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A Final Report

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Introduction

This report presents data gathered in a program designed to monitor tributyltin (TBT) levels in water and sediment from areas in the southern Chesapeake Bay which experience high boating activities. The concentrations reported will hopefully give an insight into the extent and magnitude of TBT contamination in these areas.

Sampling Locations

Water samples from two marina areas were collected weekly from June through September 1986. Sarah Creek, a tributary to the York River, contains several recreational marinas as well as areas which are more rural (Figure 1). Three sampling locations were chosen in this system. One, Station A, is near the mouth of the creek and is the site of a 288 slip marina. Station B is approximately one kilometer upstream and is a private berthing facility for a condominium complex. The third location, Station C, is on a rural segment of the creek with only occasional boat traffic. Outside of Sarah Creek, in the York River, a fourth station was established at the end of the Virginia Institute of Marine Science pier (Station D).

Hampton River flows into Hampton Roads near the entrance of the harbor (Figure 2). It contains several recreational marinas as well as a city dock used mainly for commercial fishing vessels. Stations HRM#1 and HRM#2 are two different locations at the Hampton Roads Marina; HYC is a station at another marina further upstream at the Hampton Yacht Club; CD is the station furthest upstream near the commercially used city dock, and OPC is at Old Point Comfort, a station in Hampton Roads just before its entrance into Chesapeake Bay.

Figure 3 shows the sampling sites for the Hampton Roads-James River-Elizabeth River system. Samples were collected from here in May, July and September 1986.

In September, 1986, sediment was obtained from station A in Sarah Creek (Figure 1).

Methods and Procedures:

Water samples were collected from a depth of approximately 15 cm below the surface. Samples from the marina areas were collected from piers with a sampling apparatus described previously (Huggett et al., 1986). Results are presented in Tables 1 and 2. In the Hampton Roads-James River-Elizabeth River system, samples were collected in 2 liter polycarbonate bottles from a boat. Temperature and salinity measurements were made on subsamples. All samples were acidified to pH 2 with HCl and stored in the dark at $4^{o}C$ until analysis.

The analytical procedure used to determine TBT has been described by Unger et al., (1986). Actual minimum detection levels for environmental samples was approximately 1 ngL^{-1} as TBT^{+}.

The top two centimeters of bottom sediments were collected from a sample taken by a Ponar grab sampler. The sediment was blended wet to insure homogeneity and oven dried at $60^{o}C$. The dried sediment was then ground with a mortar and pestle and sieved through either 125 or 63 micron sieves. Subsamples were taken and soxhlet extracted with hexane for 48 hrs. The hexane extract was then treated identically as those from water. Results are reported in Table 7.

Discussion

Water from Sarah Creek Stations A and B generally contained higher butyltin concentrations than previously reported for samples collected in winter and spring (Huggett et al., 1986). Station A shows the highest variability, with concentrations varying by a factor of ten within the four month period. Station B is more stable, but is still subject to TBT^+ concentrations varying by a factor of 8 within a one week time period. Relatively low TBT^+ concentrations are evident at Station C in a rural segment of the creek. York River water appears to contain much less TBT, as evidenced by the values during the last six weeks of the sampling period.

TBT concentrations are highly variable in the Hampton River over time. There are also huge differences in TBT concentrations found in samples collected from different locations at the same marina at the same time. On one occasion, TBT^+ concentrations differed by a factor of 35 in samples collected from the same marina. Unlike the recreational marinas, water samples from the commercially used city dock contained relatively consistent TBT levels over time with only an occasional spike. The station at Old Point Comfort shows relatively low concentrations of butyltins, as would be expected from the decreased boating activity and greater flushing.

In the Hampton Roads-James River-Elizabeth River system, relatively low concentrations of TBT^+ were found in open harbor areas and at the mouths of the Nansemond and James Rivers. Higher concentrations were found in the Hampton River locations and the highly industrialized Elizabeth River. One sample from the Elizabeth River contained a very high level of TBT. The sample was collected from a private shipyard where a commercial cargo ship had recently been overhauled and launched, (It had been observed one week

earlier in dry dock). Four weeks later, the TBT^{+} concentration at this site was much lower.

