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The role of sediments in the storage, movement and biological uptake of Kepone in estuarine environments : annual report to the Environmental Protection Agency for the period 10/20/76 to 10/20/77

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**The Role of Sediments in the Storage,
Movement and Biological Uptake of Kepone
in Estuarine Environments**

VIMS ARCHIVES

VIMS
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1977

Annual Report

to:

The Environmental Protection Agency

From:

**Robert J. Huggett, Project Manager
The Virginia Institute of Marine Science**

**For the period
10/20/76 to 10/20/77**

**Grant Identification Number
R804993010**

Preface

Included in this document are three sections which describe the efforts of the Virginia Institute of Marine Science's staff on the Role of Sediments in the Storage, Movement, and Biological Uptake of Kepone in Estuarine Environments. The first section is entitled: "Kepone in James River Sediment," by Maynard M. Nichols and Richard C. Trotman. The second, "Kepone Water-Sediment Elutriates," by Robert J. Huggett and the third, "Uptake of Kepone From Suspended Sediments by Oysters, Rangia and Macoma," is by Dexter S. Haven and Reinaldo Morales-Alamo.

Also attached is a progress report on the EPA funded James River Hydrographical Survey Study which was conducted in the late summer of 1977.

KEPONE IN JAMES RIVER SEDIMENTS

An annual progress report to EPA

by .

Maynard M. Nichols and Richard C. Trotman

October 1977

1. Purpose.

This study aims to determine where kepone has accumulated in the bottom sediments; that is, where are the sediment sinks for kepone? A second aim is to trace the routes and rates of transport; that is, what happens to kepone-bound sediment when released from its source? Finally, how long will it take to reduce levels of kepone in the sediment by natural processes?

Results emerging from the study are of use to advise state and federal authorities how to clean-up kepone pollution through natural processes. They provide basic data on sedimentary processes for benthic ecosystem models; they are of use for evaluating the effects of dredging kepone-rich sediments. As a tracer of sediment, kepone provides new information on sediment dispersal and the circulation of fine-grained material in a classic estuary.

2. Highlights of Activities.

Efforts during the period were highlighted by the following:

- Review of James River sediment data to predict fate of kepone for program formulation.

- Presentation of paper on results historical review, First Kepone Seminar, at VIMS, October 1976.
- Preliminary field sampling of surface sediments along length of James in three periods, September, December 1976, and March 1977; 37 to 52 stations sampled during each period; 18 cores obtained.
- Co-ordination conferences with EPA program manager, Dr. Tudor Davies, Gulf Breeze and Virginia State Water Control Board, October through December, 1976.
- Employment of project personnel, Mr. Richard Trotman, completed April 1977; sedimentologic effort in full swing.
- Liason with Battelle Northwest, Dr. Onishi, on field programs and math model formulation.
- Liason with Manhattan College, Dr. D. O'Conner and R. Thomann, concerning formulation of a math model for sediment and kepone transport.
- Development of structure for mathematical model of sediment-kepone transport with Dr. Kuo.
- Formulate plans for suspended sediment-kepone field study, May 1977.
- Follow-up sampling of bottom sediments and selected cores of dredge disposal sites, July 1977. Continued lab analyses of these samples and previous samples.

- Preparation for field study; filters, field equipment, and field labs for processing suspended sediment, June through July 1977.
- Field observations, sampling and measurement of kepone on suspended sediment, currents, and related parameters, August 1977.
- Laboratory analyses of suspended sediment samples, total concentration, organic content, September through October 1977.
- Participation in Second Kepone Seminar and kepone Symposium at the 4th International Conference on Estuaries.
- Follow-up sampling of bed sediments in Hampton Roads and lower Chesapeake Bay in conjunction with closing of area to crabbing; 12 stations occupied.
- Field sampling of bed sediments curtailed in October 1977. Data reduction largely complete.

3. Approach.

Efforts during the period mainly consisted of field sampling, laboratory analyses, and data reduction. First, historical data on kepone and James River sediments were reviewed to identify probable kepone sediment sinks and relative rates of deposition. Sampling stations were sited throughout the estuary in relation to water depth, bathymetry, oyster grounds, deposition patterns, dredge and disposal sites, and in relation to the kepone source.

Field procedures were worked out to sample freshly deposited sediment on the bed as well as in cores at selected sites. Laboratory procedures were set up to process samples for particle size and organic content. The horizontal and vertical distributions of kepone were delineated graphically and evaluated with time over one year in relation to basic information concerning sedimentary processes and transport of fine-grained sediment. An attempt was made to determine from field samples the distribution of kepone in relation to particle size and organic content.

4. Methods and Procedures.

Bed sediments were obtained by a Petersen grab with a 0.05 m² bite area or a 7.6 cm (3-inch) diameter corer. The corer was especially constructed for obtaining soft mud with minimal disturbance. Approximately 30 ml of sediment was obtained from the top sediment surface and returned to the laboratory for analyses. Stations were closely positioned by ranging or sextant bearings on buoys and landmarks. Samples were frozen prior to laboratory analyses.

In the laboratory bulk sediment samples were processed for: (1) kepone content, (2) organic matter by loss on ignition, and (3) particle size (percentage sand, silt and clay) by sieving and pipette. Additionally, the sieved fraction, less than 63 μ of samples collected in September and December 1976, was analysed for both kepone content and for particle size by a Coulter Counter. Laboratory methods follow conventional procedures described in

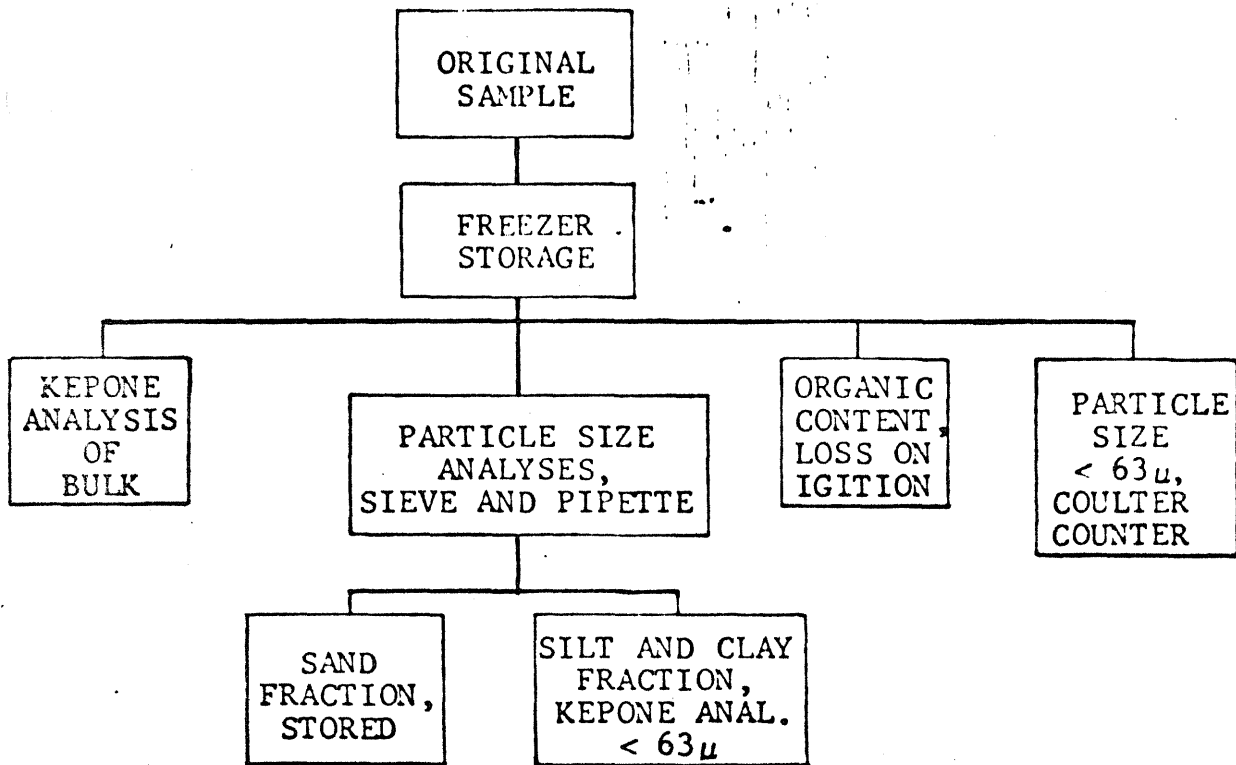


Figure 1. Scheme for laboratory processing of bed sediments.

Moncure and Nichols (1968), Standard Methods (1973) and Folk (1961). Details are given in laboratory instructions on file at VIMS sedimentological lab. Figure 1 summarizes steps in laboratory processing.

5. Results and Their Significance.

Spatial Variability. A special study of variations in kepone concentrations in bulk bed sediment over a small spatial range was conducted at two selected stations: (1) station 15 in lower reaches near Wreck Shoal with 3 m water depth and (2) station 40a in middle reaches at buoy 62 with 6 m water depth. At station 15, four samples were taken at random from the top < 2 cm of sediment and of the top < 15 cm of sediment, all from the same grab. Table 1 lists the results. Spatial variations within the 0.05 m² area of the grab are relatively small with standard deviations less than \pm 7 percent.

Table 1. Variation in kepone concentrations in the top < 2 cm and the top < 15 cm of sediment from a single grab; station 15, June 15, 1977.

<u>Depth Interval</u>	<u>Kepone, ppm</u>	
0-2 cm	0.026	Mean : 0.027 Range : 0.025 - 0.029 Std. Dev.: \pm .002 (\pm 7%)
	0.025	
	0.029	
	0.026	
0-6 cm	0.012	Mean : 0.013 Range : 0.012 - 0.013 Std. Dev.: \pm .001 (\pm 8%)
	0.013	
	0.013	
	0.013	

At station 40a one sample was taken of the top < 2 cm of sediment from 10 successive grabs. The grabs were obtained at random

while the vessel drifted over distances of 225 m downstream and 135 m upstream from the station. Results of the sampling and analyses (Table 2) indicate a very-wide range of values within a distance less than 230 m. Despite the low bottom relief and small textural differences of the sediment at the site, kepone concentrations ranged as much as 0.41 ppm. When surface samples were taken at random from 12 successive grabs at the same station, number 40a, (Table 2) (an anchor station with an area of about 200 m²) the kepone concentrations ranged 0.47 ppm with a standard deviation of 44 percent.

Table 2. Spatial variation in kepone concentrations from the top < 2 cm of sediment of successive grabs at station 40a, July 5, 1977 (drift station) and July 20, 1977 (anchor station).

<u>Drift Station</u>		
<u>Downstream</u> 225 m	<u>Upstream</u> 135 m	<u>Anchor</u> <u>Station</u>
0.062	0.021	0.27
0.074	0.025	0.17
0.081	0.029	0.44
0.067	0.023	0.21
0.096	0.017	0.14
0.110	0.013	0.27
0.130	0.027	0.33
0.340	0.033	0.39
0.360	0.029	0.34
0.470	0.023	0.61
		0.61
		0.28
	Mean : 0.024	
	Range : 0.013 - 0.033	
	Std. Dev.: 0.006 (25%)	
Mean : 0.179		Mean : 0.338
Range : 0.062 - 0.470		Range : 0.14 - 0.61
Std. Dev.: ± 0.151 (± 84%)		Std. Dev.: ± 0.153 (± 44%)

The marked variations are partly due to the sampling process whereby some surface sediment is necessarily washed in the grab or disturbed at depth. However, most local variations are inherent in the bed sediments which are affected by variations in scour and fill, variations in texture and organic matter. Such variations define rather broad limits which may be placed on the kepone distribution as a function of location. They affect "seasonal" distributions inasmuch as the navigational capability of relocating a station is no better than a circle 130 m in diameter.

Distribution of Kepone in Surface Sediments. The sediments from middle reaches are the most contaminated. As shown in Figure 2, average kepone concentrations in bulk bed sediments from the channel (> 4 m depth) are higher between mile 38 and 52 than near the source (mile 63) or farther seaward in the estuary. This is the zone of the turbidity maximum which lies landward of the inner limit of salt intrusion. Suspended sediment concentrations in this zone are higher than elsewhere most of the year.

When longitudinal distributions of kepone are compared for surveys in December 1976, March 1977, and July 1977, there are no significant trends with time. Instead the concentrations are relatively stable within a range of about 0.10 ppm. However, the average levels of concentration from December 1976 through July 1977 in middle reaches (0.15 ppm) are generally

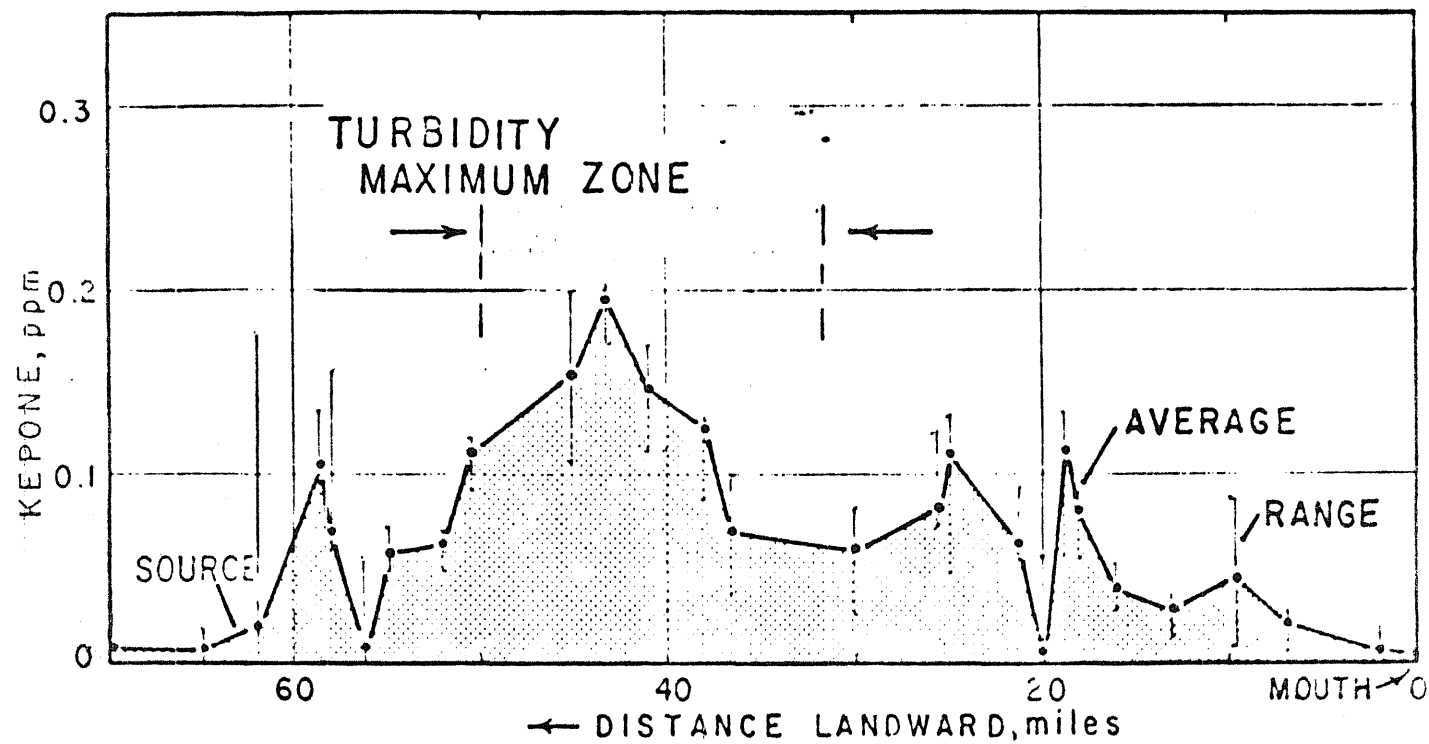


Figure 2. Longitudinal distribution of average kepone concentrations in bed sediments from the channel of the James Estuary; mean of December 1976, March and July 1977 values.

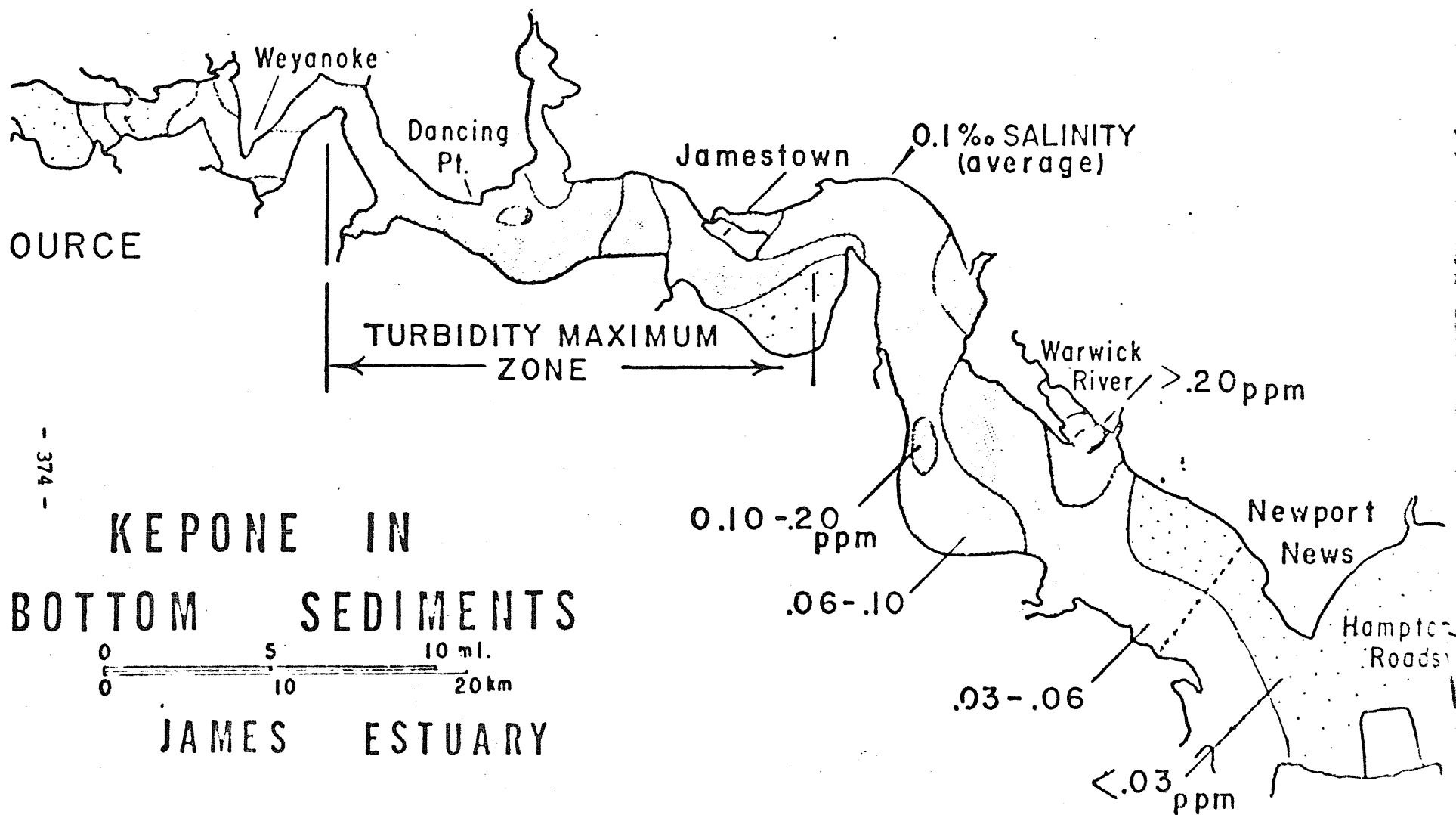


Figure 3. Horizontal distribution of average kepone concentrations in bed sediments; mean of December 1976, March and July, 1977 values.

lower than those measured earlier by VIMS in September 1976 and by the Corps of Engineers in January 1976 when concentrations were 0.27 to 0.48 ppm.

