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Recommended Citation

Smtih, C. L., deFur, P. O., & Huggett, R. J. (1985) Richmond Crater James River Water Quality Management Program, final report 1984-85 and summary, toxic organics in sediments : a final report to Richmond Regional Planning District. Virginia Institute of Marine Science, William & Mary.
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Richmond Crater James River Water Quality Management Program Final Report 1984-85 and Summary - Toxic Organics in Sediments

A Final Report

To

Richmond Regional Planning District

By

C. L. Smith
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R. J. Huggett

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July, 1985

Richmond Crater James River Water Quality Management Program

Final Report 1984-85 and Summary - Toxic Organics in Sediments

by

C. L. Smith, P. O. deFur and R. J. Huggett

Introduction

The following report contains detailed results of analyses of sediment grabs and cores from the James and Appomattox rivers and some nearby locations for a spectrum of organic toxics. Some data has been previously reported in interim progress reports, but will be included for completeness. A study of variability of replicate samples taken at a single station (JR4), not included in the proposal, presents possible limitations of interpretation of temporal and station to station results. Finally, a comprehensive summary of toxic organics in the sediments of the James River and certain tributaries over a two-year period will be presented.

Procedures for collection, preservation, extraction and the analytical methodology have been presented in the previous annual report (1) and will not be repeated here.

Results

Sediment grabs and cores from locations listed in Table 1, and depicted in Figure 1 were collected in September, 1984 and April, 1985. Six sediment grabs at Station JR4, a site at the edge of the channel, were taken in April, 1985. All samples were at the same nominal location, but because of the steep sloping bottom, some replicates were from shallow water, and others from deeper water. Considerable variation in sediment composition was observed as well. Sediment cores from Stations JR6 and JR9 were

Table 1

Station	Latitude	Longitude	Description
JR 1	37°39′57"	77°53′21"	Route 522 Bridge (Goochland County)
JR 2	37°31′37"	77°26′05"	Fall line (Mayos Bridge)
JR 4	37°29′26"	77°25′20"	Buoy 168 (below Goode Creek)
JR 6	37°26′09"	77°25′42"	Buoy 165 (at Falling Creek)
JR 7	37°25′56"	77°25′44"	Buoy 163 (below Falling Creek)
JR 8	37°24′14"	77°23′33"	Buoy 157 (below Kingsland Creek)
JR 9	37°23′10"	77°23′02"	Buoy 155 (below Proctors Creek)
JR 10	37°21′31"	77°18′08"	Buoy 137 (Curles Neck)
JR 11	37°19′20"	77°16′35"	Buoy 120 (opposite Appomattox mouth)
JR 12	37°19′05"	77°16′33"	City Point
JR 13	37°18′39"	77°13′57"	Buoy 107 (off Bailey Bay)
JR 19	37°12′51"	76°48′03"	Swann's Point (below Chickahominy)
AR 21	37°14′59"	77°22′45"	West channel at coveyor crossing
AR 23A	37°14′11"	77°24′14"	Route 600 bridge above Petersburg
JR BC	37°17′43"	77°14′58"	Mouth of Bailey's Creek
JR Almond	37°30′12"	77°25′08"	Mouth of Almond Creek