Sediments collected from Sarah Creek contained approximately four orders of magnitude more TBT than waters collected from the same location. This sediment level probably reflects both sorption of TBT from the overlying water as well as paint chips which contain the organotins.

References

Huggett, R. J., Unger, M. A., and D. J. Westbrook. 1986. Organotin Concentrations in the Southern Chesapeake Bay. In: Proceedings of the Oceans '86 Conference, September, Washington D.C., p. 1262-1265.

Unger, M. A., MacIntyre, W. G., Greaves, J. and R. J. Huggett. 1986. GC Determination of butyltins in natural waters by flame photometric detection of hexyl derivatives with mass spectrometric confirmation. Chemosphere, 15(4):461-471.

Data Report:

Table 1

Butyltins, Temperature and Salinity in Whole Water from Sarah Creek
(Concentrations as ngL^{-1})

Date	Sampling Locations	TBT^{+}	DBT^{+2}	Temp. °C	Salinity °/oo
6-3-86	A	7	9	23	20
	B	22	22	24.5	20
	C	9	9	24.5	20
	D	N.D.*	N.D.	22.5	20
6-5-86	A	27	30	23.5	20
	B	39	41	24	20
	C	5	15	24	20
	D	3	4	22.5	20
6-10-86	A	30	23	26	20
	B	22	39	27	20
	C	9	18	26.5	20
	D	N.A.**	N.A.	25	21
6-12-86	A	44	28	27.5	20.5
	B	25	33	28	20
	C	N.A.	N.A.	27.5	20.5
	D	N.A.	N.A.	26.5	21
6-17-86	A	37	16	27	22
	B	34	21	28	22
	C	8	12	28.5	22
	D	N.D.	N.D.	26	22
6-24-86	A	38	20	26	21.5
	B	29	30	26.5	22
	C	7	14	26.5	22
	D	N.D.	N.D.	25	22

Table 1 (continued)

Date	Sampling Locations	TBT^{+}	DBT^{+2}	Temp. ^{o}C	Salinity $^{o}/oo$
7-1-86	A	27	10	26	21
	B	37	27	28	21
	C	10	7	27.5	21
	D	3	N.D.	25.5	21.5
7-8-86	A	33	21	27	22
	B	37	32	28	20.5
	C	13	13	28	20
	D	3	2	26	22
7-15-86	A	11	10	26	23
	B	22	23	28	22
	C	22	26	28.5	21
	D	N.D.	N.D.	26	22
7-22-86	A	18	12	28	22
	B	26	24	30	20
	C	9	13	30	20
	D	N.D.	N.D.	28	21
7-29-86	A	76	39	30.5	20
	B	37	30	32	20
	C	14	17	31.5	21
	D	2	3	30	22
8-5-86	A	10	12	28.5	23
	B	27	24	29	22
	C	12	17	28.5	21
	D	1	2	28	23
8-12-86	A	10	6	27	23
	B	32	25	27	22
	C	12	13	27	22
	D	4	N.D.	27	23
8-19-86	A	13	15	27	22
	B	25	8	27.5	21.5
	C	8	9	27.5	22
	D	2	2	26.5	22

Table 1 (continued)

Date	Sampling Locations	TBT^{+}	DBT^{+2}	Temp. ^{o}C	Salinity $^{o}/_{oo}$
8-26-86	A	16	7	26	24
	B	24	22	27.5	23
	C	4	14	27	22
	D	N.D.	N.D.	26	24
9-1-86	A	9	9	23	22.5
	B	17	20	23.5	22
	C	8	12	23.5	22
	D	N.D.	2	23	22.5
9-9-86	A	15	8	23.5	23
	B	19	17	23	22
	C	7	9	24	22
	D	N.D.	1	23.5	23
9-16-86	A	24	18	23	23
	B	39	19	23.5	22
	C	12	10	23.5	22
	D	N.D.	N.D.	23	22
9-23-86	A	24	12	24.5	23
	B	5	7	25.5	22
	C	4	7	25	22
	D	N.D.	N.D.	24	23.5
9-30-86	A	29	13	24.5	23.5
	B	20	25	25	22
	C	8	9	25	23
	D	N.D.	1	24	23