The zone of high sediment contamination covers both channels and contiguous shoals. As shown in plan view, Figure 3, average concentrations are higher in the reach between Jamestown and Weyanoke than elsewhere. The highest average concentration is in sediment from a shoal off Dancing Point. Elsewhere, concentrations are locally high off mouths of tributary creeks such as Bailey's Creek near the kepone source, Chippokes Creek, The Thorofare, Jamestown and the Warwick River. Substantial concentrations, ranging 0.66 to 1.20 ppm, are found in Burwell Bay. However, concentrations are relatively low in narrowed reaches around Hog Point. Kepone content generally diminishes seaward from Burwell Bay to Hampton Roads where concentrations are less than 0.010 ppm. Twelve sediment samples from lower Chesapeake Bay in September 1977 all had concentrations less than 0.010 ppm.

Distribution of Kepone at Depth in Sediments. Contamination of bed sediments in zones of natural fill (undredged) extends to about 40 cm below the bed surface (Figure 4). Greatest contamination, often exceeding 0.50 ppm, occurs at depths of 10 to 20 cm below the surface. However, in cores from shoals in the shipping channel where sedimentation is locally fast (i.e., 30a), concentrations increase downward to a depth of 60 to 80 cm. This trend reflects the diminished supply of kepone-rich sediment with

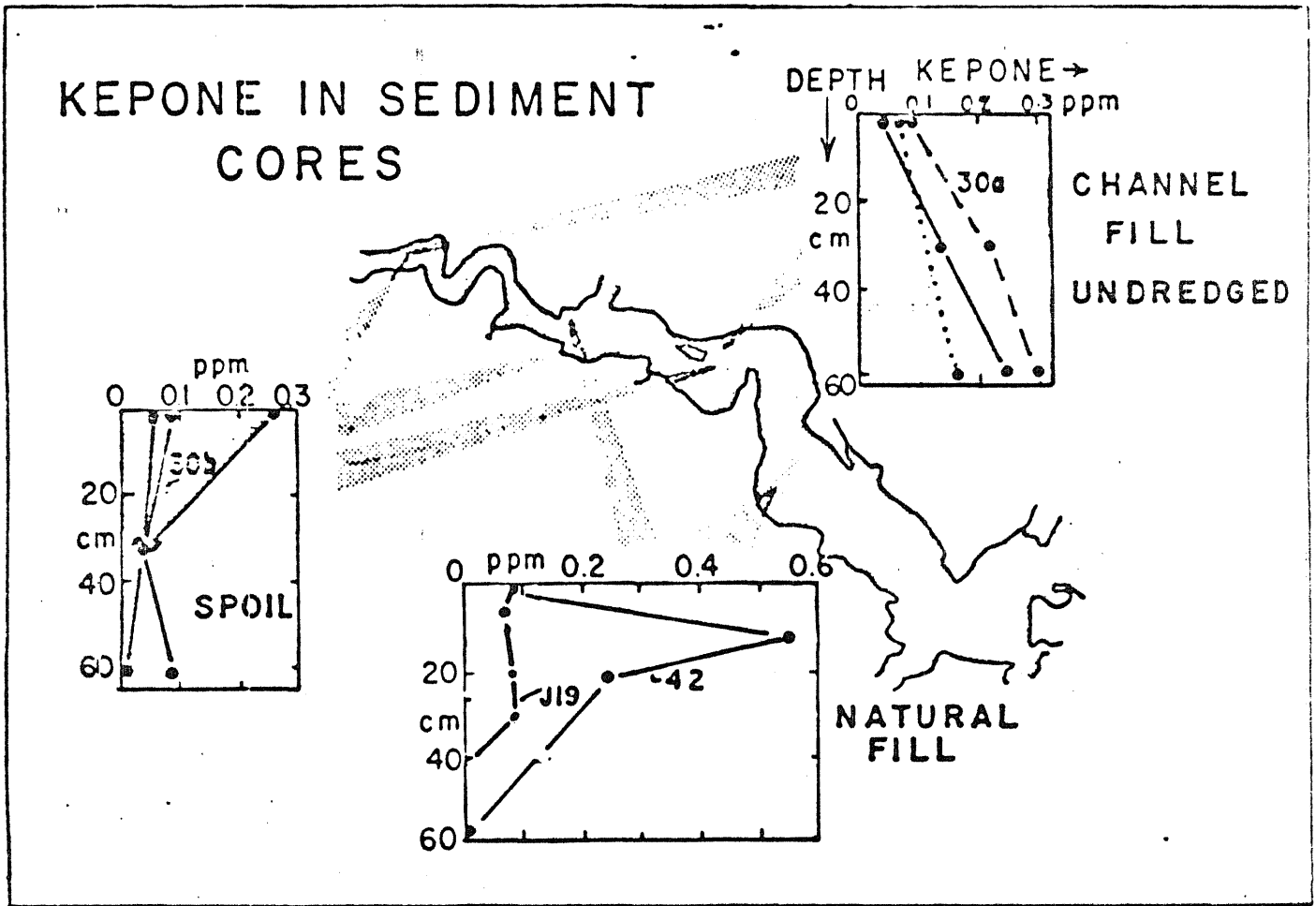


Figure 4. Depth distribution of kepone in cores from selected sites.

time since the Summer of 1975. Kepone content of old dredged material decreases slightly with depth (i.e., cores 41a, 30b, 1.9-7.5). The depth trend results from mixing of sediment during dredging and disposal. The contaminated sediment is most likely mixed and "diluted" by uncontaminated sediment and thus reduces the overall concentration.

A few samples from the Jamestown-Dancing Point reach collected in May 1967 showed dectable amounts of kepone (.038 and .018 ppm). Although the content is low, the samples suggest that the life span of kepone in the sediments is at least 10 years.

State of Kepone in Sediments. The concentrations of kepone are orders of magnitude greater in the bed sediments than dissolved in estuary water. An indication of the state of kepone storage in the sediments is gained by examining its relation to percent clay content, mean particle size and organic content.

Finer-grained sediments are generally the most contaminated. A plot of mean grain size versus kepone concentrations throughout the estuary (Figure 5a) shows a great deal of scatter. Likewise a plot of percent clay content versus kepone concentrations varies widely (Figure 5b). Part of the scatter results from the great variation in textural types throughout the estuary whereas kepone content partly varies in relation to its source. When kepone content of samples from a single reach of the estuary is considered, however, there is a trend for higher kepone content in the fine-grained sediment with high clay content.

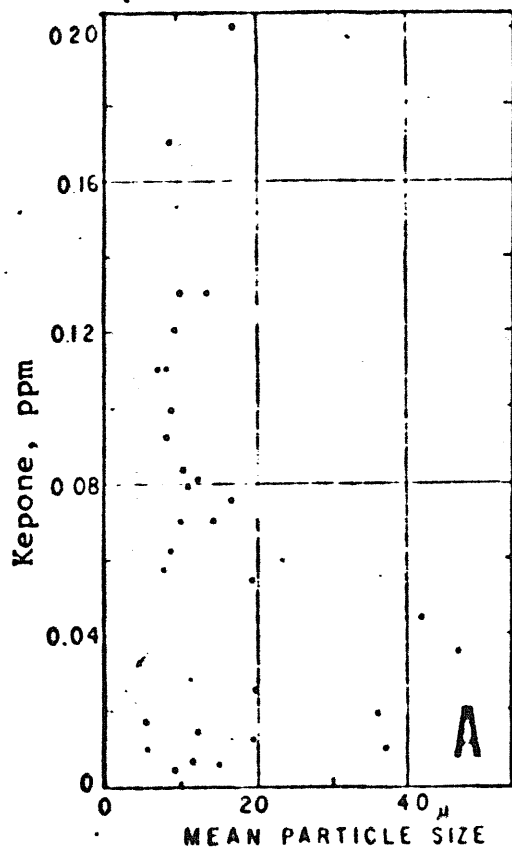
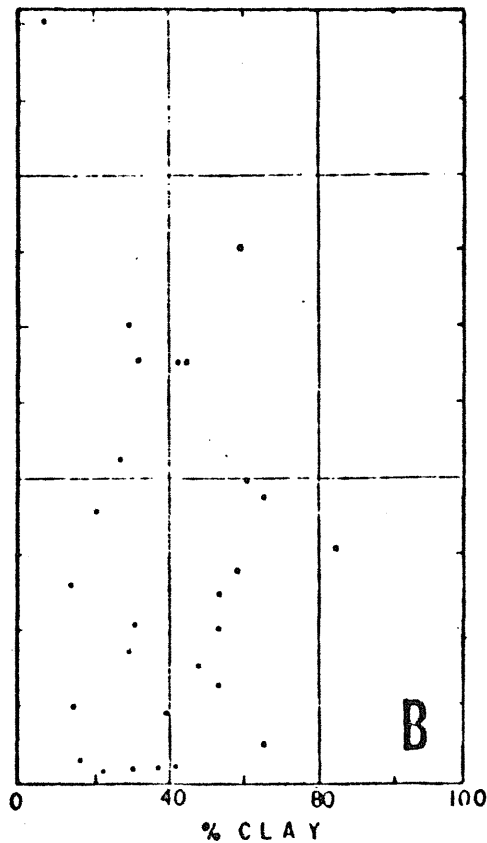
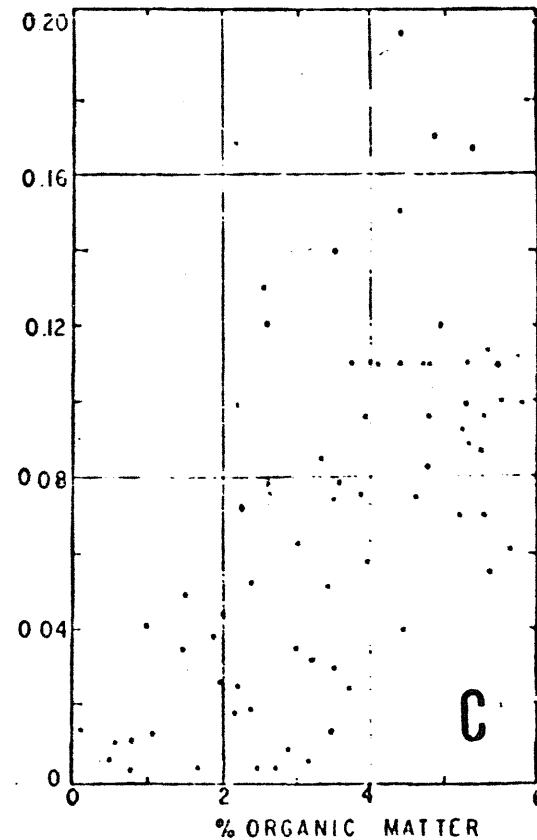


Figure 5a. Kepone content versus mean particle size.



5b. Kepone content versus percent clay content.



5c. Kepone content versus organic matter indicated by loss on ignition.

There is a distinct trend of increasing kepone content with increasing organic content. As shown in Figure 5c, organic-rich sediments have higher kepone content than sediments with low organic content. As expected, samples landward from the kepone source or from zones of scour, display wide scatter. The trend indicates kepone prefers organic matter, either adsorbed on detrital particles or ingested when the organic matter was produced. As organic matter slowly decomposes in the sediment, there is an opportunity for kepone to escape into interstitial or overlying water.

6. Discussion.

Sedimentary Sinks for Kepone. The James Estuary is an environment where much river-borne sediment accumulates. Zones of active deposition may be expected to be areas of relatively high sediment contamination. On the other hand, zones where the bed is scoured into older sediment or zones where river-borne sediments are by-passed, are zones of relatively low contamination. Inasmuch as sedimentary processes are relatively slow, deposition sites are indicators of long-term processes. They are an end product of short-term variations induced by local wave and current transport.

Kepone contamination is generally greatest in sites of active sedimentation: (1) the Jamestown-Dancing Point reach which is also the site of the turbidity maximum, (2) Burwell Bay, and (3) tributary creek mouths. Zones of sedimentation have been

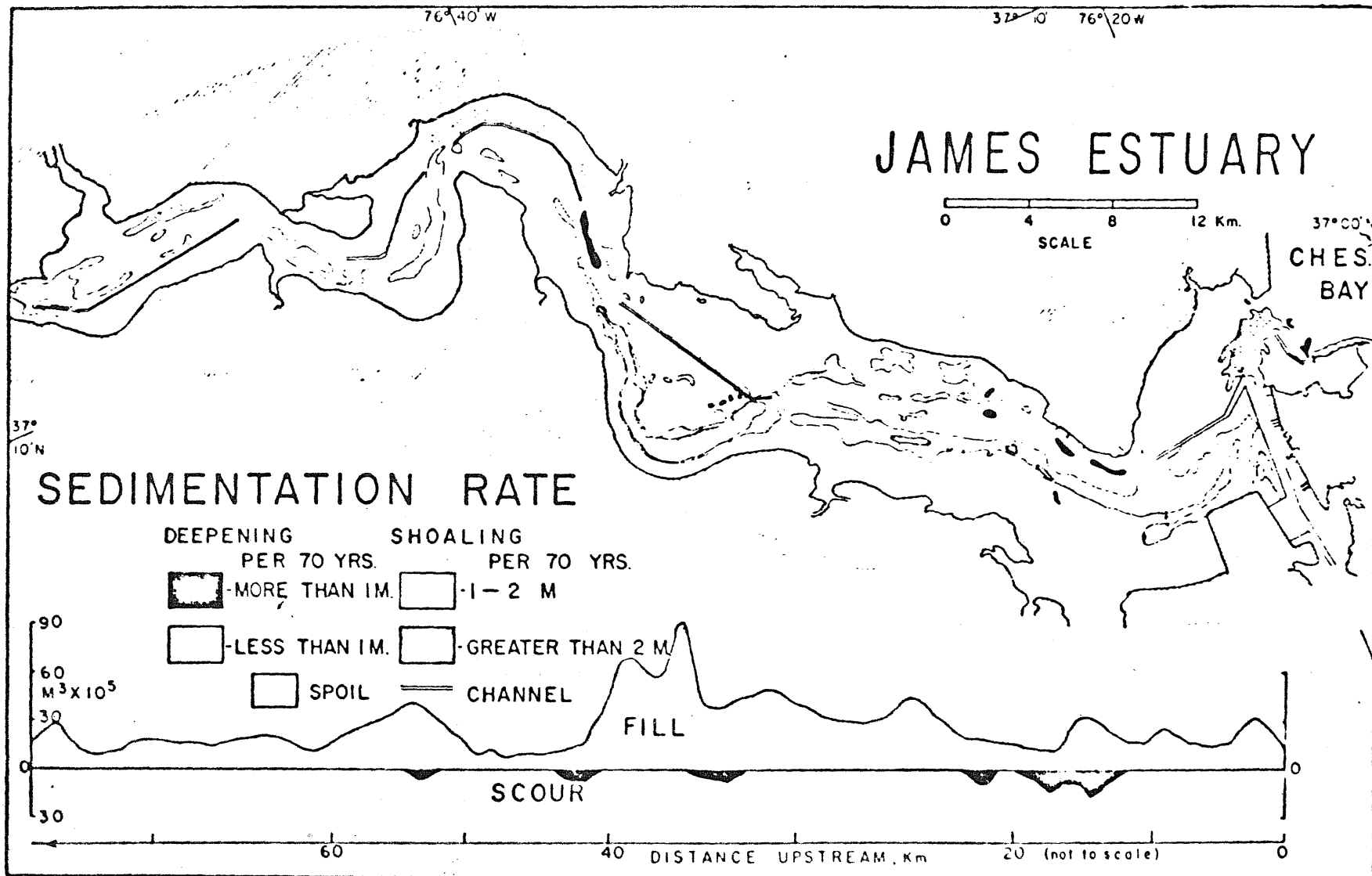


Figure 6. Sedimentation rates in the James Estuary based on water depth changes over 70 years, from Nichols (1972).

delineated in a former study (Nichols, 1972) (Figure 6) from differences in water depths over 35 and 70 years. The rates of sedimentation within the zones probably change with time but the sites of deposition persist.

Kepone concentrations are locally high off the mouth of Bailey's Creek, the kepone source. However, the main distribution does not display decreasing concentrations with distance away from the source. Instead, the main sink is in the middle estuary, the zone of the turbidity maximum where suspended sediments are trapped and deposited. Sediments in this zone are finer-grained than elsewhere, less than 8μ mean size. Clay content in this zone is also higher than elsewhere in the estuary.