Figure 1

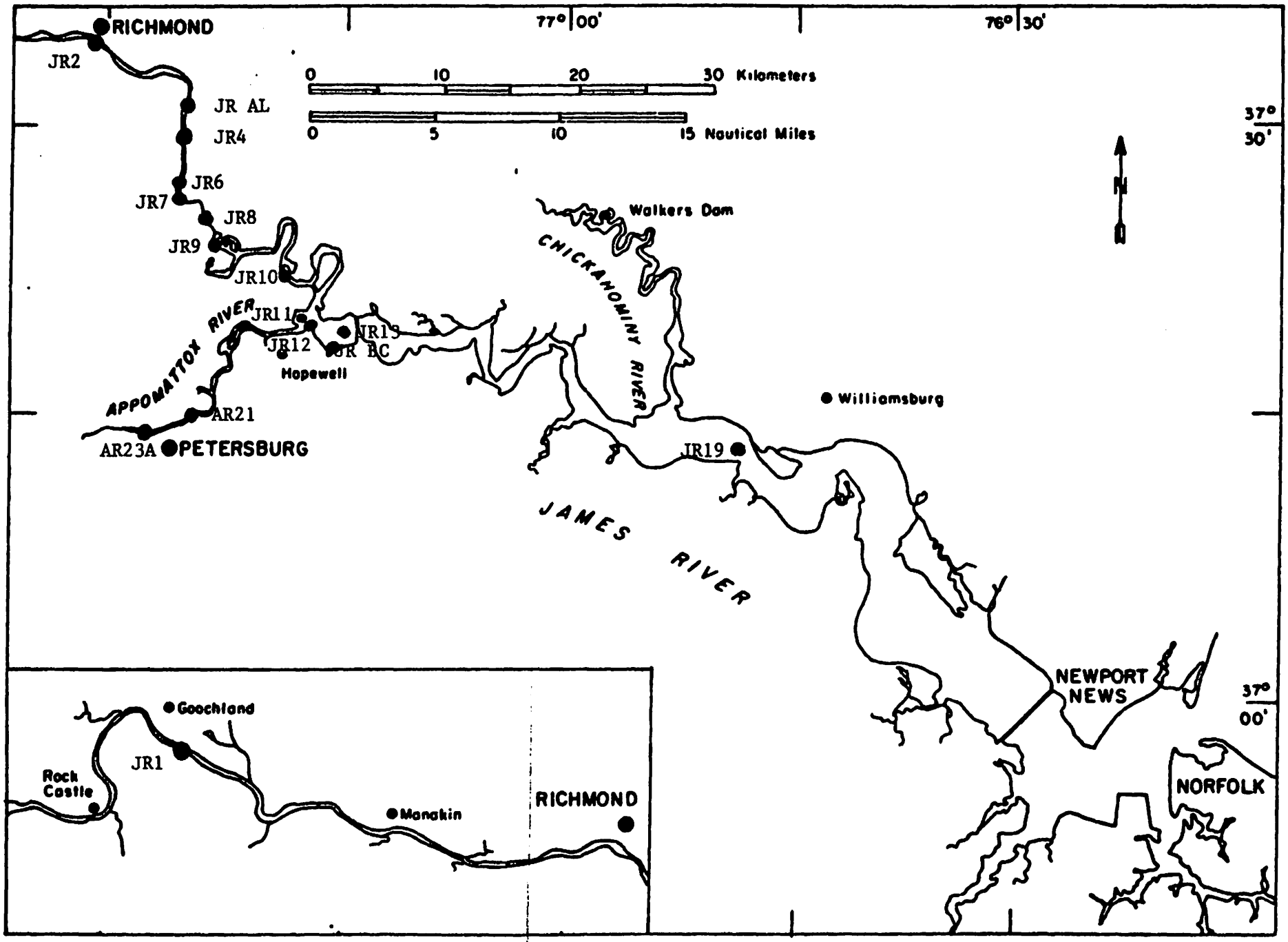

RICHMOND
77° 00'
76° 30'
JR2
0 10 20 30 Kilometers
0 5 10 15 Nautical Miles
JR AL
JR4
37° 30'
JR6
JR7
JR8
JR9
JR10
JR11
JR12
JR13
JR BC
Hopewell
Walkers Dam
CHICKAHOMINY RIVER
APPOMATTOX RIVER
AR21
AR23A
PETERSBURG
Williamsburg
JR19
JAMES RIVER
NEWPORT NEWS
37° 00'
NORFOLK
Goochland
JR1
Rock Castle
Manakin
RICHMOND

Table 2

JAMES RIVER SURFACE SEDIMENT GRAB SAMPLES - 9/84
TOTAL AND PYROGENIC PAH'S (PPB DRY WT)

