

KEPONE MONITORING AT SKIFFES CREEK

in fulfillment of contract number

DACW65-79-C-0027

by

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April 1980

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Introduction

Kepona entered the James River estuary from point sources of production and through runoff from unauthorized disposal sites in the vicinity of Hopewell, Virginia. The total quantity of Kepona released to the river is not known, however, about 1.5×10^6 kg were produced between 1966 and 1975. At present we estimate that 30,000 kg reside in contaminated sediments of the estuary.

Bed sediments are contaminated from the source at Hopewell to Hampton Roads, a distance of 88 kilometers. Patterns of contamination vary with sediment type and distance from the source. Major Kepona sinks exist in the Jamestown - Dancing Point reach and in Burwell Bay. Sediments from these zones are generally finer-grained and more enriched in organic matter than elsewhere and these zones are sites of relatively high sediment accumulation and fast deposition.

This extensive contamination of the river sediments by Kepona presents problems for managers having to make decisions on dredging actions in the river. The most important questions which need to be answered concerning dredging activities are:

- 1) Will dredging result in significant quantities of Kepona being released to the environment?
- 2) Will the releases spread the contamination or result in increased bioaccumulation of Kepona in organisms?
- 3) Will the spoil disposal methods release Kepona to the marine environment or ground water?

In the Skiffes Creek area of the James River the most important marine organism which could be affected by dredging is the oyster. Deep Water Shoals, the most upstream oyster rock in the river, lies just below Skiffes Creek

(Figure 1). Residue levels in oysters vary considerably as a function of time as is shown in Figure 2. Residues usually peak in the summer, decline after spawning then increase briefly and decline during the winter months.

Kepone is available to oysters in both the dissolved and suspended forms. The relative importance of each route is not known with certainty, but it appears that the dissolved form is more important. Uptake from solution at 10 ng/l resulted in residues of 0.12 ug/g (U. S.-EPA), while exposure to similar concentrations on solids resulted in residues of only 0.04 ug/g (Haven, VIMS).

Skiffes Creek Monitoring Program

The monitoring study for Skiffes Creek was divided into four segments: 1) biological monitoring of residue levels in oysters to detect increases which might result from the dredging, 2) monitoring of the disposal site, 3) determination of the levels of Kepone in the suspended and dissolved phases prior to, during and after dredging and 4) delineation of the sediment plume by measuring suspended sediments during dredging.

Natural populations of oysters were sampled at stations I, II, III, IV and V, and in addition, oysters transplanted from the Rappahannock River were sampled at stations A, B, I and II. Samples were collected prior to, during and after dredging.

Dissolved and suspended Kepone was determined at station B, at the surface and bottom, during high slack, low slack, mid-flood and ebb tides. These determinations were made one week prior to dredging, twice during dredging and one week after dredging.

Suspended sediments were determined at the stations shown in Figure 3 on 30 April and 1 May to coincide with remote sensing operations.

The overflow from the disposal site and groundwater site was also monitored.

Procedures

Dissolved Kepone (H₂O) - A 20 liter sample of freshly collected river water was passed through the continuous centrifuge which was operating at ~ 27,000 G's. After centrifugation, the water was vacuum filtered through a 0.8 u pore size Millipore filter.

Sixty grams of XAD-2 resin was added to the filtered water and the mixture stirred for 16 hours, then filtered through Whatman #1 paper.

The resin from the filter paper was stirred for 16 hours in 200 mls of a mixture of toluene-ethyl/acetate (1:3). The mixture was vacuum filtered through Whatman #1 paper and the residual water removed by separatory funnel, followed by percolation through sodium sulfate. The filtrate was concentrated and eluted through a Florisil column to remove organic compounds that interfere with Kepone detection by EC chromatography.

The toluene-ethyl/acetate extraction of the resin was repeated, and the two extracts quantitated separately.

Suspended Sediment - Kepone - The precipitated sediment from the continuous centrifuge was oven-dried, desiccated with a mixture of sodium sulfate - Quiso (9:1) and Soxhlet extracted with ethyl ether - petroleum ether (1:1) for 16 hours.

The extract was concentrated and eluted through a Florisil column to remove interfering organic compounds before injection into the EC gas chromatograph.