* N.D. = nondetectable @ 1 ngL^{-1}

** N.A. = data not available

Table 2

Butyltins, Temperature and Salinity in Whole Water from Hampton River

(Concentrations as ngL^{-1})

Date	Sampling Locations	TBT^{+}	DBT^{+2}	Temp. ^{o}C	Salinity $^{o}/oo$
6-19-86	HRM#1	60	25	24.5	N.A.*
	HRM#2	110	58	24.5	N.A.
	HYC	19	11	24	N.A.
	CD	22	13	23	N.A.
	OPC	4	2	23.5	N.A.
6-26-86	HRM#1	92	38	25	24
	HRM#2	320	85	25	23.5
	HYC	68	23	25	24
	C.D.	41	18	25	24
	OPC	6	5	24.5	23.5
7-3-86	HRM#1	31	20	25	23
	HRM#2	68	40	25	22.5
	HYC	45	14	25	23
	CD	44	20	25.5	23
	OPC	5	6	24	23.5
7-10-86	HRM#1	20	18	27.5	22.5
	HRM#2	150	71	28.5	23
	HYC	31	17	28	23
	CD	29	14	29	23
	OPC	3	2	27	24
7-17-86	HRM#1	28	20	27.5	22
	HRM#2	220	140	28	22
	HYC	29	13	27.5	22
	CD	26	15	28	22
	OPC	4	5	26	23

Table 2 (continued)

Date	Sampling Locations	TBT^{+}	DBT^{+2}	Temp. ^{o}C	Salinity $^{o}/oo$
7-24-86	HRM#1	13	11	28	22
	HRM#2	480	130	28.5	22
	HYC	44	17	28	22
	CD	25	15	28.5	22
	OPC	5	2	28	22
7-31-86	HRM#1	53	22	28	22
	HRM#2	110	74	29	22
	HYC	37	19	28.5	22
	CD	95	33	28.5	22
	OPC	4	8	27	23
8-7-86	HRM#1	180	41	27.5	24
	HMR#2	140	53	28	24
	HYC	31	22	28	24
	CD	24	16	28.5	24
	OPC	3	2	27	24.5
8-14-86	HRM#1	63	19	26.5	22
	HRM#2	120	80	26	20
	HYC	79	22	27	20.5
	CD	53	20	27	22
	OPC	4	4	26	25
8-21-86	HRM#1	23	8	26	23
	HRM#2	83	29	26	22.5
	HYC	32	10	26	23
	CD	15	13	26	22
	OPC	2	2	26	23.5
8-28-86	HRM#1	45	27	24	20.5
	HRM#2	670	580	23	18
	HYC	36	16	24	20.5
	CD	41	25	24	20
	OPC	3	2	24	23.5
9-4-86	HRM#1	33	11	24	23
	HRM#2	140	50	24	23
	HYC	29	10	23.5	23
	CD	17	9	23.5	23
	OPC	1	2	23	24.5

Table 2 (continued)

Date	Sampling Locations	TBT^{+}	DBT^{+2}	Temp. ^{o}C	Salinity $^{o}/oo$
9-11-86	HRM#1	13	8	25.5	24
	HRM#2	89	32	25	24
	HYC	15	8	25	23.5
	CD	9	6	25	24
	OPC	3	2	24.5	25
9-18-86	HRM#1	51	17	21	23.5
	HRM#2	93	37	21	24
	HYC	24	15	21	24
	CD	19	8	21	24
	OPC	4	2	21.5	25
9-25-86	HRM#1	29	11	25.5	23
	HRM#2	66	31	25.5	23
	HYC	190	38	26.5	24
	CD	23	13	26	24
	OPC	6	5	25	25

*N.A. = data not available.