Routes of Transport. From the sedimentation patterns, kepone distributions and existing hydraulic knowledge of the James, it is possible to sketch the probable route of kepone-sediment transport. Both the source of kepone and the major source of suspended sediment come from the same direction, landward or upstream of the estuary. Since the influx of sediment from Bailey's Creek is very small in proportion to the influx of sediment from the main river, it is probable the kepone was mainly introduced in the dissolved form and bound to suspended sediment from the main river. Since the estuary is fresh above Jamestown most of the year, net transport from Hopewell to Jamestown is directed seaward. When suspended sediment reaches

the Jamestown area, transport is slowed down because net velocity approaches zero in the null zone at the salt intrusion head. The null zone acts as a dynamic barrier that restricts seaward transport of river-borne suspended sediment carried near the bottom. Only sediment carried near the surface is transported farther seaward through the upper layer. If this sediment settles downward, it is carried back upstream to the null zone by landward density currents through the lower estuarine layer. However, sediment carried over the shoals may escape the estuary through the upper layer especially during floods like Agnes. Nonetheless, the bulk of the sediment load is trapped landward of the null zone. As a tracer of sediment, kepone supports this fact. Most kepone concentrations are located in or above the null zone and they persist with time, both over the short-term, 8 months of sampling, and over the long-term as demonstrated from the distributions at depth in cores. The data indicate that it will take a long time, many years, to reduce levels of kepone in the sediment by natural processes of decay and dispersal. Part of the kepone will be buried by "new" sediment but the most significant reduction will come by "dilution" with uncontaminated sediment introduced during freshets and floods. This trend has already started on the floor of the shipping channel where sedimentation is locally fast.

KEPONE WATER-SEDIMENT ELUTRIATES

Many pollutants have an affinity to sediments which is governed by the surface charges on particles. This is particularly true for some of the trace metals - such as zinc - with the clay mineral portion of the sediments. The magnitudes of the surface charges are affected by pH and salinity (Parks, 1967). Therefore, it was necessary to determine if Kepone behaved in a similar manner because, in the James River, both the estuarine and the tidal fresh water portions with their wide ranges of pH and salinity were contaminated by the pesticide. As well the distribution of Kepone in the bottom sediments of the James show a marked increase in that portion usually in the vicinity of the freshwater - saltwater interface. At this boundary the waters change from fresh, (salinity $<0.5\%$) to saline, (salinities 0.5% to $20 - 25\%$). Also in this region the pH of the water increases from near 7 to 8 due to the buffering capacity of seawater. With these abrupt changes in pH and salinity coinciding with the change in Kepone concentration, it appeared possible that fresh water sediments, highly contaminated with the pesticide, were being "extracted" by estuarine waters as they traversed this boundary progressing seaward or that Kepone in solution was not adsorbed by sediments in saline waters. Therefore, experiments were conducted in the laboratory to determine the extractibility of sediment-Kepone by waters with varying ranges of salinity and pH.

The experimental design included two phases. The first phase was to determine the accuracy and precision of the analysis of water for dissolved Kepone and the second phase was to determine the amount of Kepone removed from contaminated freshwater sediments by waters with pH's ranging from 6 to 9 and salinities of $<0.5\%$ and 20% .

These ranges of pH's and salinities bracket those found in the James River.

Phase I, Water-Kepone Analysis

The method utilized for the Kepone-water extraction was one developed by The Environmental Protection Agency, Research Triangle Park (1975). It involves liquid extraction using benzene as the organic solvent. The extractions are carried out in separatory funnels with 3 successive treatments of the same water with benzene at a ratio of 1:10 benzene to water. The extracts are combined and then dried by passing them through anhydrous sodium sulfate. The combined extracts are then analyzed by electron capture gas chromatography.

To check the efficiency and accuracy of the procedure, Kepone free water, (obtained either from Kepone noncontaminated estuaries such as the York or from laboratory deionized-double distilled stocks), was spiked with known amounts of Kepone, extracted and analyzed (Table I).

Phase II, Water Extraction of Kepone From Sediments.

The experimental design for this phase involved subjecting Kepone contaminated sediments from the James River, obtained from the fresh water portion, near Hopewell, to waters with varying pH's and salinities. The salinities were either fresh, (0.06‰), obtained from the James River or saline, (19.5‰), gotten from the mouth of the York River at the Virginia Institute of Marine Science's facility. The pH's of these waters were adjusted to the desired levels by addition of either reagent grades of hydrochloric acid or sodium hydroxide.

After the desired pH and salinity were achieved, a portion of wet sediment (100 g) was placed in a flask and the water (250 ml)

added and the mixture was agitated with a Wrist-Action Shaker for 1 hr. Following this the sediments were separated by centrifugation and the supernatant water was extracted for dissolved Kepone by the method previously described in the Phase I section of this report.

In all, 36 separate extraction were analyzed and the resulting water Kepone concentrations were compared to that in the exposed sediments. The comparisons are reported as the percent removed by a water of a given pH and salinity in Table II.

Discussion:

The data from Phase I clearly show that the Benzene method of extracting Kepone from water yields approximately 85% or better of the amount of the pesticide from solutions spiked at 1 ppb to 10 ppb. However, at concentrations below 1 ppb the efficiency drops greatly - for instance, 64% yield at 0.5 ppb. These yields can be used to judge the accuracy obtained for Kepone analyses of water by this method. The precision estimates can be seen from the standard deviations which show $\pm 14\%$ or better for spiked solutions of 1 to 10 ppb. The precision of the method for concentrations of 0.5 ppb are in the same range which suggests that a portion of the "spike" may be sorbed to the walls of the glassware or lost by some other means.

Attempts were made to try solvents other than benzene, for extraction, (ethyl acetate - toluene, methylene chloride) but with the similar results - dissolved Kepone at concentrations less than 1 ppb may be 100% in error.

Since only at the 10 ppb Kepone concentration were the effect varying salinities on the analysis compared, it is risky to judge salinity effects on the method. Evenso, there is no obvious effect using natural waters of 0.06 and 19.5‰.

The extraction experiments, the results of which are given in Table II and Figure 1, show that there is no apparent affect of either salinity or pH, within the ranges used which approximate those found in the James River, on the extractibility of Kepone from sediments by water. It must be kept in mind, however, that the amounts of Kepone extracted were in the tenths of ppb range. Since the analytical methodology is less than ideal at these concentrations some differences could go undetected. Figure I shows that all results are within 2 standard errors of each other which implies no difference at the 95% confidence interval.

The data indicate that, if the analyses are correct, the partitioning coefficient of Kepone from sediment to water is approximately 6×10^{-4} , irrespective of natural ranges of pH and salinity. It follows then, that the relatively high concentrations of Kepone at the fresh water-salt water interface and upstream are likely due to the turbidity maximum (mentioned in the sediment section) rather than chemical factors such as partitioning.

References

Environmental Protection Agency, 1975, Preliminary Report on Kepone levels from Hopewell, Va area. Briefing at Research Triangle Park, North Carolina

Parks, G. A., 1967. Aqueous Surface Chemistry of Oxides and Complex Oxide Minerals: Equilibrium Concepts in Natural Water Systems, p. 121-160. In Gould, F. (Ed),--Advances in Chemistry, Series 67. American Chemical Society Publications.

TABLE I

Extraction Efficiencies of Kepone from
Water by the Benzene Method

Salinity	Adjusted pH	Spiked Kepone Concentration	% Recovery
0%, Deionized H ₂ O	7.0	10ppb	96%
"	"	"	99%
"	"	5ppb	87%
"	"	"	90%
"	"	"	78%
"	"	"	94%
"	"	"	95%
"	"	1ppb	97%
"	"	"	72%
"	"	"	93%
"	"	"	69%
"	"	"	93%
"	"	"	56%
"	"	"	102%
"	"	"	85%
"	"	"	86%
"	"	"	96%
"	"	"	83%
"	"	0.5ppm	72%
"	"	"	51%
"	"	"	67%
"	"	"	71%
"	"	"	67%
"	"	"	55%
"	"	"	80%
"	"	"	48%
"	"	"	69%
0.06% James R. H ₂ O	7.0	10ppb	86%
"	"	"	99%
"	"	"	92%
"	"	"	85%
"	"	"	83%
"	"	"	77%
"	"	"	76%

TABLE I (continued)

<u>Salinity</u>	<u>Adjusted pH</u>	<u>Spiked Kepone Concentration</u>	<u>% Recovery</u>
19.5% York R. H ₂ O	8.0	10ppb	74%
"	"	"	85%
"	"	"	73%
"	"	"	99%
"	"	"	74%
"	"	"	103%
"	"	"	99%

TABLE I

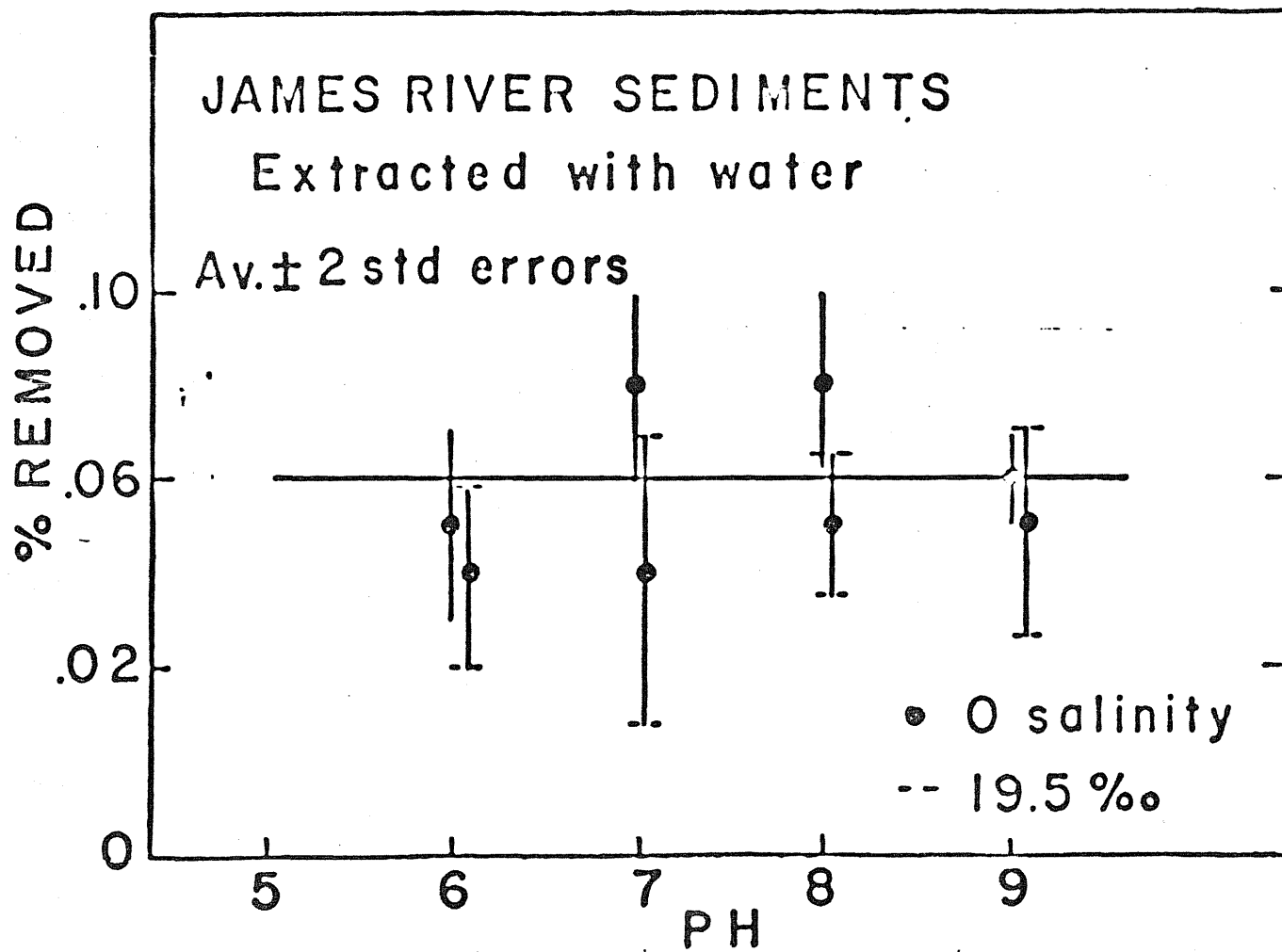
Summary

Salinity	Adjusted pH	Spiked Kepone Concentration	Average yield And Standard dev
Deionized + Distilled	7.0	10ppb	98 ± 2%
"	"	5ppb	89 ± 7%
"	"	1ppb	85 ± 14%
"	"	0.5ppb	64 ± 11%
0.06% James River H ₂ O	7.0	10ppb	85 ± 8%
19.5% York River H ₂ O	8.0	10ppb	87 ± 13%

Elutriate Results

Alkalinity	(Sediment \pm ppm Kepone) pH	Removed	\pm Sd
0.06%	6.0	0.04%	STD. ERROR - 0.01 0.05 \pm 0.01 of total Kepone in sediment recovered at a pH 6.0 + 0.06
"	"	0.06%	
"	7.0	0.11	0.08 \pm 0.04 of total Kepone in sediment recovered at a pH 7.0 + 0.06 STANDARD ERROR 0.01
"	"	0.11	
"	"	0.09	
"	"	0.12	
"	"	0.01	
"	"	0.07	
"	"	0.06	STANDARD ERROR 0.01
"	"	0.06	
"	"	0.11	
"	8.0	0.06	0.08 \pm .02 of total Kepone in sediment recovered at pH 8.0 + 0.06 STANDARD ERROR 0.01
"	"	0.09	
"	"	0.09	
"	9.0	0.05	0.06 \pm 0.01 of total Kepone in sediment recovered at pH 9.0 + 0.06 STANDARD ERROR 0.005
"	"	0.06	
19.5%	5.0	0.03	0.03 \pm ?
"	6.0	0.04	0.04 \pm 0.02 of total Kepone in sediment recovered at pH 6 + 19.5 STANDARD ERROR 0.009
"	"	0.06	
"	"	0.03	
"	7.0	0.02	STANDARD ERROR 0.015 0.04 \pm 0.03 of total Kepone in sediment recovered at pH 7 & 19.5
"	"	0.07	
"	"	0.04	

"	8.0	0.09	
"	"	0.06	
"	"	0.05	
"	"	0.06	
"	"	<0.01	0.05 + 0.02' of total Kepone
"	"	0.05	in sediment recovered at pH
"	"	0.04	8.0 + 19.5'
"	"	0.06	
"	"	0.02	STANDARD ERROR 0.007
"	"	0.05	
"	9.0	0.07	0.05 + 0.02' of total Kepone
"	"	0.05	in sediment recovered at pH
"	"	0.03	9 + 19.5'
			STANDARD ERROR 0.012



UPTAKE OF KEPONE FROM SUSPENDED SEDIMENTS
BY OYSTERS, RANGIA AND MACOMA

Introduction

Laboratory studies on the uptake of Kepone from sediments in suspension by bottom-dwelling organisms were undertaken by the Virginia Institute of Marine Science at Gloucester Point, Virginia on December 1, 1976. The first two months were spent in acquisition and preparation of laboratory equipment and space for the experiments.

In the period of time since then, three series of laboratory experiments were conducted with three species of bivalves. Eight experiments were completed with the oyster Crassostrea virginica, five with the clam Rangia cuneata and one with the clam Macoma balthica. Most of these experiments involved exposure of the animals to contaminated sediments in suspension. In two of them, however, the animals were placed in a bed of contaminated sediments with uncontaminated river water flowing over them.

This report presents the results of three series of experiments followed by a discussion.

Materials and Methods

Apparatus

A diagram of the basic arrangement of the apparatus used to conduct these experiments is shown on Figure 1. The units labelled A through D were used only during the first series of experiments when ambient river water temperature was below 10 C most of the time. York River water was piped

into a constantly-overflowing box (A) from which it was pumped through heat exchangers (C) into a rectangular cascading trough (D). The latter served to allow bubbles created by the escape of dissolved gases to dissipate before reaching the animal trays. This section of the system was not used in the last two series of experiments when river water temperatures were above 10 C. Then, York River water was piped directly into a rectangular trough (E) which was suspended from the ceiling directly above the wet table that held the experimental trays. Water depth in the trough was maintained at 20 cm by a drain standpipe of that height.

Water to supply the experimental trays was siphoned out of trough E with plastic tubing. In the first series of experiments water flow rates were controlled by inserting glass flowmeters (F) in the tubing siphons ahead of the mixing chambers (I). In the last two series of experiments the flowmeters were omitted. Instead, flows were regulated by the bore size of the plastic tubing used for siphons. This eliminated constrictions in the tubing caused by adjustable clamps which enhanced flow interruptions due to clogging. Siphons were cleaned daily and flow measurements made before and after the siphons were cleaned.

Water from the siphons entered a rectangular mixing chamber made of acrylic plastic (I), 25 cm in length, 16 cm in width and 14 cm in height, through a smaller chamber (2 cm long, 3.5 cm wide and 14 cm high). The smaller chamber was connected to the larger one by a circular opening with a 2 cm

diameter. Contaminated sediment suspensions also entered the mixing chamber through the same small chamber. Stock suspensions were kept well mixed in flasks (H) by magnetic stirrers (J). They were metered into the mixing chamber at a constant rate by peristaltic pumps (G).

River water and sediment suspensions were mixed in the mixing chamber by magnetic stirrers. Observation showed that the mixing was complete before the mixture flowed out of the mixing chamber. Sedimentation in the chamber was negligible. The diluted sediment suspensions flowed into the experimental trays (K) through a standpipe located at the end opposite to the one through which water and sediments entered the chamber. The system set up was the same for trays holding control animals except for elimination of components G and H.

In experiments with the clam Rangia cuneata, York River water salinity was reduced to between 5 and 6^o/oo by addition of fresh ground water pumped from a shallow well. A second rectangular trough (P) was suspended below the one receiving York River water (E). York River water was siphoned (Q) from trough E into trough P. Fresh water was also piped into a cascading trough similar to D to eliminate gas bubbles generated by the change in pressure the ground water was subjected to before it flowed into trough P. Water of the resulting lower salinity was then siphoned into the trays holding Rangia clams following the same system setup labelled F through K in Figure 1.

Figure 2 shows a partial view of the apparatus used in the series of experiments.

A system of sediment traps was used to insure that no contaminated sediments from our experiments escaped into the floor drain which emptied into the York River. The first component was the wet table on which the experimental trays were set (L in Figure 1). A standpipe about 2.5 cm high inserted in the drain hole of the wet table converted the table into a sediment trap. A plastic circular tank (50 cm high and 30 cm in diameter) received water from the wet table through a pipe reaching close to the bottom. The tank overflowed near its top into a series of three rectangular boxes (114 cm long and 25 cm wide), each with a 15 cm high standpipe overflow. The third box overflowed into the floor drain. The sediments and other excess solids obtained in the experiments were collected in carboys for disposal.