SAMPLE	TOTAL UCM + RESOLVED	RESOLVED	% UCM	PYROGENIC	% PYRO
JR2D	37801.	33624.	11	19215	51
JR4D	1989	1279	36	629	32
JR6D	5845	3695	37	1632	28
JR7D	5031	3397	32	1574	31
JR8D	3362	2338	30	1198	36
JR9D	5423	3494	36	1467	27
JR12D	17881	12242	32	4673	26
AR21A	1827	1827	0	148	8
AR23A	144	144	0	20	14

Table 3

JAMES RIVER SEDIMENT CORE JR6 9-84
TOTAL AND PYROGENIC PAH'S (PPB DRY WT)

SAMPLE	TOTAL UCM + RESOLVED	RESOLVED	% UCM	PYROGENIC	% PYRO
JR6D1	7135	3764	47	1676	23
JR6D2	8619	5163	40	2172	25
JR6D3	12395	8487	32	3060	25
JR6D4	21970	7164	67	2617	12
JR6D5	19601	9222	53	3129	16
JR6D6	17116	6800	60	2452	14
JR6D7	10645	10517	1	3750	35
JR6D8	16127	10277	36	2989	19
JR6D9	21667	8767	60	2729	13
JR6D10	10886	9455	13	2930	27
JR6D11	17360	8934	49	2777	16

Table 4

JAMES RIVER SEDIMENT CORE JR9 9-84
TOTAL AND PYROGENIC PAH'S (PPB DRY WT)

SAMPLE	TOTAL UCM + RESOLVED	RESOLVED	% UCM	PYROGENIC	% PYRO
JR9D1	6742	4617	32	1824	27
JR9D2	9287	6579	29	2444	26
JR9D3	12064	9790	19	3912	32
JR9D4	24520	16673	32	5620	23
JR9D5	20747	15084	27	5200	25
JR9D6	13071	10710	18	2897	22
JR9D7	21002	20086	4	5769	27
JR9D8	5315	4978	6	1784	34
JR9D9	2599	2310	11	847	33
JR9D10	3082	1632	47	399	13
JR9D11	1788	1788	0	367	21
JR9D12	2814	2186	22	214	8

Table 5

JAMES RIVER SURFACE SEDIMENT GRAB SAMPLES - 4/85
TOTAL AND PYROGENIC PAH'S (PPB DRY WT)

SAMPLE	TOTAL UCM + RESOLVED	RESOLVED	% UCM	PYROGENIC	% PYRO
JR2E	6359	6359	0	3561	56
JR4.1E	6754	4583	32	2099	31
JR4.2E	3982	2224	44	1003	25
JR4.3E	11835	4160	65	1865	16
JR4.4E	23490	9589	59	4046	17
JR4.5E	575	308	46	153	27
JR4.6E	29967	9242	69	3868	13
JR6E	10524	7253	31	2971	28
JR7E	10127	5693	44	2374	23
JR8E	24140	13896	42	6117	25
JR9E	15515	7115	54	2634	17
JR12E	9621	6216	35	2866	30
AR21E	43897.	39506.	10	7915	18
AR23AE	91	91	0	51	56
BA CR	220496.	108064.	51	9758	4

Table 6

Table . James River Sediment Grab and Core Results
Total and Pyrogenic PAH's (ppb dry wt) - 9/84

STATION	JR6			JR9		
CORE SECTION	TOTAL + UCM	TOTAL RESOLVED	PYROGENIC	TOTAL + UCM	TOTAL RESOLVED	PYROGENIC
SURFACE GRAB	5845	3695	1632	5423	3494	1467
0-10 CM	7135	3764	1676	6742	4617	1824
10-20 CM	8619	5163	2172	9287	6579	2444
20-30 CM	12395	8487	3060	12064	9790	3912
30-40 CM	21970	7163.9	2617	24520	16673	5620
40-50 CM	19601	9221.7	3128.8	20747	15084	5200
50-60 CM	17116	6800.2	2452	13071	10710	2897
60-70 CM	10645	10517	3750.4	21002	20086	5769
70-80 CM	16127	10276.6	2988.9	5315	4978	1784
80-90 CM	21667	8766.8	2728.8	2599	2310	847
90-100 CM	10886	9454.9	2930.1	3082	1631.8	399.1
100-110 CM	17360	8934.3	2776.5	1788	1788.3	367
110-116 CM	-	-	-	2814	2186.4	214.2

sectioned into 10 cm lengths which were individually analyzed to obtain information on variations of organic content with sediment depth.