Table 3

Butyltin Concentrations and Salinity in Whole Water From the Hampton Roads-James River-Elizabeth River System in May, 1986

(Concentrations as ngL^{-1})

Date	Station	TBT^{+}	DBT^{+2}	Salinity, °/oo
5-21-86	1	5.9	1.6	16.0
	2	2.2	2.2	19.
	3	3.4	2.4	18.
	4	7.1	1.8	20.
	5	4.6	1.6	21
	6	1.7	1.6	21.
	13	8.5	3.7	23
	14	3.7	2.5	22
	15	5.4	2.9	21
	17	21.	11.	22
	19	18.	8.8	21
	A*	7.1	3.5	22
	B*	12.	3.5	22

* Samples collected uptide (A) and downtide (B) of the Coral Sea, CV43, an aircraft carrier painted with tributyltin containing paint.

Table 4

Butyltin Concentrations, Temperature and Salinity in Whole Water From the Hampton Roads-James River-Elizabeth River System in July 1986 (Concentrations as ngL^{-1})

Date	Station #	TBT^{+}	DBT^{+2}	Temp. °C	Salinity °/oo
7-25-86	1	1	2	29	18.5
	2	2	2	29	20
	3	4	3	28.5	22
	4	5	3	28	22
	5	6	3	28	22
	6	7	4	28	23
	7	16	12	28	22
	8	19	14	28.5	22
	9	33	22	28.5	22
	10	21	14	28.5	23
	11	17	13	28.5	22
	12	2	3	28	22.5
	13	6	4	28	22.5
	14	3	3	28	21.5
	15	5	5	28.5	22
7-30-86	16	8	6	28	21
	17	14	5	29	22
	18	13	9	29	21
	19	5	4	30.5	21
	20	3	5	31.5	20
7-25-86	21	2	3	28.5	22.5
	22	N.D.*	1	28.5	21
	23	1	N.D.	29	21
	24	N.D.	N.D.	29.5	20.5
	25	N.D.	2	29	20.5

* N.D. = not detectable at 1 ngL^{-1}

Table 5

Butyltin Concentrations, Temperature and Salinity in Whole Water From the Hampton Roads-James River-Elizabeth River System in August 1986 (Concentrations as ngL^{-1})

Date	Station #	TBT^{+}	DBT^{+2}	Temp. °C	Salinity °/oo
9-2-86	1	1	2	23	18
	2	1	2	23	20
	3	4	3	23	23
	4	4	4	23	23
	5	2	3	23	23.5
	6	N.D.	8	23	23
	7	25	9	23.5	23
	8	39	13	24	23
	9	30	15	24	22
	10	15	11	24	22.5
	11	17	11	24	22
	12	4	3	23	23
	13	2	3	23	24
	14	3	3	23	24
	15	2	2	23	22
	16	5	9	24	22
	17	17	13	24	22
	18	920	59	24.5	22
	19	17	12	25.5	21
	20	14	8	26	20.5
	21	2	3	23	21
	22	1	1	22	20
	23	N.D.*	1	22	18.5
	24	N.D.	N.D.	22.5	19
	25	N.D.	1	22	20

*N.D. = not detectable at 1 ngL^{-1}

Table 6

Butyltin Concentrations, Temperature and Salinity
in Whole Water From the Hampton Roads-, James River-
Elizabeth River System in September 1986
(Concentrations as ngL^{-1})

Date	Station #	TBT^{+}	DBT^{+2}	Temp. ^{o}C	Salinity $^{o}/oo$
9-29-86	1	3	2	23	19
	2	2	2	23.5	22
	3	5	4	24	25
	4	7	6	24	25
	5	3	3	24	28
	6	3	3	24	23
	7	14	10	25	24
	8	15	11	25	24
	9	42	21	25.5	24
	10	17	18	25	24
	11	17	10	25	24
	12	3	3	24	24
	13	2	4	23.5	20
	14	3	4	24	23
	15	5	6	24	22
	16	11	11	24	22
	17	30	16	24.5	22
	18	49	18	24.5	22
	19	10	7	26	22
	20	7	6	27	22
	21	2	3	24	20
	22	N.D.*	N.D.	24	19
	23	1	2	24	19
	24	N.D.	2	23.5	19
	25	1	3	24	20