Experimental Trays

Two types of trays were used to hold experimental animals. In most experiments, a tray made of acrylic plastic 49 cm long, 26 cm wide, and 8 cm high, were used. The overflow end was 6 cm high and that also was the depth of the water in the tray. This tray was not compartmentalized and the animals laid directly on the bottom (Figure 3).

A larger acrylic plastic tray, 81 cm long, 54 cm wide and 8 cm deep was used in the third series of experiments to hold oysters whose biodeposits were collected. A baffle

at the overflow end of the tray maintained water level at a depth of 6.5 cm. These trays were divided into 25 compartments by plastic strips 2.5 cm high. Each compartment held one oyster. The compartments facilitated separation and collection of biodeposits.

Biodeposits

Biodeposits produced by oysters receiving contaminated sediments in suspension in the large trays were collected every day with a bulb pipette. The aggregates collected at the end of each weekly period were then analyzed for Kepone. Every time biodeposits were collected, sediments settling out by gravity in the same tray were also collected and the weekly accumulation also analyzed for Kepone contents. Each day, after biodeposits and sediments had been collected, every compartment was cleaned of any remaining sediments.

Animals Buried In Mud

A modification to the manner usually used to expose animals to contaminated sediments, i.e., by flowing sediment suspensions over them, was introduced in the third series of experiments. Oysters and Rangia were buried partially and fully, respectively, in beds of contaminated sediments held in the smaller of the trays described above (Figure 4). The sediment bed was 4 to 5 cm deep. It was made up of unsieved sediments from the same batch used in simultaneous experiments with flowing suspended sediments.

Oysters were pressed into the sediments at about a 30° angle. Up to one-third of their height was below the sediment surface level. The valve area over the gills protruded above the sediment surface. Rangia were pressed into the mud so that almost the whole animal was below the sediment surface level. Within several hours they had buried themselves fully into the sediment so that only their siphons showed. Water flowing over the animals and the sediment bed had no sediments added to it and was approximately two to three cm deep.

Source of Experimental Animals

The animals used were obtained from areas to be free of Kepone^R. Rangia and Macoma were collected from the Rappahannock River and oysters came from the Piankatank River. All three species were acclimated to the experimental temperatures and salinities under flowing-water conditions at least one week prior to use. Analysis before start of each experiment showed them to be free of contamination with Kepone^R.

Preparation of Sediment Suspension

Figure 5 presents a flow chart outline of the steps taken in preparation of Kepone^R contaminated sediment suspensions. All contaminated sediments were collected with a sediment grab sampler at Jordan Point, in the James River at Hopewell and represented the top 6 cm of the bottom. They were trans-

ported to the laboratory in 2 or 3 large plastic bags each containing about 20 kg of material. The contents of each bag was mixed and transferred to smaller bags in fractions of approximately 500 ml in volume. The smaller bags were stored in a freezer until needed. Only sediments collected on the same date were used in any one series of experiments.

When needed, a bag of sediments was thawed, mixed with well water and shaken mechanically in flasks for 12 hours or more. The sediments were then wet-sieved through a 63 μ and the resulting suspension diluted up to 7000 ml with well water. This volume was labelled as stock suspension and given an identification number. It was maintained in suspension by continuous agitation with a magnetic stirrer and bar. Subsequently, to insure homogeneity in dosage, it was divided into measured portions by alternately siphoning a small volume into each of six containers and repeating the cycle until each container had been filled to the desired volume.

The samples in two of the containers, with volumes of approximately 400 and 200 ml, were used to determine the concentration of Kepone in the suspension and the dry weight per unit volume of the sediments in the suspension, respectively. The suspension in the other four containers, usually with volumes of 1200 and 1600 ml, was the material to be introduced into the trays holding experimental animals. The suspensions in the four containers were diluted in a ratio of 1:4 and pumped into the mixing chambers.

medium and high, mean hourly concentrations ranged between 0.040 and 0.153 ppm.

Mean hourly concentrations for the total duration of exposure (one, two, three or four weeks) in experiments where levels were classified as low ranged between 0.027 and 0.058 ppb (Tables 4 and 5). In experiments where levels were classified as medium or high the range of mean hourly concentration was between 0.057 and 0.153 ppb.

Results are presented separately for each of the three bivalve species. No data are presented for the Kepone concentration in animals examined before the start of each experiment or for control animals because in every case they were under the level of detectability of the analytical procedure.

C. sstrea virginica

Figures 6-8 show the concentration of Kepone in oysters examined at weekly intervals after exposure to contaminated sediments in suspension in three series of experiments. The values in parentheses give the mean hourly concentration of Kepone in the sediments for the weekly period that immediately preceded removal for analysis of that particular sample of oysters.

Results of the first series of experiments showed a uniform progression in the concentration of Kepone in oysters with time (Figure 6). There was indication that an asymptotic level had been reached after two weeks. There also was a clear separation between the three lines which represented high, medium and low concentrations in sediments. A uniform progression was also evident in the second series of experiments although the

absolute concentrations attained in oyster meats were lower than in the first series and there was no indication that an asymptotic level had been reached (Figure 7). In the third series there was neither a uniform progression nor suggestion of an asymptotic level.

The three sets of lines in Figures 6-8 did not appear to share a common pattern. However, they did show that the higher concentrations in oyster meats were associated with the higher concentrations in the sediments and vice versa. When the values for Kepone concentration in oyster meats in the three series of experiments (Tables 1-3) were grouped into three classes according to selected concentration ranges it was found that the values for Kepone in sediments also separated into three fairly distinguishable groups with different means. Eleven sediment values associated with concentrations in oyster meats between 0 and 0.10 ppm had a mean of 0.038 ppb (range: 0.020 - 0.098 ppb). Twelve values for concentration in sediment associated with concentrations in oyster meats between 0.101 and 0.199 had a mean of 0.058 ppb (range: 0.023 - 0.088 ppb). Five values for sediments associated with concentrations in oyster meats of 0.20 ppm or greater had a mean of 0.095 ppb (range: 0.070 - 0.113 ppb).

A plot of concentration of Kepone in oyster meats as a function of concentration in suspended sediments appears in Figure 9. Regression analysis showed a correlation between the two sets of data (correlation coefficient = 0.781).

Having obtained this correlation, the values for concentration in oyster meats were normalized on the basis of a constant, hourly

concentration of Kepone in the sediments. The mean hourly concentration of Kepone in sediments for the whole duration of each experiment (approximately four weeks) was chosen as the normalization constant. The computed means appear in Table 4.

Plots of the normalized values for oyster meat concentrations appear in Figure 10 and 11. The marked dips in meat concentrations after two and three weeks of exposure during the third series of experiments have been eliminated in the normalized curves. The normalized curves suggest that an asymptotic level is reached after the first week of exposure in that series.

The curves for the first and second series were slightly altered by the conversion but the original trends shown were not appreciably changed. The curves for the first series still indicate an asymptotic plateau. Curves for the second series, on the other hand, still show a trend of increasing concentration in oyster meats with time. The high value seen for the third week in the broken line for the first period results from a relatively high value in the meats in the original data while the corresponding value in the suspended sediments was relatively low (medium concentration, Table 1).

There were significant differences in the temperatures at which the three series of experiments with oysters were conducted (Table 6). In the first series, York River water had to be heated to raise it to desirable levels. The minimum and maximum daily temperatures recorded near the source of our river water supply for each of the weekly periods included in the experiment were: 1st week, 3.2-7.6°C; 2nd week, 6.4-10.4°C; 3rd week, 9.0-12.8°C; and 4th week, 10.0-12.0°C. Water temperatures in the

experimental trays ranged between 14.0 and 21.0°C during the four weeks included, with the average being between 17 and 18°C for each of the weekly periods.

The second and third series of experiments were conducted at ambient temperatures. These ranged between 18.3 and 25.7°C during the four weeks of the second series with an average for each week in the range of 20.9 to 23.5°C (Table 6). During the third series the overall range was 25.0 to 34.0°C with the weekly average ranging between 26.6 and 29.6°C.

During the first series of experiments, daily salinities ranged between 17.5 and 22.1‰ for the four weeks, and the weekly average ranged from 18.4 to 20.4‰ (Table 6). During the second series, the corresponding salinity ranges were 16.2 - 20.3‰ and 17.1-19.4‰. Likewise, the ranges of the corresponding averages for the third series were 20.2-23.6‰ and 20.6-23.1‰.

One of the experiments in the third series involved weekly analysis of Kepone concentration in the meats of oysters that had been held partially buried in an undisturbed bed of contaminated sediments. York River water flowing over the sediment bed was uncontaminated by Kepone. The concentration of Kepone in the sediments forming the bed averaged 1.77 ppm in two samples analyzed before the oysters were introduced (Table 7). A mixed sample from the same tray analyzed after the oysters were removed showed a concentration of 2.89 ppm. A sample collected from the top one centimeter layer of the tray after the oysters were removed had a Kepone concentration of 2.24 ppm.

After one week in the sediment bed the Kepone concentration in two samples of oysters averaged 0.037 ppm (Table 7). The

concentration in oyster meats decreased gradually during the next three weeks below the detectability level of the analytical techniques, i.e., 0.02 ppm.

Mean sizes of oysters used in the three experiments appear in Table 9. They ranged between 7 and 8 cm in height during the first and third series of experiments and between 5 and 6 cm in the second series.

Oyster Biodeposits

Oysters concentrated Kepone in their biodeposits to levels thousands of times higher than those found in the suspended sediments (Table 8). The concentration factors for feces ranged from 11,000 to 55,000. In pseudofeces, the range was between 3,000 to 20,000. The concentration in feces was always higher than that in pseudofeces but the magnitude of the difference varied considerably between the paired samples compared.

Concentration of Kepone in sediments that settled by gravity in the tray compartments was usually slightly higher than those in pseudofeces. However, it was also significantly lower than that in feces.

Rangia cuneata

Five experiments were conducted with the wedge clam Rangia cuneata during the second and third series of experiments. In four, animals were exposed to contaminated sediments in suspension and in one they were buried in a bed of contaminated sediments.

The results obtained for Rangia during the second series of experiments are almost identical to those obtained for oysters during the same series (Table 2, Figures 12 and 7). Most of the actual values found at any one weekly interval were close and the line trends are similar.

The data for Rangia in the third series of experiments were somewhat different from those for oysters (Table 3, Figures 13 and 8). Distribution of the weekly values for Rangia meats tended to remain at approximately the same level after the first week with a slight dip in the third week samples. The oyster data showed a greater vertical displacement of the weekly values. The data for both animals showed a fairly distinct separation between the lines for low and high Kepone concentrations in the sediments.

Rangia buried in undisturbed contaminated sediments accumulated Kepone to low levels (Table 7, Figure 13). After the first week high of 0.05 ppm there was a gradual decrease with time to 0.03 ppm after four weeks. Rangia receiving low concentrations of Kepone in suspension accumulated slightly more Kepone than those buried in the sediments even though the latter had a Kepone concentration several thousand times greater (2 ppm in the bed sediments vs. 0.02 to 0.06 ppb in the water column).

Water temperatures in the trays holding Rangia during the second series of experiments were slightly lower than during the third series (Table 6). The range during the second series was between 18 and 20°C and during the third series it was between 20 and 22°C. There was substantially no difference in water salinities during the two series.

Mean sizes and Rangia used in these experiments appear in Table 10. They ranged between 4 and 5 cm in height.

Macoma balthica

A single experiment was conducted with the clam Macoma balthica during the second series. The Macoma were held in the

same tray with oysters receiving sediments in suspension at a high concentration of Kepone. However, they were placed in the tray one week later than the oysters and consequently, they remained in the tray one week after all the oysters had been removed.

The Macoma laid directly on the bottom of the tray and, being fairly small (average height was between 1.4 and 1.7 cm; Table 11) were in close contact with the contaminated sediments that settled on the tray bottom. Sediments settling to the bottom of the experimental trays were removed every two or three days.

The Macoma accumulated Kepone at the fastest rate of the three species studied to date. After three weeks the concentration was 0.33 ppm (Figure 14). During the fourth week there was a slight drop to 0.30 ppm.

Mean water temperatures in the trays holding Macoma ranged between 21 and 24°C during the four weekly periods (Table 6). Mean water salinities ranged between 17 and 20‰.

Mean sizes of Macoma used in these experiments appear in Table 11. They ranged around 1.5 cm in height.

Condition index. Measurements of the meat quality of samples of the experimental animals showed no significant differences between those analyzed at the start of the experiments and those analyzed after approximately four weeks in the experimental trays.

Discussion

The bivalves Crassostrea virginica, Rangia cuneata and Macoma balthica concentrated Kepone from suspended sediments by factors ranging between 1000 and 3000 over that in the water column.

There was little difference in the results obtained for Crassostrea and Rangia. Macoma, however, accumulated Kepone in greater concentrations than the other two species.

Crassostrea and Rangia showed similar trends in uptake of Kepone from suspension. This showed that the two species have similar feeding habits. As suspension feeders, they are reacting in a similar manner to the presence of the sediments in suspension. Such a similarity was reinforced by the experiments in which individuals of the two species were buried partly or fully in a bed of contaminated sediments. Neither one of the two species accumulated much Kepone under those circumstances. Water flow over the sediment beds was relatively slow and the water-sediment interface was not disturbed. Therefore, very little of the sediment was re-suspended. Concentrations in Rangia were slightly higher than those for oysters and if there is any significance to the difference it may be an indication that by being fully buried with its siphon close to the sediment surface, Rangia had access to sediments not available to oysters.

The data for oysters showed a strong correlation between the mean hourly concentration of Kepone in suspended sediments, computed for weekly intervals, and the mean concentration in oyster samples exposed to those sediments during the same weekly period. As illustrated in Figures 6-8, usually the Kepone in oyster meats decreased or increased from one week to the next following a decrease or increase in Kepone in the sediments during the intervening week. The validity of such a correlation is further reinforced by the similarity between the patterns of the curve for low and high sediment concentrations in each of the three series of experiments.

A weaker correlation (0.614) was also found in the data for Rangia. Further collection of data for Macoma will be necessary before it can be determined if the relationship holds for that species.

This correlation indicates that, at the temperatures included, oysters and possibly other bivalves such as Rangia and Macoma depurate themselves of Kepone continuously at the same time that they ingest and accumulate it. Therefore, in order for the Kepone level to remain at a high level, the Kepone concentration in suspension will also have to remain at a correspondingly high level.

Consequently, disturbance of river bottoms contaminated with Kepone by natural processes or other processes initiated by man, which would result in an increase in the suspended sediment load, appear to be capable of causing a sharp increase in the levels of Kepone in individuals of bivalve populations within reach of the increased load. On the other hand, it would appear that such an increase in Kepone in the affected animals would also decrease sharply once the disturbance is terminated.

It is difficult to evaluate with the data obtained to date the influence of temperature on the uptake and depuration of Kepone by oysters and Rangia. More data are required to establish that.

Further studies are planned to investigate this relationship between Kepone in sediments and in bivalves. The effect of concentrations in the sediments higher than those tested so far will be considered. The effect of higher water flows capable of

causing suspension of surface sediments in a bed holding buried animals will also be studied. Experiments that include combinations of contamination and depuration of bivalves will also be conducted.

The levels of Kepone flowing over animals in experimental trays have been fairly low - never higher than 0.15 ppb in the water column - in the experiments conducted so far. This has been dictated by restrictions in the capability of our system and personnel to maintain larger quantities of sediments in stock suspensions and flowing over the animals around the clock for four weeks. Changes required to achieve higher sediment concentrations will be implemented in the forthcoming series of experiments.

The data indicate that a leveling in the concentration of Kepone in oysters and Rangia occurs after the first week of exposure. This was seen best in the curves obtained by normalization of the data using as a constant the mean hourly concentration of Kepone in the sediments for the duration of each experiment. Since no animal samples were analyzed for a period shorter than one week it is quite possible that the leveling may occur sooner than one week. Either way, this is another indication of the efficiency of these bivalves to depurate themselves of Kepone since it is evidently a balance between uptake and depuration that is responsible for the leveling off in the curves.

Analysis of oyster biodeposits indicated that Kepone is concentrated in feces to levels many thousand times higher than it is present in the water column. These observations re-emphasize the importance of the effect biodeposition can have on the physico-chemical characteristics of sediments. At the same time

oysters accumulate Kepone in their tissues to levels up to 1000 times that in the water column, they are also re-depositing high concentrations of the chemical on the bottom. This re-deposition is being done in the form of material less likely to be resuspended because of its nature as an aggregate.

Kepone concentration in oyster pseudofeces was not much different than that found in sediments that settled by gravity onto the tray bottom. Therefore, there appears to be no indication that pseudofeces contribute to the deposition of Kepone-rich sediments any more than natural sedimentation would. However, pseudofeces form an aggregate which like feces may also resist re-suspension to a greater extent than naturally-settling sediments.

There is no way to establish to what extent sediments settling by gravity in experimental trays are included in the samples of feces and pseudofeces collected. However, the concentrations recorded for feces are so much greater than in the natural sediments and the bulk of the feces was so obviously greater than the fine blanket of sediments on the bottom of the tray, that it can be safely inferred that their contribution to the values recorded for feces are minimal.

Literature Cited

Haven, D. S. 1950. Seasonal cycle of condition index of oysters in the York and Rappahannock Rivers. Proc. Nat'l Shellfish Assoc. 54: 42-65.

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Table 1. Concentration of Kepone in sediments and in the meats of oysters during successive exposure periods in first series of Kepone uptake experiments. 24 February - 27 March, 1977

Exposure Period	No. days	Sediments Range	(ppb) Hourly Mean	Meats Mean (ppm)	Concentration Factor
<u>Low Sediment Concentration</u>					
1	6.9	0.014 - 0.039 ¹	0.027	0.086	3185
2	14.8	0.014 - 0.066	0.037	0.125	3289
3	21.8	0.003 - 0.045	0.023	0.135	5625
4	29.2	0.015 - 0.046	0.033	0.113	3228
<u>Medium Sediment Concentration</u>					
1	6.9	0.027 - 0.083	0.057	0.130	2281
2	14.8	0.027 - 0.142	0.073	0.160	2078
3	21.8	0.006 - 0.091	0.045	0.185	3854
4	29.2	0.029 - 0.092	0.067	0.133	1900
<u>High Sediment Concentration</u>					
1	6.9	0.040 - 0.197	0.082	0.185	2256
2	14.8	0.054 - 0.197	0.104	0.250	2294
3	21.8	0.008 - 0.133	0.070	0.210	2838
4	29.2	0.044 - 0.137	0.098	0.257	2495

¹Short period of time when no contaminated sediments were being added to the water flowing over the animals (i.e., sediment concentration = 0) are not included in range. However, they were used in computing the mean. This includes the final 8-9 hours when animals were allowed to flush out sediments in their digestive tract prior to removal for analysis.