Oysters - The meats of 12 oysters were homogenized in a food blender and frozen to facilitate the breakdown of the tissue. A 30 gram aliquot of the sample was allowed to thaw, desiccated with a mixture of sodium sulfate - Quso (9;1) then refrozen.

The frozen sample was ground in a food blender and Soxhlet extracted for 16 hours with a mixture of ethyl ether - petroleum ether (1:1).

The extract was concentrated and eluted through a Florisil column to remove interfering organics prior to injection into the EC chromatograph.

Total Kepone (Dissolved and Suspended) - A 50 ml aliquot of well mixed water sample was put into a separatory funnel. Five mls of benzene was added and the funnel shaken for 2 minutes. After separating, the aqueous phase was again shaken with an additional 5 mls of benzene.

The two benzene extracts were combined and treated with 1% methanol prior to injection into the EC chromatograph.

Suspended Sediment (Sediment Plume) - A 500 ml aliquot of sample was passed through a pre-weighed 0.8 u pore size Millipore filter. The filter pad with residue was oven-dried @ 55°C and desiccated to constant weight.

$$\text{mg/l suspended solids} = \frac{\text{wt. of residue}}{\text{sample vol.}} \times 1000$$

Results

The results of the instream monitoring program for dissolved and suspended Kepone are presented in Table 1. All of these data were collected at Station B as shown in Figure 1. Four sets of samples, collected at different tidal stages, were taken prior to dredging (2 & 11 April). Eight sets were collected during dredging (15 May - 12 June) and 4 sets were collected after the dredging was completed.

Over the study period, the average dissolved Kepone concentration at the surface was 5.1 ng/l. Bottom samples were slightly higher averaging 5.6 ng/l. Before and after dredging the dissolved surface average was 4.7 ng/l compared to 5.5 ng/l during dredging. During the dredging bottom samples averaged 5.8 ng/l compared to 5.3 ng/l for non-dredging periods. None of the differences noted above were statistically significant when comparing means using analysis of variances, ($\alpha = 0.05$).

Concentrations of Kepone on the suspended solids during the study averaged 0.056 ppm and 0.049 ppm for surface and bottom samples, respectively. Prior to and after dredging the suspended samples averaged 0.059 ppm compared to 0.054 ppm during dredging. Bottom samples during dredging averaged 0.049 ppm compared to 0.050 for non-dredging periods. None of the differences were statistically significant.

Residue levels of Kepone in oysters collected during the study are shown in Table 2. Prior to dredging, the natural populations had average residues of 0.1 ppm, compared to 0.06 ppm during dredging and 0.09 ppm after the dredging was completed. At Station 1, the oyster rock closest to Skiffes Creek, the pre-dredging average residue was 0.13 ppm compared to 0.08 ppm during and 0.07 ppm after the completion of the project.

Oysters transplanted from the Rappahannock did not show any measurable Kepone uptake during the first 2 weeks of exposure. The low salinities observed during this period undoubtedly reduced pumping rates and thus lowered the animals' ability to concentrate Kepone. Salinities continued to be depressed (Table 1) and resulted in mortalities of the transplanted oysters at the upstream stations. The Rappahannock oysters, which originated from areas of higher salinity, are less resistant to low salinities than those resident in the James. They therefore cannot be considered representative of conditions when salinities are depressed.

The dredged material was pumped to the upland disposal site shown in Figure 3. Samples for Kepone analysis were collected at the overflow and from a nearby test well to detect ground water contamination. The results of these tests are shown in Table 3.

No Kepone was detected in water from the test well during the study which extended until 16 July.

High levels of solids were found to escape from the disposal area. These solids although similar in Kepone concentrations to those observed in the river were found in high concentrations, i.e. grams/liter. This caused relatively high Kepone levels to be observed in the effluent throughout the study period.

Measurements of suspended solids obtained during the remote sensing operation are tabulated in Table 4. The levels of suspended solids observed are very similar to those expected in the area (Nichols, 1972) and do not indicate any additional suspension due to the dredging operation.

Discussion

In the James River, neither the biological or chemical monitoring studies could detect any effect of the dredging operation. Kepone levels remained at background in both the dissolved and suspended phases and residues in oysters were not increased. Suspended solids in the river were not increased above background levels.

The disposal area, however, did not function effectively. Kepone contaminated sediments were being released even after the dredging operation had terminated. In future operations the design of the containment structure should be given greater attention to assure they have proper capacity and do not allow for short circuits to occur.