*N.D. = not detectable at 1 ngL^{-1}

Table 7

Tributyltin Concentrations in Replicate Sediment Samples from Sarah Creek

Subsample	Sieve Size	TBT^+ µg/kg
1	125 µ	1000
2	125 µ	1300
3	125 µ	1000
4	125 µ	950
5	125 µ	930
6	125 µ	1000
7	63 µ	1200
8	65 µ	920
9	63 µ	1100
10	63 µ	1200
11	63 µ	1100
12	63 µ	1100

Overall mean = 1075 $\pm$ 121 µg/kg

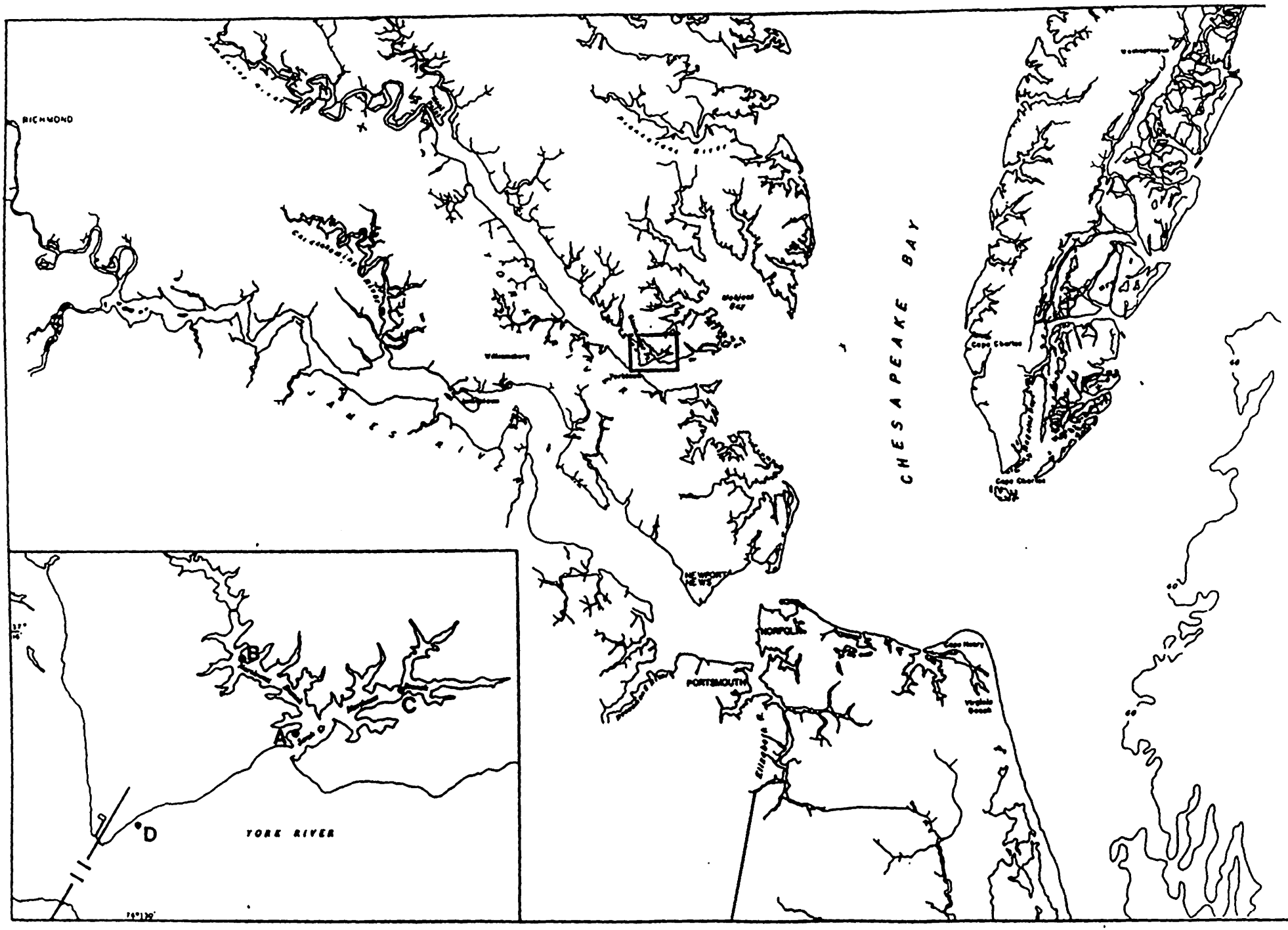

Figure 1. Sarah Creek Sampling Sites