Table 2. Concentration of Kepone in sediments and in animal meats during successive exposure periods in second series of Kepone uptake experiments. 13 May - 19 June, 1977.

Exposure Period	No. Days	Sediments (ppb)		Meats Mean (ppm)	Concentration Factor
		Range	Hourly mean		
<u>Low Concentration</u>					
Oysters:					
1	7.3	0.024 - 0.078 ¹	0.042	0.039	931
2	14.8	0.024 - 0.058	0.035	0.058	1667
3	22.0	0.017 - 0.040	0.026	0.064	2424
4	29.0	0.028 - 0.055	0.038	0.096	2526
<u>Rangia:</u>					
1	7.3	0.024 - 0.077	0.039	0.025	641
2	14.8	0.024 - 0.057	0.034	0.050	1453
3	22.0	0.016 - 0.039	0.025	0.048	1912
4	29.0	0.028 - 0.054	0.037	0.083	2237
<u>High Concentration</u>					
Oysters:					
1	7.2	0.054 - 0.178	0.098	0.09	905
2	14.7	0.058 - 0.139	0.086	0.16	1860
3	21.9	0.040 - 0.095	0.063	0.11	1732
4	28.9	0.068 - 0.132	0.093	0.23	2484
<u>Rangia:</u>					
1	7.2	0.057 - 0.188	0.104	0.05	521
2	14.7	0.061 - 0.147	0.091	0.14	1545
3	21.9	0.043 - 0.100	0.067	0.11	1644
4	28.9	0.071 - 0.140	0.098	0.22	2254
<u>Macoma:</u>					
1	7.5	0.058 - 0.139	0.086	0.13	1512
2	14.7	0.040 - 0.095	0.063	0.19	2992
3	21.7	0.068 - 0.132	0.093	0.33	3564
4	29.0	0.095 - 0.131	0.098	0.30	3067

¹ Short periods of time when no contaminated sediments were being added to the water flowing over the animals (i.e., sediment concentration = 0) are not included in range. However, they were used in computing the mean. This includes the final 8-9 hours when arrivals were allowed to flush out sediments in their digestive tracts prior to removal for analysis.

Table 3. Concentration of Kepone in sediments and in the meats of oysters and Rangia during successive exposure periods in third series of Kepone uptake experiments. 8 July - 9 August, 1977.

Exposure Period	No. Days	Sediments (ppb)		Meats Mean (ppm)	Concentration Factor
		Range	Hourly mean		
<u>Low Sediment Concentration</u>					
Oysters:					
1	8.0	0.018 - 0.087 ¹	0.047	0.113	2404
2	15.4	0.012 - 0.058	0.020	0.067	3350
3	23.4	0.007 - 0.041	0.020	0.049	2450
4	31.0	0.008 - 0.085	0.035	0.067	2030
<u>Rangia:</u>					
1	8.0	0.020 - 0.097	0.058	0.053	1000
2	15.4	0.014 - 0.066	0.026	0.063	2423
3	23.4	0.008 - 0.044	0.024	0.041	1703
4	31.0	0.008 - 0.082	0.041	0.068	1658
<u>High Sediment Concentration</u>					
Oysters:					
1	8.1	0.046 - 0.223	0.113	0.21	1858
2	15.5	0.031 - 0.096	0.043	0.10	2325
3	23.5	0.019 - 0.078	0.040	0.069	1725
4	31.0	0.019 - 0.195	0.088	0.16	1818
<u>Rangia:</u>					
1	8.1	0.058 - 0.284	0.153	0.12	784
2	15.5	0.039 - 0.121	0.065	0.12	1846
3	23.5	0.021 - 0.086	0.053	0.085	1604
4	31.0	0.023 - 0.230	0.126	0.125	992

Short periods of time when no contaminated sediments were being added to the water flowing over the animals (i.e., sediment concentration = 0) are not included in range. However, they were used in computing the mean. This includes the final 8-9 hours when animals were allowed to flush out sediments in their digestive tract prior to removal for analysis.

Table 4. Normalized values for Kepone concentration in oysters exposed in laboratory trays to suspensions of sediments contaminated with Kepone. Presented as a function of the mean hourly concentration in sediments for the duration of each experiment.

Exposure Period	Length of Exposure (days)	Mean hourly conc. Kepone for each period (ppb)	Mean hourly conc. Kepone for accumulated time periods (ppb)	Actual conc. Kepone in oyster meats ¹ (ppm)	Normalized conc. Kepone in oyster meats (ppm)
<u>First series of experiments (24 Feb - 27 March 1977)</u>					
1	6.9	0.027	0.027	0.087	0.097
2	14.8	0.037	0.032	0.125	0.101
3	21.8	0.023	0.029	0.136	0.177
4	29.2	0.033	0.030 ³	0.113	0.100
1	6.9	0.057	0.057	0.130	0.137
2	14.8	0.073	0.066	0.160	0.137
3	21.8	0.045	0.059	0.188	0.252
4	29.2	0.067	0.061 ³	0.133	0.121
1	6.9	0.082	0.082	0.185	0.203
2	14.8	0.104	0.094	0.250	0.217
3	21.8	0.070	0.085	0.209	0.269
4	29.2	0.098	0.090 ³	0.257	0.236
<u>Second series of experiments (13 May - 11 June 1977)</u>					
1	7.3	0.042	0.042	0.039	0.030
2	14.8	0.035	0.038	0.058	0.059
3	22.0	0.026	0.034	0.064	0.080
4	29.0	0.038	0.035 ³	0.096	0.088
1	7.2	0.098	0.098	0.090	0.078
2	14.7	0.086	0.092	0.160	0.157
3	21.9	0.063	0.083	0.110	0.148
4	28.9	0.093	0.085 ³	0.230	0.213

Table 4, (con'td)
Normalized values in oyster meats

Exposure Period	Length of Exposure (days)	Mean hourly conc. Kepone for each period (ppb)	Mean hourly conc. Kepone for accumulated time periods (ppb)	Actual conc. Kepone in oyster meats ¹ (ppm)	Normalized conc. Kepone in oyster meats ² (ppm)
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Third series of experiments (8 July - 9 Aug. 1977)

1	8.0	0.047	0.047	0.110	0.072
2	15.4	0.020	0.034	0.067	0.104
3	23.4	0.020	0.029	0.049	0.076
4	31.0	0.035	0.031 ³	0.067	0.059
1	8.1	0.113	0.113	0.210	0.133
2	15.5	0.043	0.080	0.100	0.167
3	23.5	0.040	0.066 ³	0.069	0.124
4	31.0	0.088	0.072 ³	0.160	0.131

- 1 Determined analytically
- 2 Normalized value computed proportionally
- 3 Mean value reference used in computing normalized values in oysters

Table 5. Mean hourly concentration of Kepone in sediment suspensions flowing over Rancia and Macoma during the total duration of each period of exposure in experimental trays.

<u>Species</u>	<u>Total duration of exposure (days)</u>	<u>Mean hourly concentration for each weekly period (ppb)</u>	<u>Mean hourly concentration for full period (ppb)</u>
<u>Rangia: Second series of experiments (13 May - 11 June 1977)</u>			
<u>Low sediment concentration</u>			
	7.3	0.039	0.039
	14.8	0.034	0.037
	22.0	0.025	0.033
	29.0	0.037	0.034
<u>High sediment concentration</u>			
	7.2	0.104	0.104
	14.7	0.091	0.097
	21.9	0.067	0.087
	28.9	0.093	0.090
<u>Third series of experiments (8 July - 9 August)</u>			
<u>Low sediment concentration</u>			
	8.0	0.053	0.058
	15.4	0.026	0.043
	23.4	0.024	0.036
	31.0	0.041	0.037
<u>High sediment concentration</u>			
	8.1	0.153	0.153
	15.5	0.065	0.111
	23.5	0.053	0.091
	31.0	0.126	0.100

Table 5, Continued

<u>Species</u>	<u>Total duration of exposure (days)</u>	<u>Mean hourly concentration for each weekly period (ppb)</u>	<u>Mean hourly concentration for full period (ppb)</u>
<u>Macoma:</u>	Second series of experiments (8 July - 9 August 1977)		
	<u>High sediment concentration</u>		
	7.5	0.086	0.036
	14.7	0.063	0.075
	21.7	0.093	0.081
	29.0	0.098	0.085

Table 6. Range and mean of water temperature and salinity in trays holding animals during Kepone uptake experiments.

Weekly Period	Temperature (C)		Salinity (o/oo)	
	Range	Mean	Range	Mean
<u>1st Series (Feb. 24 - March 27, 1977)</u>				
<u>Oysters:</u>				
1st	14.0 - 20.8	17.2	19.3 - 22.1	20.6
2nd	15.0 - 21.0	17.7	19.1 - 20.6	20.2
3rd	16.1 - 20.8	18.5	19.1 - 20.1	19.7
4th	14.8 - 19.6	17.0	17.5 - 19.2	18.4
<u>2nd Series (May 13 - June 19, 1977)</u>				
<u>Oysters:</u>				
1st	18.3 - 25.0	20.9	17.5 - 19.2	18.3
2nd	21.3 - 25.0	22.4	16.2 - 17.9	17.1
3rd	22.3 - 25.7	23.5	17.5 - 19.5	18.3
4th	20.5 - 25.0	21.5	18.9 - 20.3	19.4
<u>Macoma:</u>				
1st	21.3 - 25.0	22.4	16.2 - 17.9	17.1
2nd	22.3 - 25.7	23.5	17.5 - 19.5	18.3
3rd	20.5 - 25.0	21.5	18.9 - 20.3	19.4
4th	20.7 - 25.9	23.7	19.9 - 20.0	19.9
<u>Rangia:</u>				
1st	16.6 - 21.2	18.6	0.5 - 7.3	5.5
2nd	18.7 - 20.8	19.5	5.0 - 6.4	5.4
3rd	19.0 - 22.3	20.4	1.3 - 7.9	5.1
4th	18.0 - 21.3	19.2	3.2 - 6.4	5.0
<u>3rd Series (July 8 - August 9, 1977)</u>				
<u>Oysters:</u>				
1st	26.9 - 34.0	29.6	20.2 - 20.8	20.6
2nd	26.8 - 32.0	29.3	20.9 - 22.1	21.6
3rd	25.0 - 30.0	26.6	21.9 - 22.9	22.5
4th	26.5 - 30.9	28.5	22.9 - 23.6	23.1
<u>Rangia:</u>				
1st	20.5 - 24.3	22.9	2.8 - 8.7	5.9
2nd	20.4 - 24.9	22.5	3.9 - 8.8	6.1
3rd	19.0 - 22.0	20.3	4.2 - 6.0	5.4
4th	20.0 - 23.2	21.4	2.3 - 6.8	5.4

Table 7. Concentration of Kepone in the meats of oysters and Rangia held in control trays receiving no contaminated sediments and in test trays partially or fully buried in unsieved sediments contaminated with Kepone. July 8 - August 9, 1977. Means in parentheses.

<u>Exposure Period</u>	<u>Cumulative No. Days</u>	<u>Kepone Conc. in Animals Buried in Sediments (ppm)</u>	<u>Kepone Conc. in Control Animals (ppm)</u>
<u>A. Oysters (partially buried in test trays):</u>			
1	8.5	0.034 0.040 (0.037)	≤ 0.007
2	15.9	0.024	≤ 0.009
3	23.9	0.014 0.015 (0.016)	≤ 0.005
4	31.6	0.014 ≤ 0.009 (≤ 0.007)	≤ 0.004
<u>Rangia (fully buried in mud)</u>			
1	8.5	0.067 0.035 (0.051)	0.011
2	15.9	0.053 0.039 (0.046)	≤ 0.006
3	23.9	0.029 0.038 (0.033)	≤ 0.003
4	31.6	0.034 0.031 (0.032)	≤ 0.007

Table 7 (Continued)

B. Concentration of Kepone (in ppm) in unsieved sediments used in test trays in which animals were fully or partially buried.

1. Mixed samples at start of experiment:	0.71
(Same sediments used in both trays)	2.83
	(1.77)
2. Fractionated and mixed samples at end of experiment:	
a. Mixed sample from oyster trays	2.89
b. Sample from top 1-cm layer in oyster tray	2.24
c. Mixed sample from <u>Rangia</u> tray	2.12
d. Sample from top 1-cm layer in <u>Rangia</u> tray	0.64

Concentration of Polychlorinated Biphenyls (PCBs) and related chemicals settling out by gravity in water during the 1970s

Sample	Year	Number of Samples	PCB Concentration in Sample (ppb)	PCB Concentration in Sample (ppb)	PCB Concentration in Sample (ppb)	PCB Concentration in Sample (ppb)	PCB Concentration in Sample (ppb)	PCB Concentration in Sample (ppb)	PCB Concentration in Sample (ppb)	PCB Concentration in Sample (ppb)	PCB Concentration in Sample (ppb)	PCB Concentration in Sample (ppb)
1	1970	6	1.9	0.016								
2	1971	3	0.33	0.11								
3	1972	7	0.77	0.36	0.15	0.07	0.04	0.02	0.01	0.005	0.002	0.001
4	1973	7	0.77	0.36	0.15	0.07	0.04	0.02	0.01	0.005	0.002	0.001
5	1974	6	0.77	0.36	0.15	0.07	0.04	0.02	0.01	0.005	0.002	0.001
6	1975	7	0.77	0.36	0.15	0.07	0.04	0.02	0.01	0.005	0.002	0.001
7	1976	7	0.77	0.36	0.15	0.07	0.04	0.02	0.01	0.005	0.002	0.001
8	1977	7	0.77	0.36	0.15	0.07	0.04	0.02	0.01	0.005	0.002	0.001
9	1978	7	0.77	0.36	0.15	0.07	0.04	0.02	0.01	0.005	0.002	0.001
10	1979	7	0.77	0.36	0.15	0.07	0.04	0.02	0.01	0.005	0.002	0.001

Table 9. Mean height (in cm) of oysters in different samples analyzed for Kepone during uptake experiments. Number of animals in each sample appears in parentheses.

Exposure Period	Low Kepone conc. in sediments	Medium Kepone conc. in sediments	High Kepone conc. in sediments	Animals Buried in mud	Control Animal
<u>First series of experiments (24 Feb - 27 March 1977)</u>					
1	(4) 6.7 (3) 7.8	(4) 7.2 (3) 7.1	(4) 6.1 (3) 7.0		(4) 7.1 (3) 7.1
2	(4) 7.7 (3) 7.4	(4) 7.6 (3) 7.5	(4) 7.1 (3) 7.0		(4) 7.1 (3) 7.1
3	(4) 7.2 (3) 7.0	(4) 7.3 (3) 7.1	(4) 6.7 (3) 6.6		(4) 7.1 (3) 7.1
4	(4) 7.1 (3) 7.2 (4) 7.8	(4) 6.1 (4) 7.3 (5) 7.3	(4) 7.8 (4) 7.8 (4) 7.4		(4) 7.1 (4) 7.1 (3) 7.1
<u>Second series of experiments (13 May - 19 June 1977)</u>					
1	(8) 5.8		(8) 5.7		
2	(4) 6.0 (4) 5.4		(4) 5.6 (4) 4.3		(2) 7.1 (4) 6.1
3	(3) 6.9 (5) 5.4		(3) 6.4 (5) 4.8		(4) 6.1 (4) 4.1
4	(4) 5.7 (4) 5.1 (5) 5.6		(6) 5.1 (5) 5.5		(3) 6.1 (5) 5.1
<u>Third Series of experiments (8 July - 9 Aug., 1977)</u>					
1	(3) 8.1 (2) 7.7		(3) 7.2 (2) 7.9	(3) 6.6 (3) 7.2	(4) 7.1
2	(3) 7.9 (3) 7.6		(3) 7.6 (3) 7.6	(3) 6.1 (3) 7.4	(4) 7.1

Table 9, Cont'd)

<u>Exposure Period</u>	<u>Low Kepone conc. in sediments</u>	<u>Medium Kepone conc. in sediments</u>	<u>High Kepone conc. in sediments</u>	<u>Animals Buried in mud</u>	<u>Control Animals</u>
3	(3) 7.6 (3) 7.5		(3) 7.5 (3) 7.0	(3) 6.9 (3) 7.3	(4) 7.7
4	(4) 7.1 (4) 6.8		(3) 7.7 (4) 6.3	(4) 7.0 (3) 7.4	(3) 7.7 (3) 8.2

Table 10. Mean height (in cm) of *Rana* in different samples analyzed for Kepone during uptake experiments. Number of animals in each sample appears in parentheses.

Exposure period	Low Kepone conc. in sediments	High Kepone conc. in sediments	Animals buried in mud	Control Animals
<u>Second series of experiments (13 May - 19 June 1977)</u>				
1	(8) 4.9	(8) 4.6		(3) 4.6
2	(4) 4.9 (4) 4.9	(4) 4.3 (4) 4.8		(4) 5.0 (4) 4.8
3	(4) 4.7 (4) 4.7	(4) 4.7 (4) 4.8		(4) 4.7 (4) 4.8
4	(8) 4.6 (8) 4.7 (8) 4.8	(8) 4.7 (8) 4.7 (8) 4.6		(8) 4.5 (7) 4.7
<u>Third series of experiments (8 July - 9 Aug. 1977)</u>				
1	(4) 5.01	(2) 5.31 (3) 4.90	(3) 4.85 (3) 5.04	(5) 5.20
2	(4) 4.99 (4) 4.49	(4) 4.88 (4) 4.92	(4) 4.92 (3) 5.02	(6) 4.74
3	(4) 5.00 (4) 5.15	(5) 5.02 (4) 4.89	(4) 5.12 (4) 4.96	(6) 4.98
4	(4) 5.03 (5) 4.73	(5) 4.83 (6) 4.79	(5) 5.00 (5) 5.24	(5) 4.88 (5) 4.75

Table 11. Mean height (in cm) of Maccma in different samples analyzed for Kepone during uptake experiments. Number of animals in each sample appears in parentheses.