References

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- Haven, D. S. and R. Morales. 1977. Uptake of Kepone from suspended sediments by oysters, Rangia and Macoma. Annual Report to U.S. EPA. Gulf Breeze, Florida.
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Table 1. In-stream Kepone Monitoring

Date	Tidal Stage	Kepone		Salinity	
		Dissolved ng/l	Suspended ppm		
2 Apr. '79	Slack before flood	S	1.0	0.079	0.113
		B	1.0	0.048	-
	Mid flood	S	1.0	0.083	0.110
		B	1.0	0.033	0.561
11 Apr. '79	Slack before ebb	S	5.4	0.056	0.507
		B	6.3	0.049	1.353
	Mid ebb	S	9.2	0.064	1.157
		B	5.1	0.039	1.589
15 May '79	Slack before flood	S	3.0	0.058	1.598
		B	3.8	0.027	1.129
	Mid flood	S	6.2	0.054	1.049
		B	6.7	0.039	1.111
22 May '79	Slack before ebb	S	9.8	0.054	0.843
		B	5.2	0.061	1.347
	Mid ebb	S	3.6	0.047	0.751
		B	4.5	0.062	1.023
6 June '79	Slack before ebb	S	4.0	0.10	0.145
		B	4.0	0.039	0.120
	Mid ebb	S	6.1	0.06	0.185
		B	8.8	0.08	0.310
12 June '79	Slack before flood	S	5.5	0.03	0.106
		B	7.3	0.04	0.108
	Mid flood	S	5.4	0.03	0.110
		B	6.7	0.04	0.104
21 June '79	Slack before ebb	S	5.3	0.06	
		B	8.5	0.07	
	Mid ebb	S	3.0	0.06	
		B	7.5	0.04	

Table 1. continued

Date	Tidal Stage	Kepone		Salinity
		Dissolved ng/l	Suspended ppm	
10 July '79	Slack before flood	S	6.3	0.03
		B	7.2	0.04
	Mid flood	S	7.0	0.04
		B	5.9	0.08

$$\Sigma x = 171.4$$

$$n = 32$$

$$\bar{x} = 5.3 \text{ ng/l}$$

$$= 0.005 \text{ } \mu\text{g/l}$$

$$\Sigma x = 1.692$$

$$n = 32$$

$$\bar{x} = 0.053 \text{ } \mu\text{g/g}$$

Table 2

Oysters - Natural Populations

Date	Station				
	1	2	3	4	5
	Kepone - ppm				
12 Mar. '79	0.13	0.103	0.12	0.06	0.09
	0.12	0.069	0.13	0.06	0.08
8 May '79	0.07	0.05	0.06	0.05	0.06
	0.09	0.05	0.06	0.04	0.05
10 July '79	0.07	0.05	0.09	0.09	0.12
	0.07	0.07	0.13	0.08	0.09

Oysters - Rappahannock River Transplants

	1	2	A	B
5 Mar. '79	Date oysters were transplanted			
27 Mar. '79	ND*	ND	ND	ND
	ND	ND	ND	ND
7 May '79	ND	0.03	M	M
10 July	M	0.11	M	M

*ND = non-detectable

M = mortality

Table 3

Disposal Site Monitoring

Total Kepone (Dissolved & Suspended)

Date	Spillway			Test Well
	Kepone, Total* ug/l	Suspended Solids g/l	Kepone** on Solids ppm	Kepone, Total ng/ml
24 May '79	0.20	-		ND
31 May '79	0.47	67.1	0.03	ND
7 June '79	0.51	-		-
11 June '79	0.50	1.5	0.07	-
15 June '79	0.09	1.2	0.10	ND
20 June '79	0.21	-	-	-
16 July '79	0.17	-	-	ND