Summaries of the September, 1984 sediment grab organic fraction are contained in Table 2, core sections at JR6 and JR9 in Tables 3 and 4, and the April, 1985 grab samples in Table 5. Listings of the 25 most abundant compounds appear in Appendix Tables A1-A47, and the complete ARI-concentration files in Appendix Tables A48-A94. The reconstructed chromatograms of the G3.2 (PAH containing) fractions are shown in Appendix Figures A1-A51 and the G3.34 (Polar heterocyclic aromatics and ketones) fractions in Appendix Figures A52-A93. Gas chromatography of every JR6 core section was not completed since so little was found in chromatograms of adjacent sections contained negligible material.

Discussion

Core Sections

Some of the pertinent data from these two cores and the grab samples obtained nearby are compared in Table 6. It is observed that the PAH concentrations at station 6 increase with depth rapidly after the first 10 cm, and vary without consistent trend at greater depths. Concentration variation of PAHs with core depth at station 9 shows increasing concentration with depth down to about 100 cm, and drastic decrease at greater depth. Surface concentrations in both cores are similar to those of grab samples taken nearby. Perylene and two tetramethyloctahydrochrysenes, all diagenetically-produced PAHs from naturally-occurring biologically-produced precursors become quite abundant with depth in both cores, although the bottom 30 cm of the core at station 9 is quite depleted in almost all compounds. This core apparently penetrated a much older and-or different

sediment type. The two cores show maxima in total PAH content in the 30-40 cm range, and a second maximum at 80-90 cm in the JR6 core, and at 60-70 cm in the JR9 core. These maxima in total concentrations is not reflected in the pyrogenic fractions. It is likely that these fluctuations are produced by annual variations in river flow and terrigenous input of organic material. The rather continuous increase in pyrogenic compounds with depth is not drastic, and any hypotheses which might be ventured to explain their variation would be based on rather weak observational evidence. It is possible that the input of PAHs is now less than in the past due to increasingly better environmental controls.

Sediment grab samples: September, 1984 and April, 1985

Stations JR2 AND JR12 were considerably higher in the fall, 1984 sampling than for the spring, 1985 sampling. The reverse was true for stations JR4, JR6, JR7, JR8, and the Appomattox River station AR23A. The other Appomattox station, AR21, was exceedingly low in both seasons. Explanations for these variations represent three possible categories: changes actually occurring between sampling periods which affect the amount, but not the character of PAH content at a station, natural variability at the sampling site (this will be discussed in a later section), and introduction of PAH materials of a profoundly different type. Station JR2, very close to downtown Richmond, shows a PAH composition of mostly pyrogenic and petroleum-derived material. Its lowered concentration after the winter of 1984-85 may be due to a small difference in sampling site and different sedimentary type, or may indicate a seasonal flushing of PAHs as previously proposed. Station JR12, near Hopewell had an abundance of the naturally occurring hydrochrysenes in the fall which were far less prominent than the

following spring. A similar explanation as for JR2 is proposed. The other James River stations, which consisted of both pyrogenic PAHs and natural products showed most variation in natural product content, and their increase is probably due to increased input of terrigenous vegetation to the sediments. Appomattox River station AR23A consisted of primarily pyrogenic PAHs, but at very low concentration. The other Appomattox River station AR21A, and a sample from a creek feeding into Bailey's Bay and the James River near Hopewell showed extraordinary amounts of what appears to be an abietic acid-derived hydrocarbon. Its spring concentration at AR21, when carefully diluted and compared with a co-injected standard was near 55 ppm, and that at Bailey's Creek is estimated to be similar. This seems to be a new compound to the river in great abundance locally. Complete elucidation of this compound's structure is incomplete, and work to do so is continuing. The sudden appearance of this compound in two separate locations is intriguing. Although possible, it appears unlikely that this compound is the result of naturally occurring sedimentary diagenesis of organic matter, though it appears to be closely related to biogenic PAHs. An industrial source of the compound or a precursor appears likely, though none has been identified.