Exposure Period	High Kepone conc. ... in <u>sediments</u>	Control Animals
--------------------	---	--------------------

Second series of experiments (13 May - 19 June 1977)

1	(15) 1.7	(10) 1.6
2	(12) 1.6	(10) 1.6
3	(12) 1.5	(11) 1.6
4	(10) 1.4	(7) 1.6

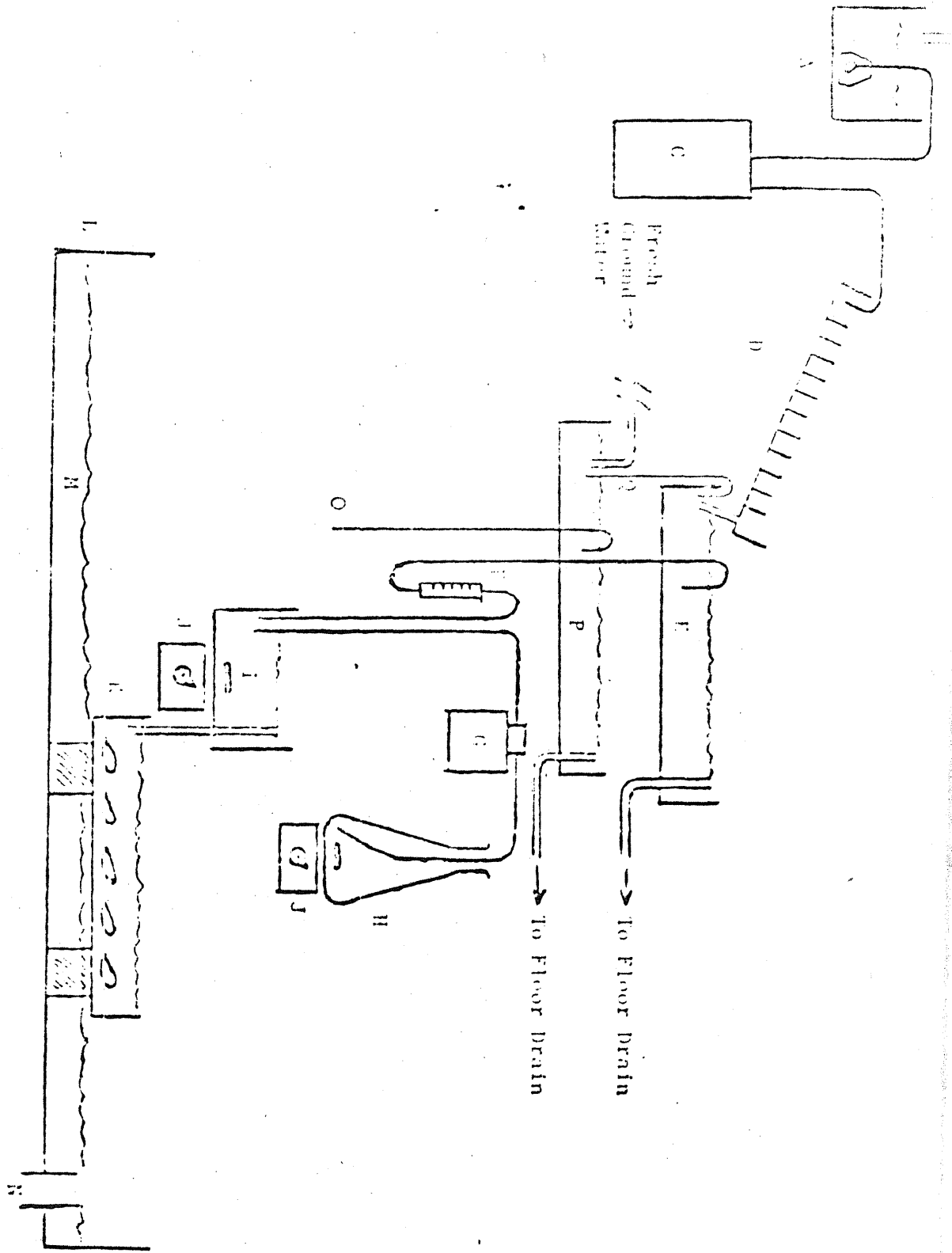


Figure 1. Schematic of apparatus used in uptake experiments with diving collases in three series of experiments. Identification of individual components appears on next page.

Key to identification of components in Figure 1

- A. Constantly-overflowing box providing York River water supply to system.
- B. Submersible pump.
- C. Heat exchanger system.
- D. Cascading trough used to allow escape of gases coming out of suspension as result of river water being heated up.
- E. Constantly-overflowing overhead trough from which water for experimental trays was siphoned.
- F. Flow meter.
- G. Peristaltic pump used to meter out sediment suspension.
- H. Flask holding sediment suspension.
- I. Mixing chamber receiving simultaneously York River water and sediment suspension.
- J. Magnetic stirrer.
- K. Experimental tray holding oysters.
- L. Wet table holding experimental trays.
- M. Drain pipe maintained a water level of about one-inch on wet table. This served as first component of a series of sediment trays.
- N. Water from wet table overflowed into a series of three other sediment traps.
- O. Siphon to mixing chamber of Rangia trays.
- P. Constantly-flowing overhead trough from which water of low salinity for experimental trays was siphoned.
- Q. Siphon used to add river water from Trough E to fresh water in Tray P.

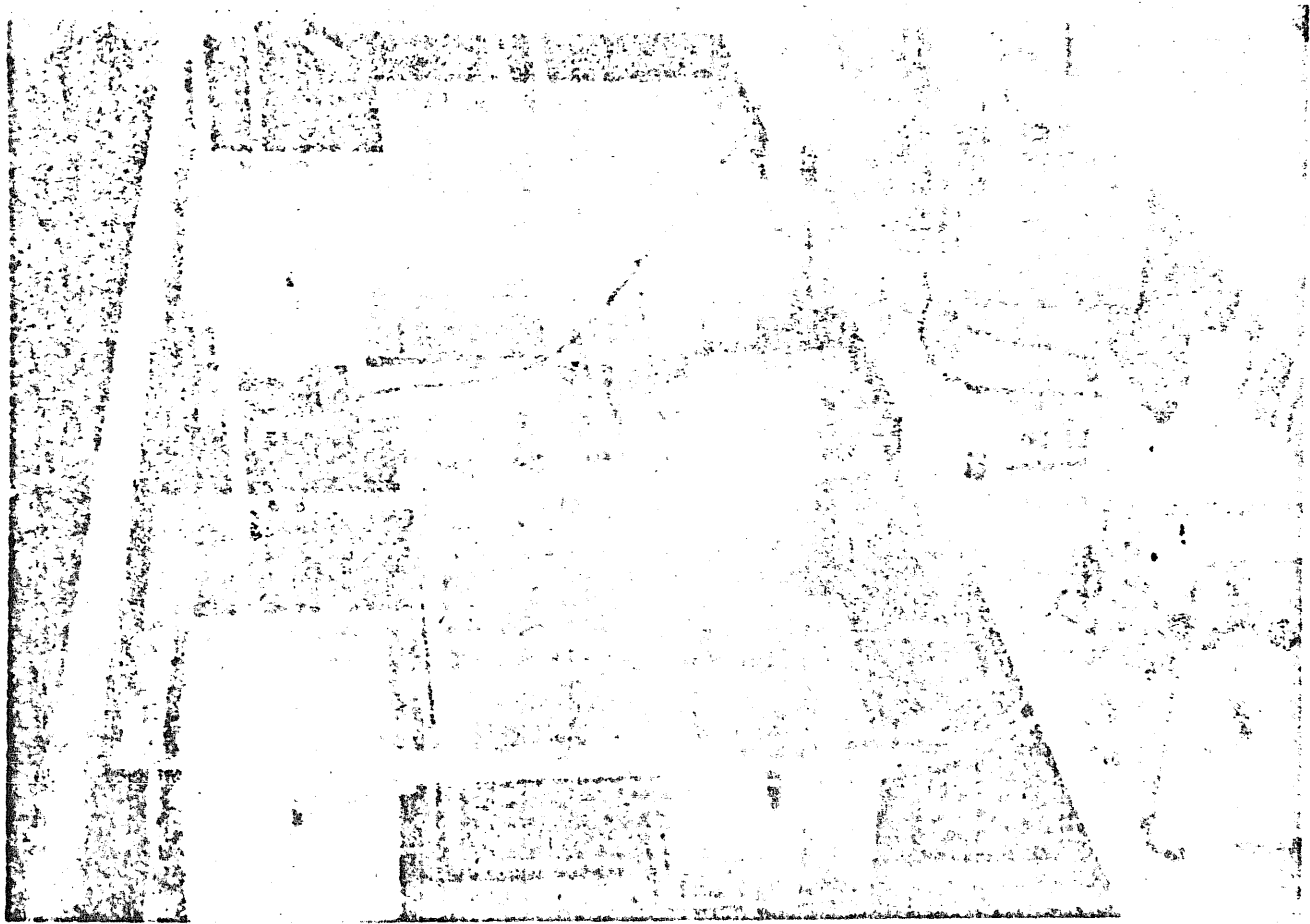


Figure 2. Arrangement of trays, mixing chambers and peristaltic pumps in third series of experiments in which animals received contaminated sediments in suspension. Oysters in large trays and Rangia in small ones.

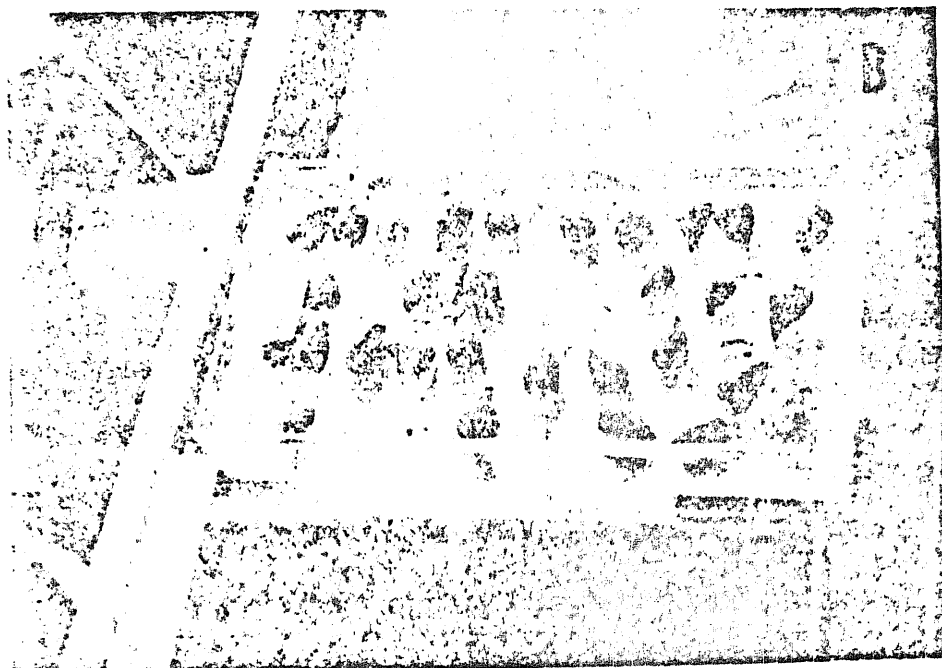
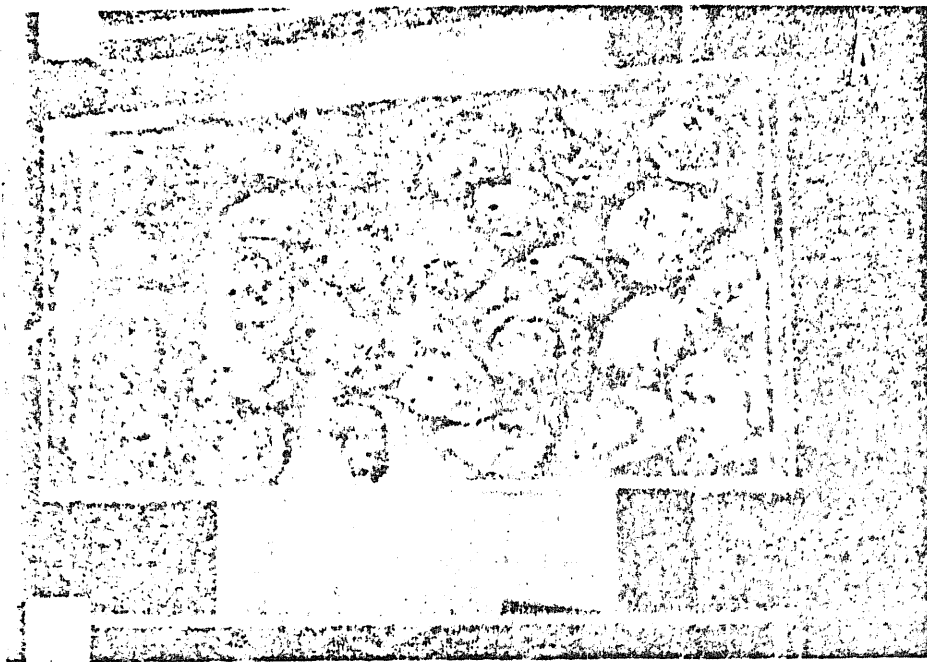


Figure 3. Control oysters (A) and Rangia (B) in small trays at start of third series of experiments.

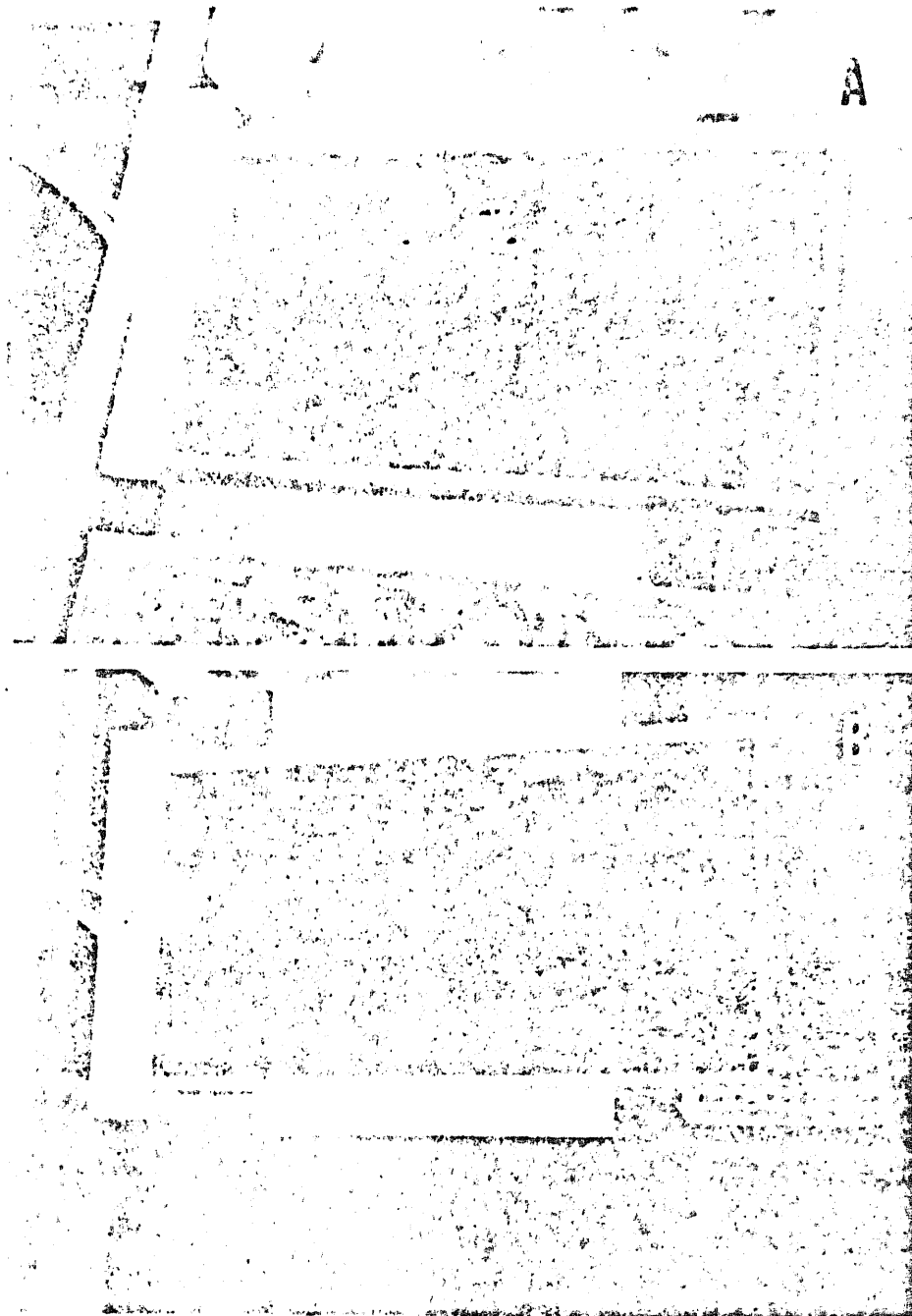


Figure 4. Oysters (A) and Rangia (B) partially buried in bed of sediments contaminated with Kepone at start of third series of experiments. Subsequently Rangia buried themselves fully.

Grab samples collected at
Jordan Point, James River.



Mixed and divided into sub-
samples approximately 500 ml
in volume. Bagged and stored
in freezer.



Bag of sediments thawed.



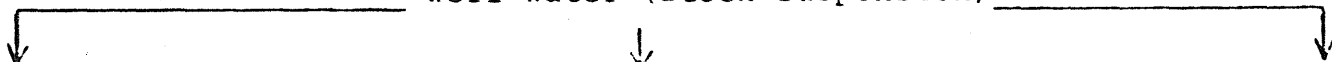
Mixed with well water and shaken
mechanically for 12 hours or
more.



Wet-sieved through 63 u sieve.



Diluted up to 7000 ml with
well water (stock suspension)



Sample taken for determination
of Kepone concentration.

Divided into measured portions

Sample taken for determination
of sediment concentration
(dry weight per unit vol).



Diluted with well water 1:4



Metered into experimental trays
and mixed with inflowing river
water at predetermined rates to
approximate predetermined dilutions.

Figure 5. Flow chart showing steps taken in preparation of sediments contaminated with Kepone for introduction into trays holding experimental animals.