*Analyzed by benzene partitioning

**Analyzed by Soxhlet

0.0045 ug/l

Table 4
Suspended Solids

Station	Date	Time EDT	Depth	Suspended Solids Mg/l	Station	Date	Time	Depth	Suspended Solids Mg/l	Current Velocity (Knots)	Current Direction (Degrees)
1	30 Apr 79	1314	S	24.4	5	4/30/79	1312	S	30.5	0.44	350
		1550	S	8.4			"	M	31.5	0.48	345
							"	B	24.4	0.49	347
2	30 Apr 79	1315	S	39.4			1541	S	27.3	0.08	360
		1600	S	33.0			"	M	29.5	0.14	190
3	30 Apr 79	1319	S	36.4			1541	B	25.9	0.12	120
		1607	S	24.6			6	"	1326	S	18.2
4	30 Apr 79	1335	S	16.8				M	33.1	0.66	312
		1615	S	14.4			"	B	50.2	0.58	312
1	1 May 79	0826	S	35.4			1548	S	30.8	0.10	360
		1212	S	30.0			"	M	16.1	0.08	290
							"	B	38.1	0.09	155
2	1 May 79	0832	S	39.2	7		1335	S	32.0	0.68	310
		1217	S	33.8			"	M	37.1	0.58	330
3	1 May 79	0838	S	59.6				B	40.7	0.45	340
		1225	S	27.6			"	1558	S	16.0	0.34
4	1 May 79	0845	S	16.6				M	34.2	0.27	350
		1231	S	21.6			"	B	48.2	0.04	340
							8	"	1346	S	34.2
							M	40.0	0.80	332	
							B	35.4	0.55	320	
							1604	S	27.7	0.27	080
								M	30.6	0.32	140
								B	38.1	0.20	155