Replicate Sampling

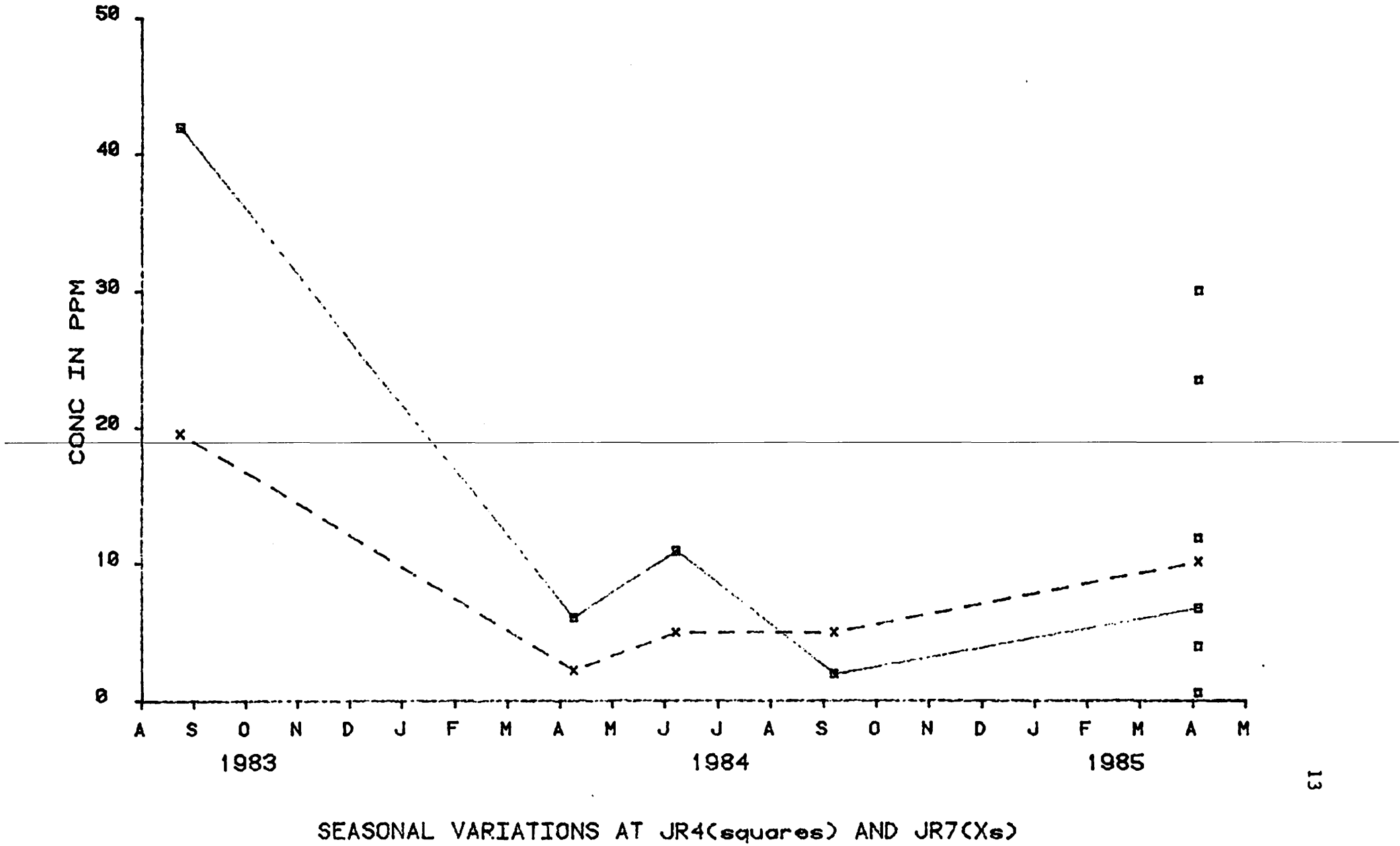
In order to assess the possible variability in samples from a given station and time, six replicate grab samples were collected at JR4 in April, 1985. This station was selected because significant variation had been observed here in the past, and because the station was on the very edge of a steeply cut channel, it should indicate a worst case site. The station was at a channel marker, and samples were gotten as the boat swung between shoal

Table 7

Table . TOTAL RESOLVED PEAKS + UNRESOLVED CONCENTRATIONS(ppb dry sed.)