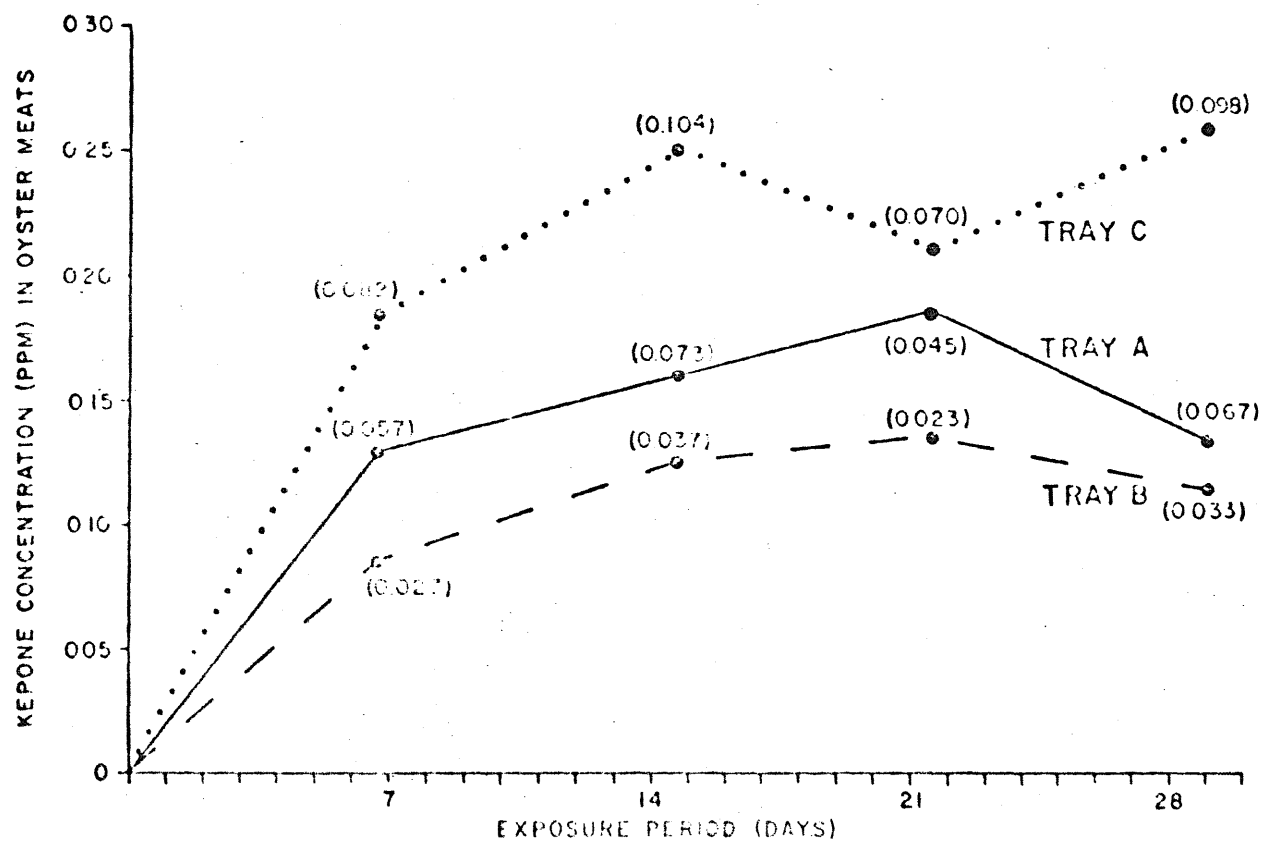


Figure 6. Mean concentration of Kepone in meats of oysters exposed to contaminated sediments in suspension. First series of experiments, 24 Feb.-27 March 1977. Figures in parentheses are mean hourly concentration of Kepone in sediments for the period ending at that point.

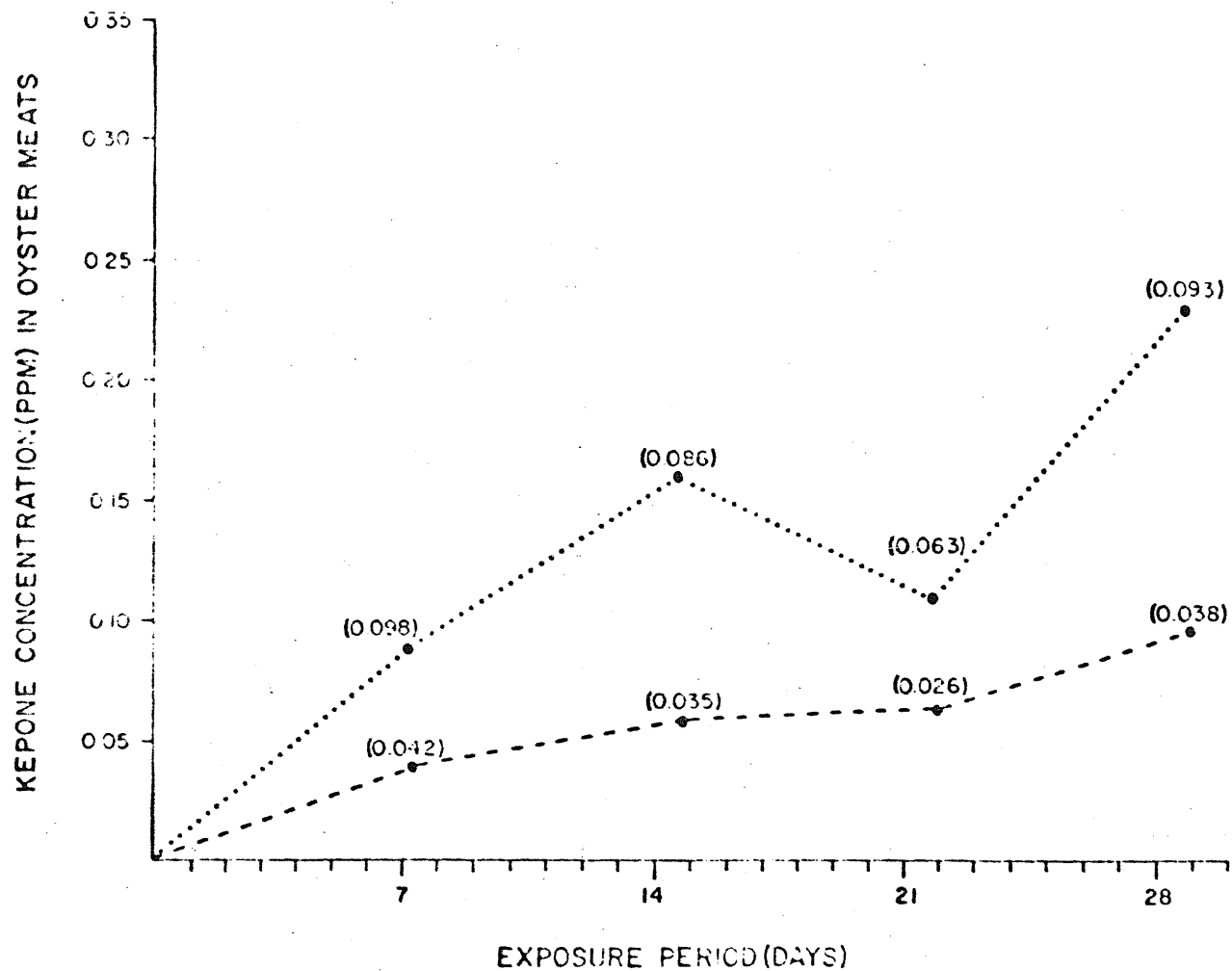


Figure 7. Mean concentration of Kepone in meats of oysters exposed to contaminated sediments in suspension. Second series of experiments, 13 May-11 June 1977. Figures in parentheses are mean hourly concentration of Kepone in sediments for weekly period ending at that point.

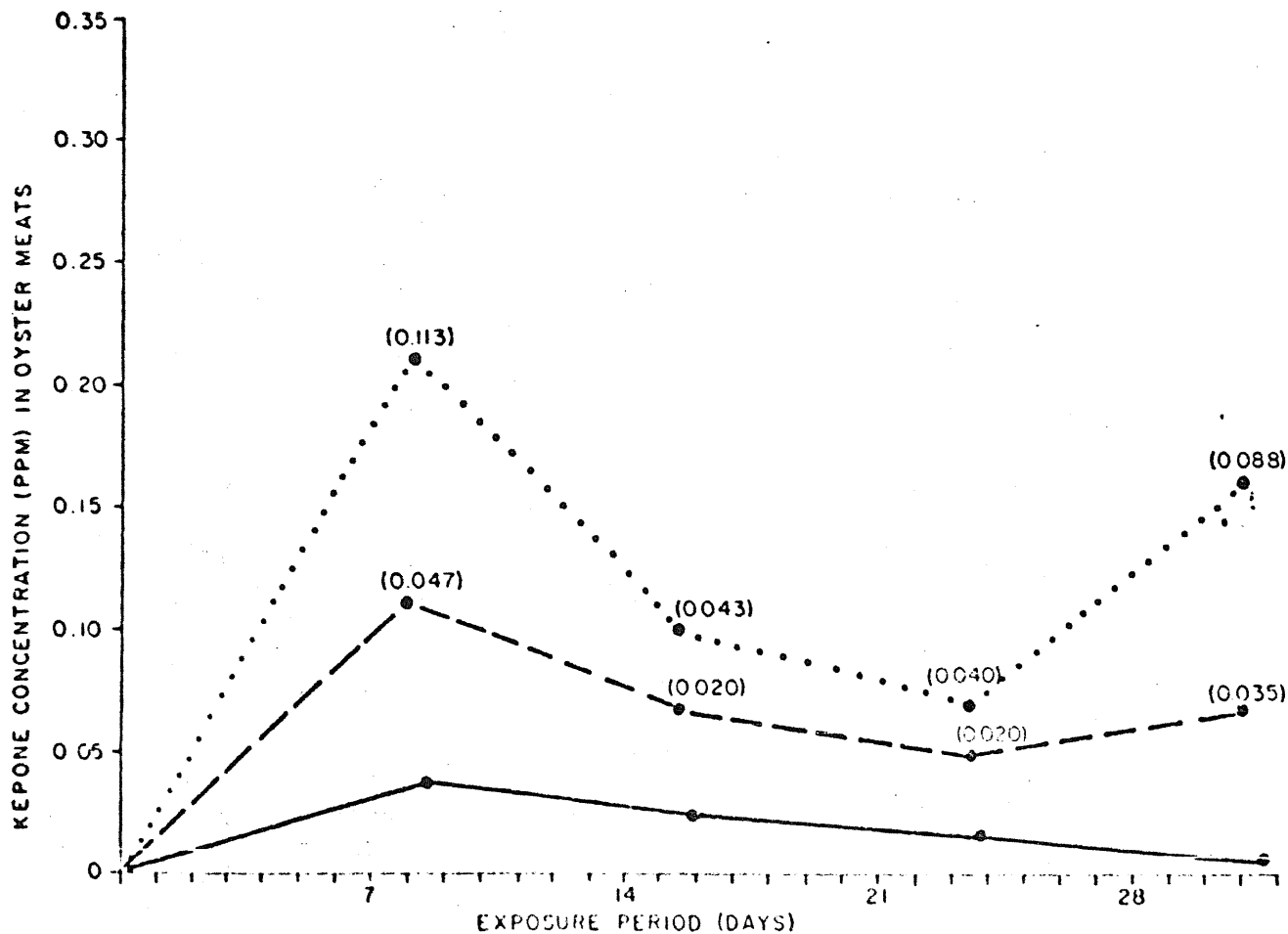


Figure 8. Mean concentration of Kepone in meats of oysters exposed to contaminated sediments in suspension (broken lines) or partially buried in bed of contaminated sediments (solid line). Third series of experiments, 8 July-9 August 1977. Figures in parentheses are mean hourly concentration of Kepone in sediments for weekly period ending at that

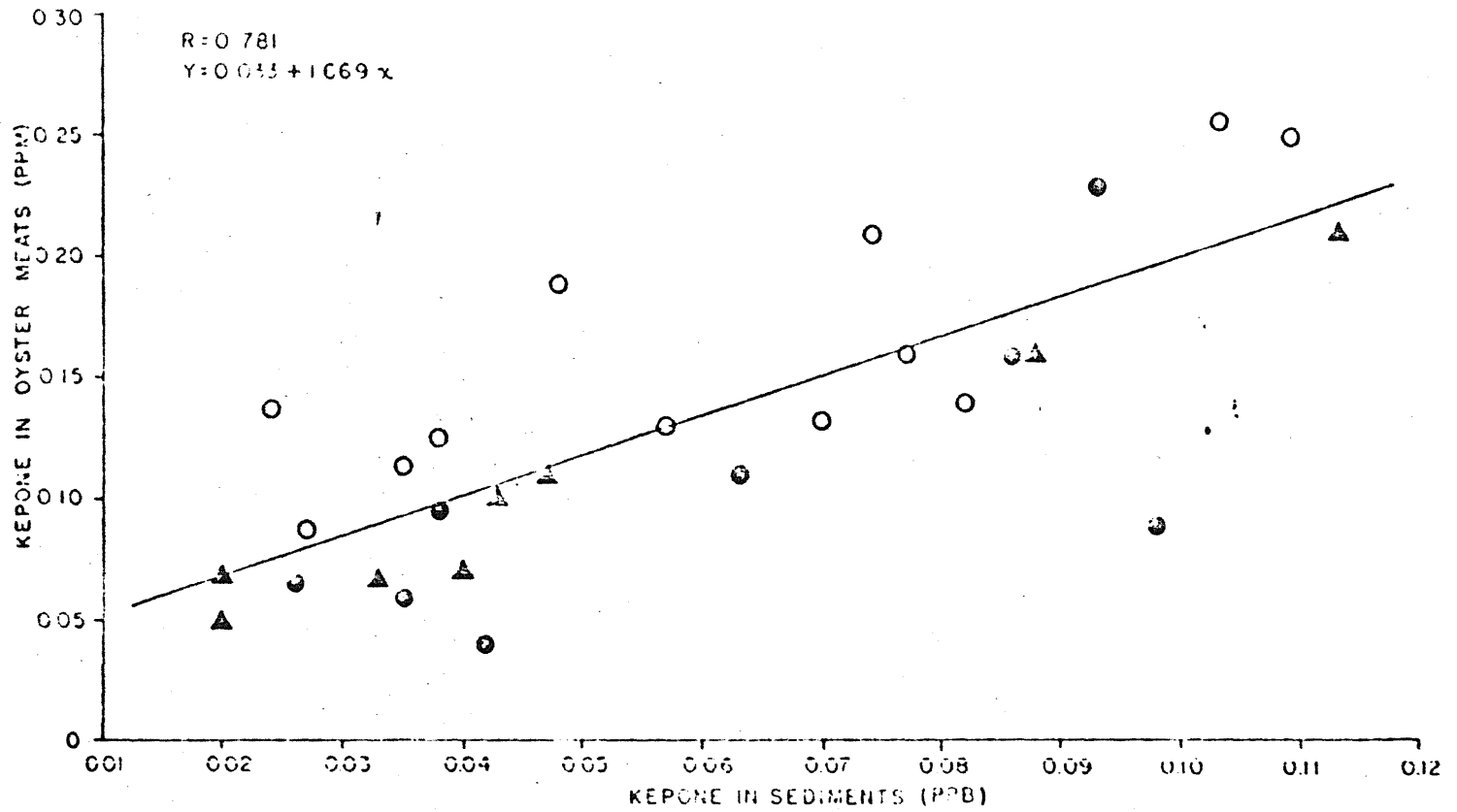


Figure 9. Regression of concentration of Kepone in oyster meats on mean hourly concentration of Kepone in suspended sediments for weekly periods in three series of experiments. Open circles: first series, closed circles: second series, triangles: third series.

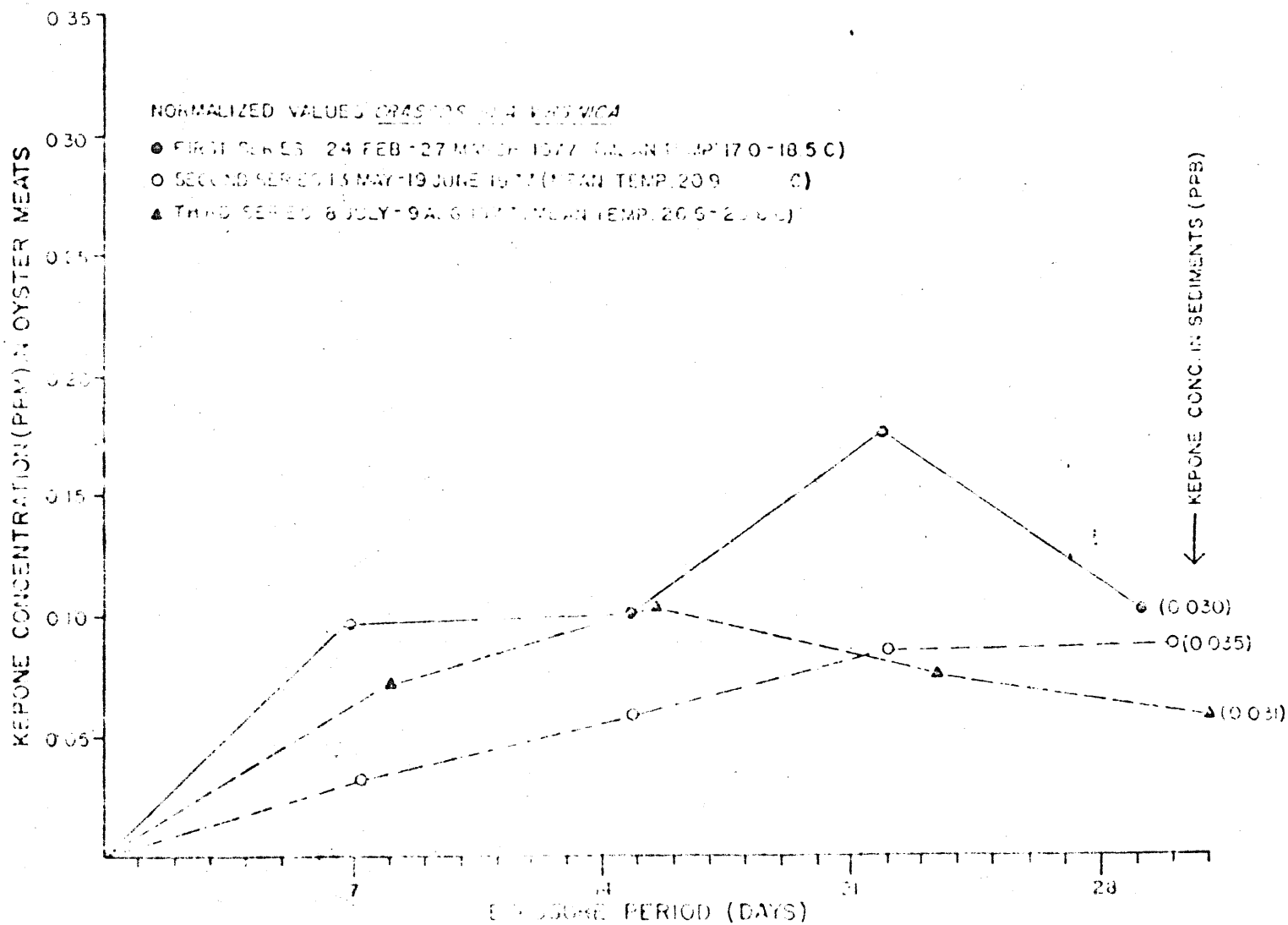


Figure 10. Mean concentration of Kepone in meats of oysters exposed to contaminated sediments in suspension. Normalized to a constant hourly concentration for the four-week period in each series. Mean given in

