a similar geographic map of sediment quality. Therefore, even though a direct cause and effect relationship between PNAH contamination and biological effects cannot be proven, the coincidence of the patterns strongly suggests a relationship. Perhaps more intensive investigations in the future can gather data on steady state sediments which are specifically indicative of known sources to classify sediments statistically by most probable source(s) (e.g. creosote, petroleum, combustion, coal dust, etc.) and/or by ecological characteristic (e.g. toxic, carcinogenic, mutagenic, inert, etc.).

One final observation made concerns the effect of maintenance dredging on the characteristics of the sediments. Both the toxicological and the PNAH data indicated a change in the sediment quality between Stations N and P between the summer of 1981 and the spring of 1982. Toxicity of the sediments diminished during this period and PNAH's in sediments decreased in concentration by nearly two orders of magnitude. The level of toxicity and the concentration of PNAH's appeared to have increased in the 1983 experiments. This indicates a "re-invasion" of contamination into the area, probably via suspended particulates. PNAH concentrations from the pre-dredging period were higher than any levels which could be found in the published literature for marine or estuarine sediments. The post-dredging return of contamination should be viewed as substantiation for the recommendations concerning a ban on ocean disposal of sediments from this region.

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