STATION	8/83	4/84	6/84	9/84	4/85
JR1	288	na	na	na	na
JR2	na	na	na	37801	6359
JR3	na	4223	70888	na	na
JR4	41959	6071	10910	1989	6754
					3982
					11835
					23490
					575
					29967
JR6	na	na	na	5845	10524
JR7	19584	2245	5011	5031	10127
JR8	na	na	na	3362	24140
JR9	na	na	na	5423	15515
JR10	11343	1637	na	na	na
JR11	16932	1470	na	na	na
JR12	na	na	na	17881	9621
JR13	1543	460	na	na	na
JR19	4666	512	na	na	na
AR21A	na	na	na	1827	43897
AR23A	na	na	na	144	91
ALMONDS CR.	na	na	7912	na	na
DUPONT EST.	na	na	6583	na	na
BAILEYS CR.	na	na	na	na	220496

Figure 2



SEASONAL VARIATIONS AT JR4(squares) AND JR7(Xs)

water on one side and deep in-channel water on the other. One replicate, #5, was a crumbly rock-like mineral, which would have been discarded under other circumstances. It proved to be almost devoid of hydrocarbons. The other replicates had a more usual appearance but still showed a 7-fold variation in total concentration. The PAH composition of all these replicates was remarkably constant. This replicate experiment must serve a warning of the high possible small scale geographic variability (in this case less than 30 feet) at a sample site. At station JR4, this could account for most if not all the temporal variability observed, and the variability of total PAH concentration from one station to the next.

Summary

Sediment samples from various parts of the upper James River were sampled on five dates between August, 1983 and April, 1985. The total resolved and unresolved PAH hydrocarbon concentrations are summarized in Table 7. Only two of the stations, JR4 and JR7, were sampled at every occasion. Their variations in total PAH concentrations, including the six replicates at JR4, are plotted vs time in Figure 2. Although considerable differences occur from one sampling time to the next, it is apparent that, with the exception of the initial sample, all of the variation may be attributed to small scale geographic variation at the nominal station site. Nonetheless, it is also apparent that certain stations at certain times show very high concentrations of pyrogenic, petroleum derived, or otherwise abnormal PAHs which represent an unhealthy situation for the river. Inability to repeat measurements of these high values at a later data may be due to sampling at a slightly different place, or it may truly represent

river flushing and normal sediment scour. The upper James is a fast flowing stream, and it is not unreasonable to expect such activity.

Some of the conclusions that may be drawn from this project of two year's sampling are:

1. The organic compounds in sediments above the fall line and Richmond are quite low in concentration, and consist primarily of pyrogenic PAHs, probably from precipitation of airborne particulates.
2. The sediments in the immediate vicinity of metropolitan Richmond are likely to contain highly variable amounts of pyrogenic and petroleum-derived PAHs, originating from urban runoff from streets, industrial spills, etc.
3. The lower portions of the river are likely to contain a constant background of pyrogenic PAHs from upstream sources as well as airborne input, and contain occasionally large amounts of biogenous PAHs and their diagenetic products such as retene, perylene, and the hydrochrysenes.
4. The Appomattox River and certain areas of the James River near Hopewell may contain occasionally very large amounts of PAHs which look like biogenous compounds, but are probably created by industry as a product or by-product and lost to the river.
5. Small scale geographic variability may be so large in certain portions of the river as to obscure observation of long term temporal study of changes or some large scale geographic differences.

References

Smith, C. L., P. O. deFur and R. J. Huggett. 1984. Organic Chemicals in Pore Water and Sediments from the Upper James River. Final Report to the Richmond Regional Planning District. Virginia Institute of Marine Science, Gloucester Point, VA.