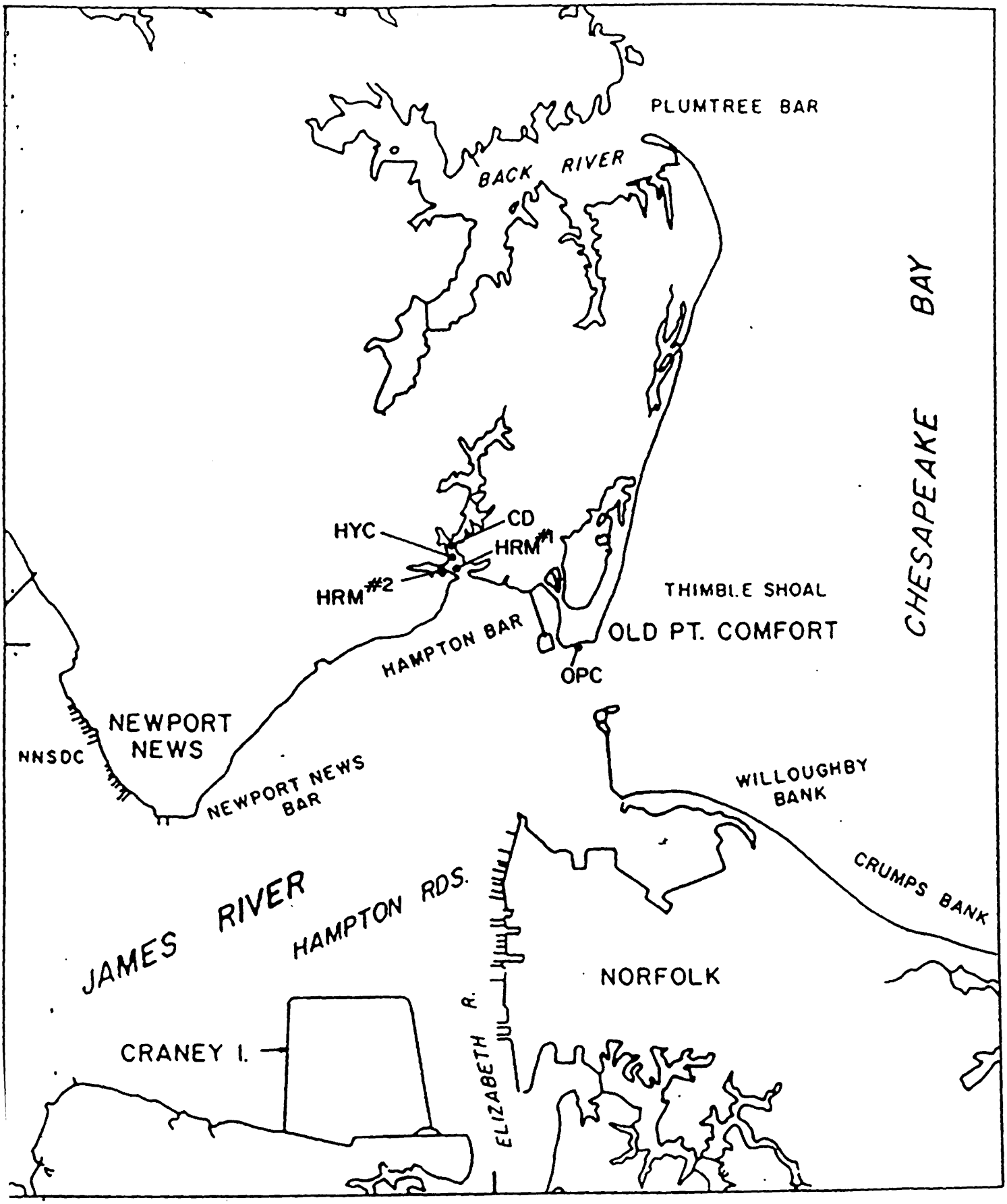

Figure 2. Hampton River Sampling Sites

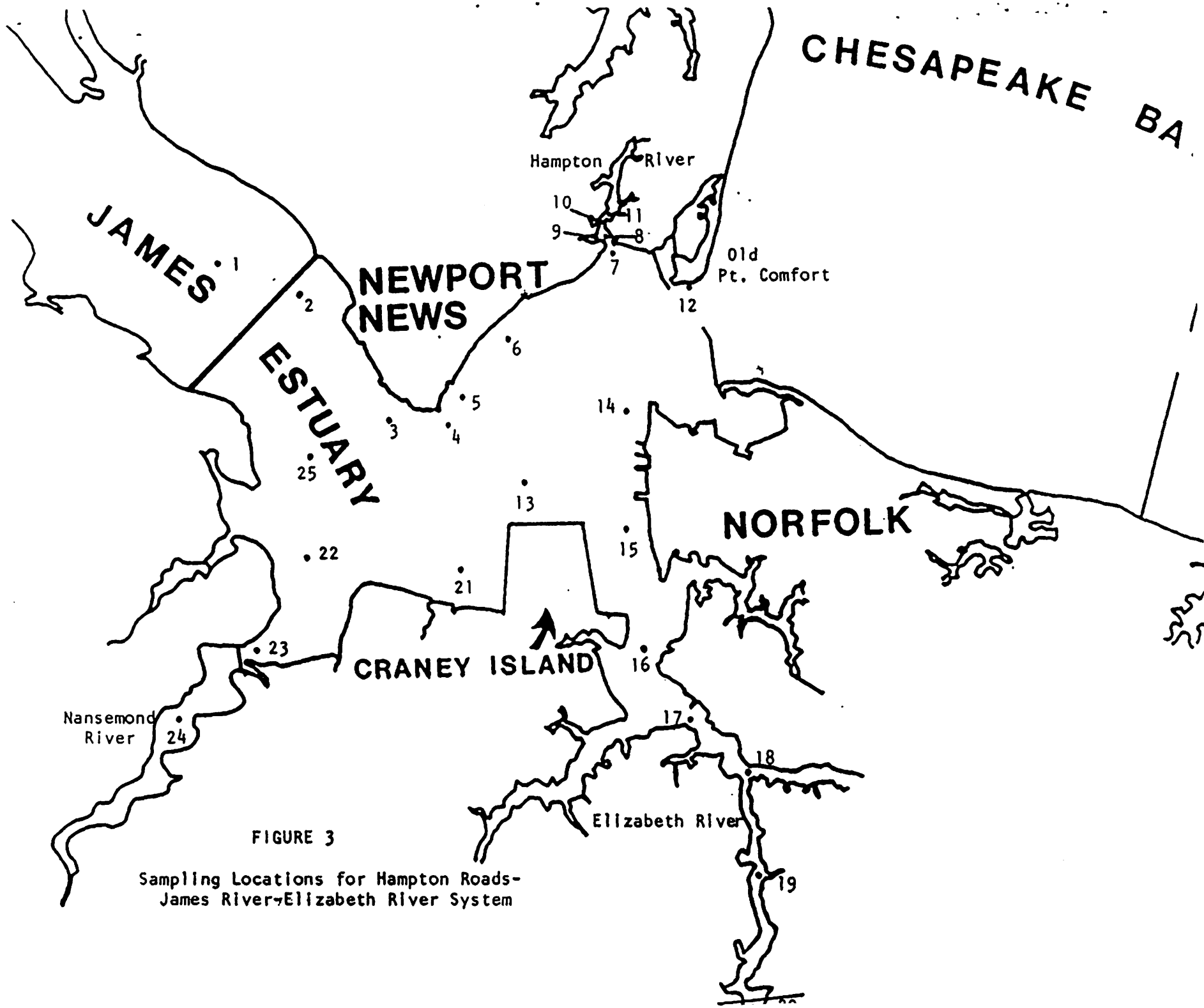

FIGURE 3

Sampling Locations for Hampton Roads-James River-Elizabeth River System