S = Surface + 1 Meter
M = Mid-depth
B = Bottom - 1 Meter

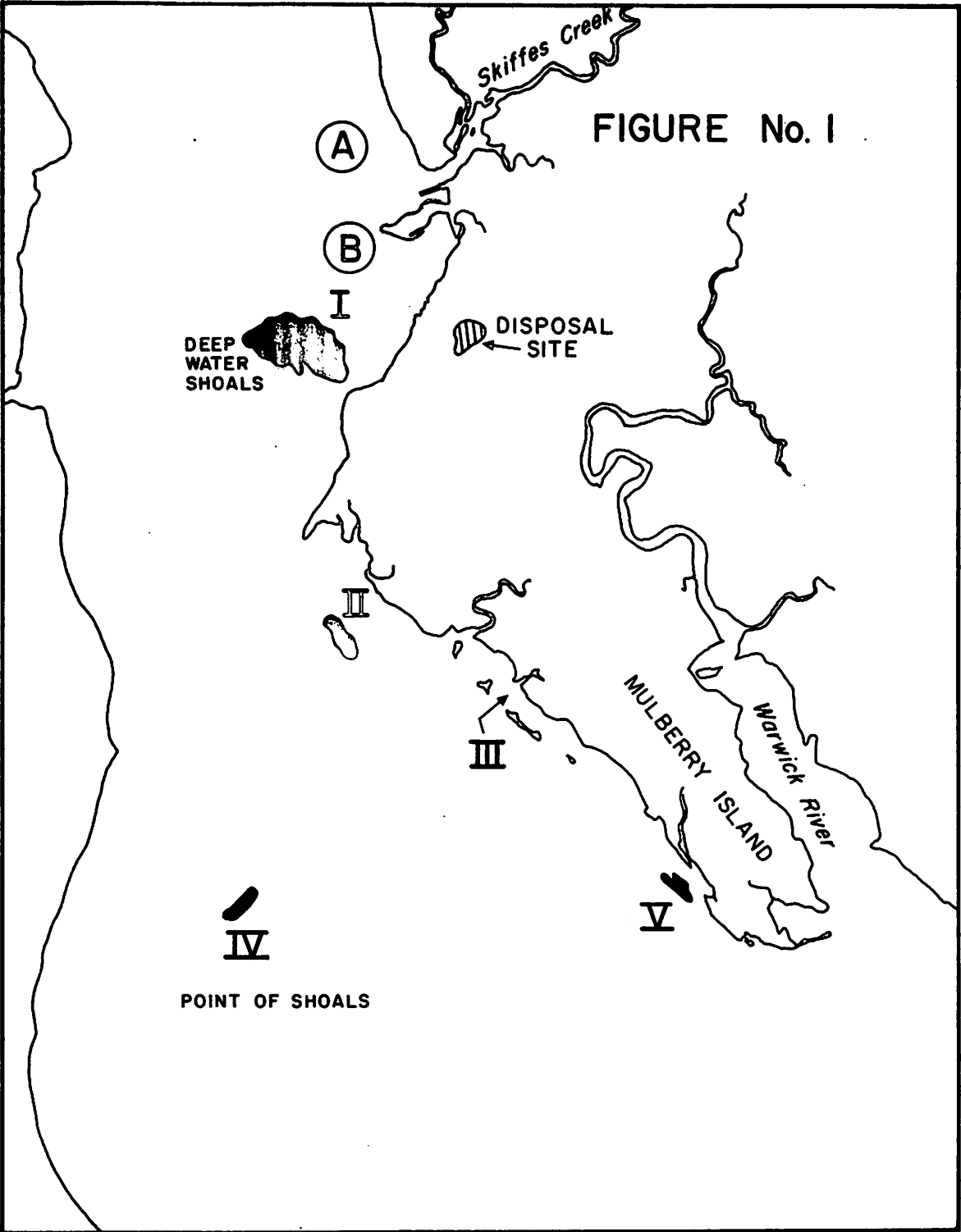


FIGURE 2
DEEP WATER SHOALS

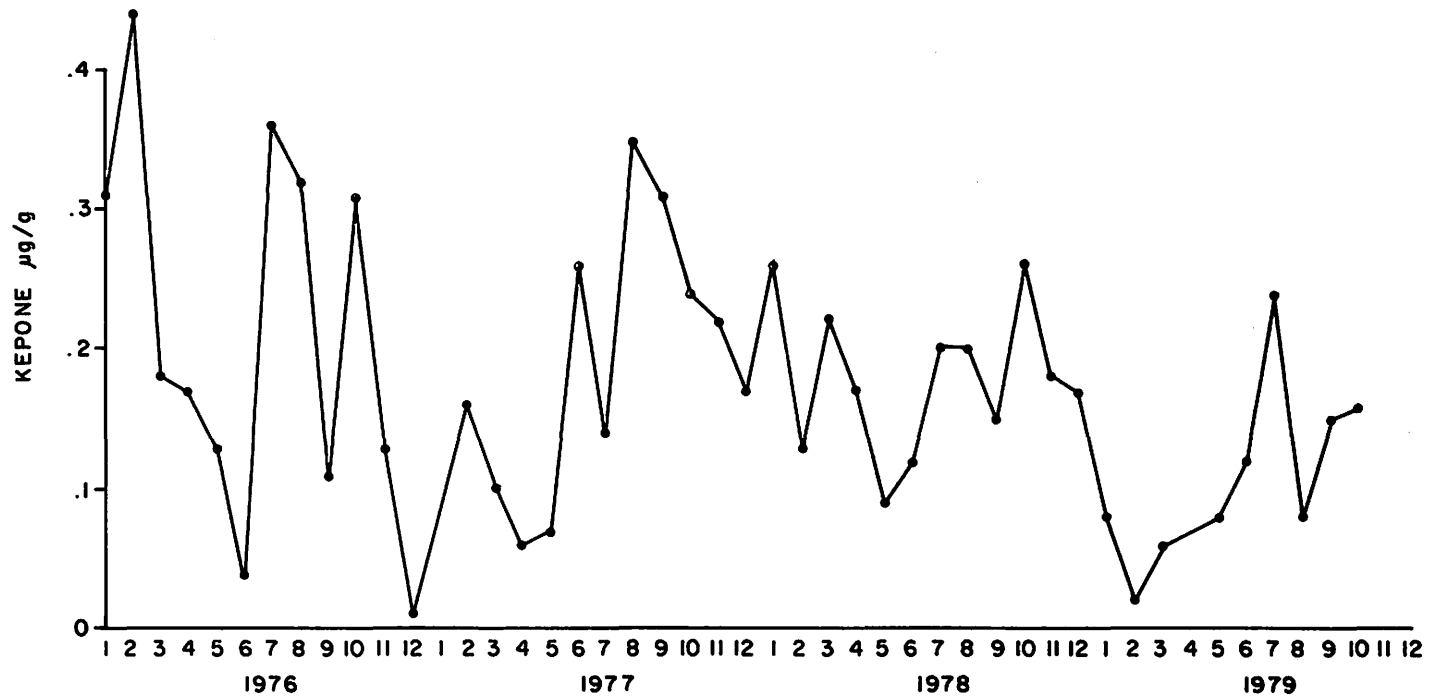


FIGURE 3