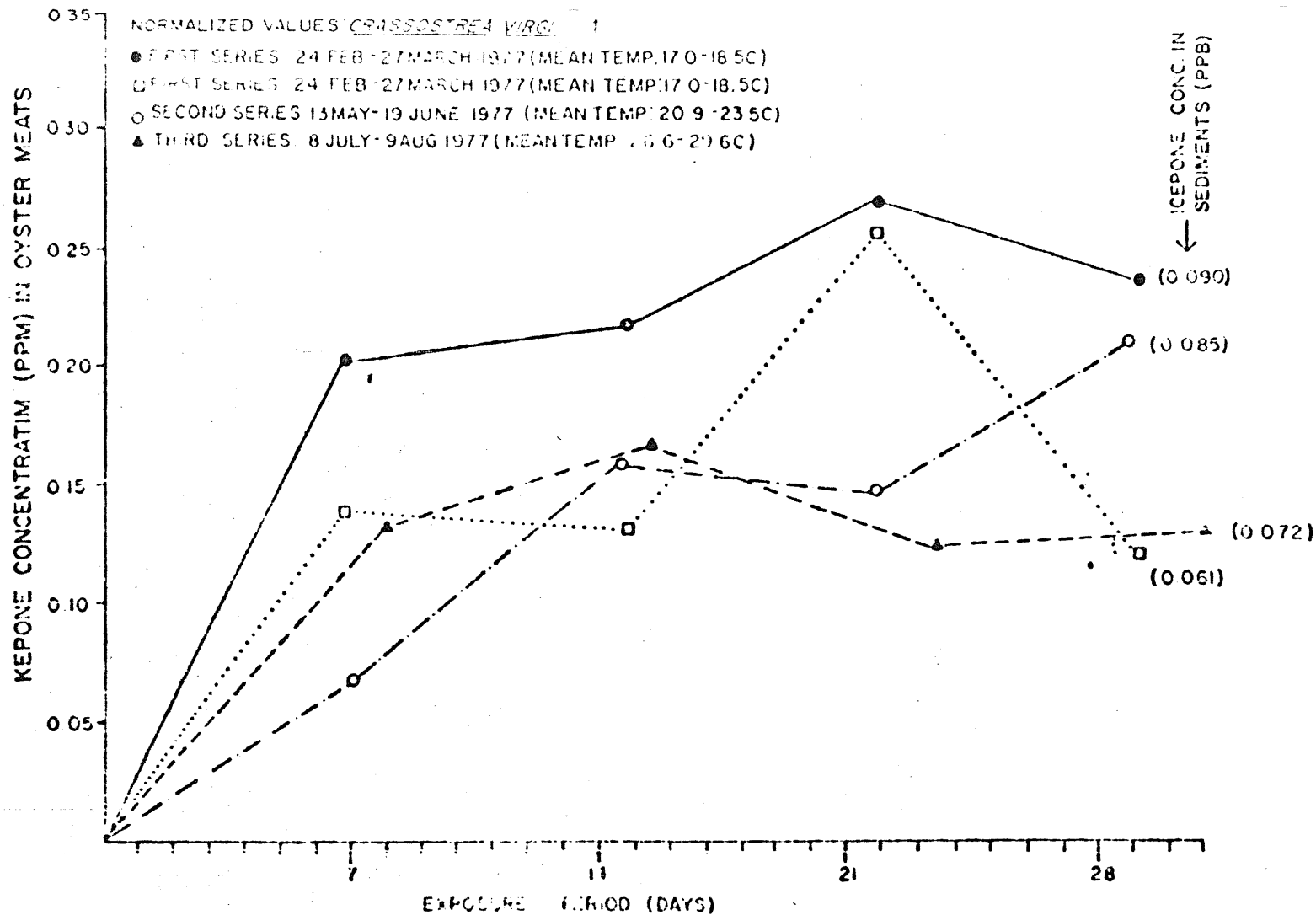


Figure 11. Mean concentration of Kepone in meats of oysters exposed to contaminated sediments in suspension. Normalized to a constant hourly concentration, the mean for the four-week period in each series. Mean given in parentheses.

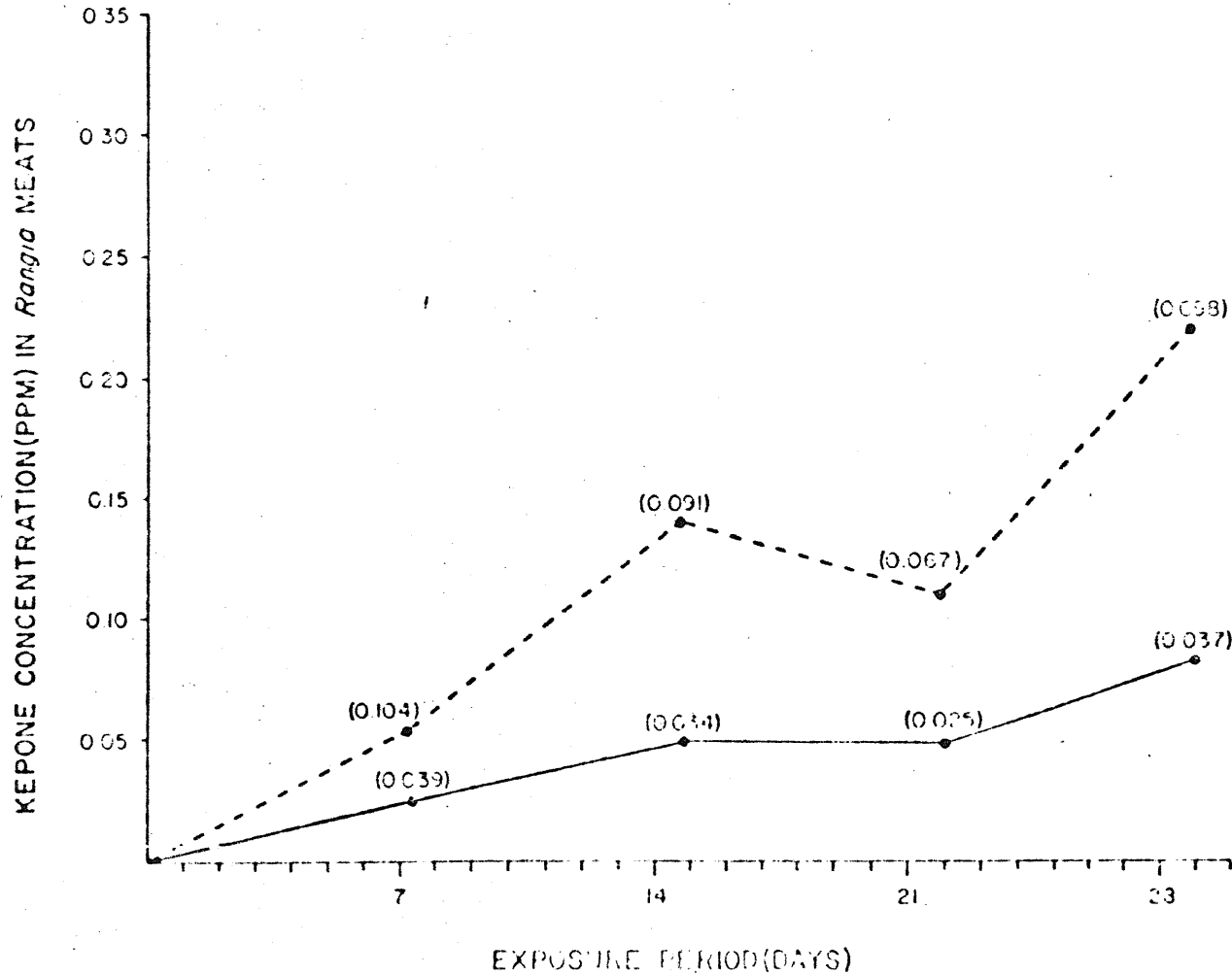


Figure 12. Mean concentration of Kepone in meats of *Rangia cuneata* exposed to contaminated sediments in suspension. Second series of experiments, 13 May-11 June 1977. Figures in parentheses are mean hourly concentration of Kepone in the water column only period ending at that point.

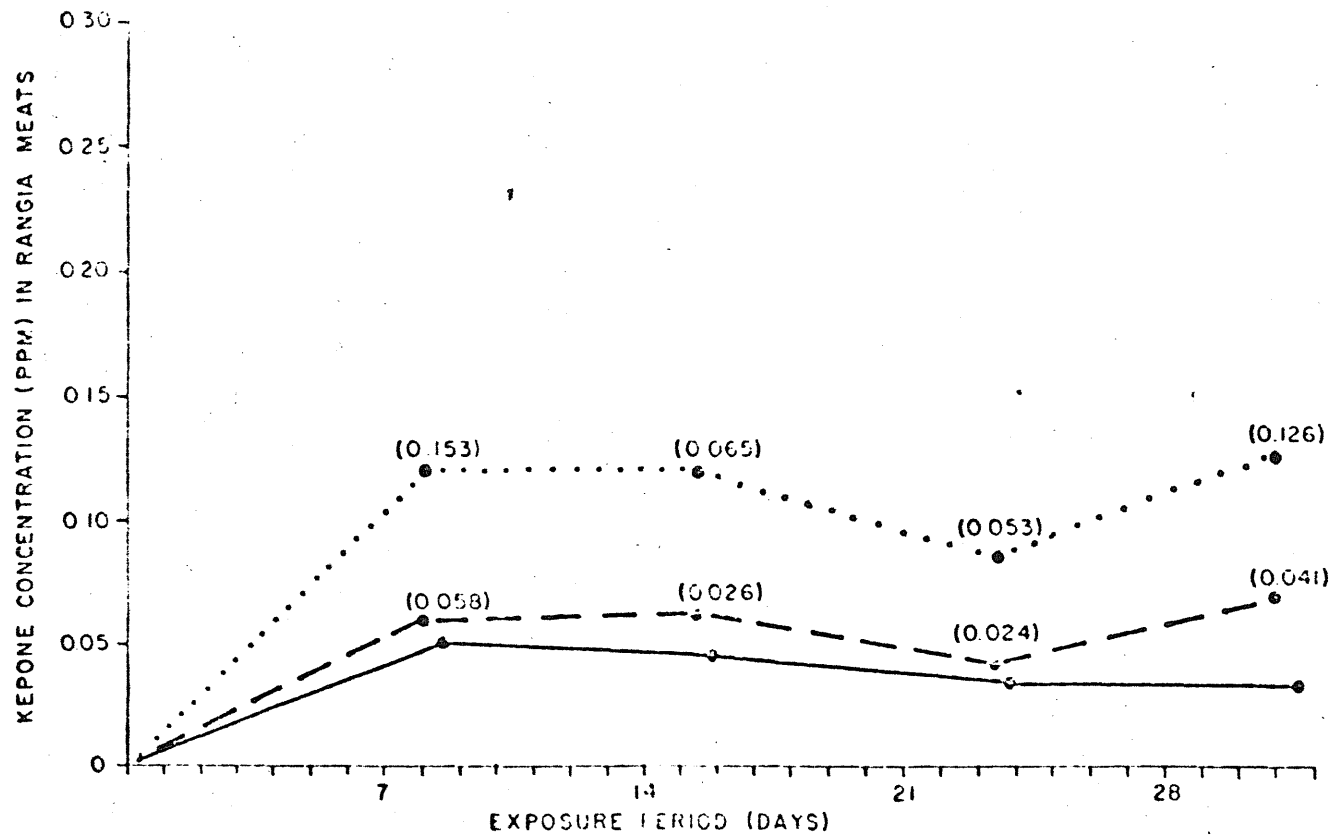


Figure 13. Mean concentration of Kepone in meats of *Rangia cuneata* exposed to contaminated sediments in suspension (broken lines) or buried in bed of contaminated sediments (solid line). Third series of experiments, 8 July-9 August 1977. Figures in parentheses are mean hourly concentration of Kepone in sediments for weekly periods ending at that point.

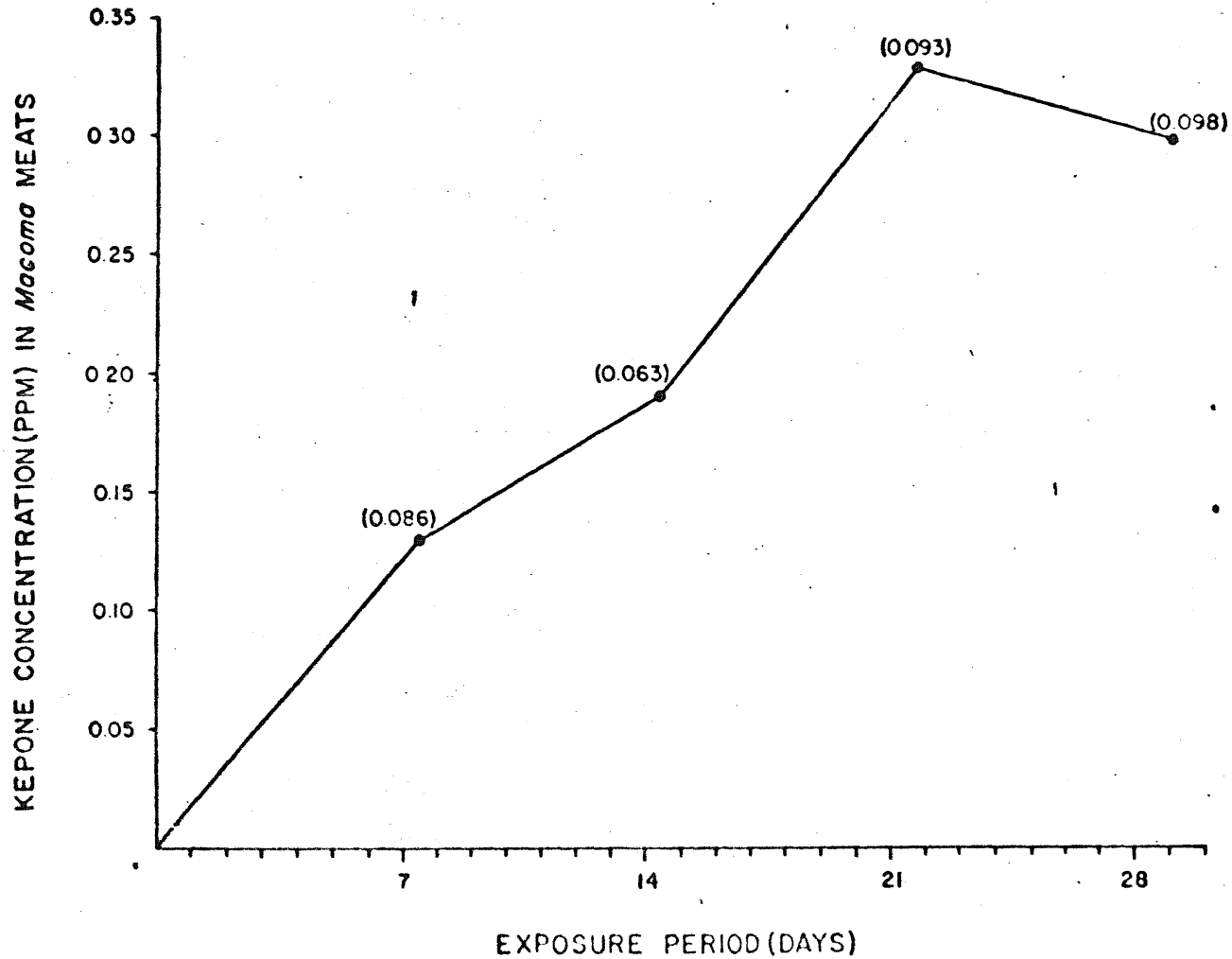


Figure 14. Mean concentration of Kepone in meats of Macoma balthica exposed to contaminated sediments in suspension. Second series of experiments, 20 May-19 June 1977. Figures in parentheses are mean hourly concentration of Kepone in sediments for weekly periods ending at that point.

EPA James River Kepone Hydrographical Survey Study

Progress Report (Nov. 1, 1977)

I. Hydrographical Survey (Aug., 1977)

Four transects were occupied for the field study with three stations included in each transect. The middle (primary) station or primary station, measured top, middle and bottom depth, while the two side channel stations measured top and bottom depths. (figures of the transect positions are included within).

The following is a compilation of information concerning each station.

Station 46.51, River mile 46.51, sampled from 8/26/77
at 1500 to 8/28/77 at 1500.

Station 46.51A - total depth 17 feet

Current meter depth off the bottom:
2 feet and 7.5 feet

Current meter time in:
8/23/77 at 1015

Current meter time out:
8/29/77 at 1935

Samples taken at mid depth, included all parameters
except kepone

Station 46.51 B - total depth 19.5 feet

Current meter depth off the bottom:
3 feet and 10.5 feet

Current meter time in:
8/23/77 at 1050

Current meter time out:
8/29/77 at 1925

Samples taken at top, mid and bottom depths, included
all parameters

Station 46.51 C - total depth 23 feet

Current meter depth off the bottom:
2 feet, 6.5 feet and 12.5 feet

Current meter time in:
8/23/77 at 0940

Current meter time out:
8/29/77 at 1915

Samples taken at mid depth, included all parameters,
except kepone

Station 73.24 sampled from 0800 8/27/77 to 8/29/77 1100

Station 73.24 A - total depth 15.5 feet

Current meter depth off the bottom:

6 feet

Current meter time in:

8/23/77 at 1550 ..

Current meter time out:

8/29/77 at 1523

Samples taken at mid depth, included all parameters
except kepone

Station 73.24 B - total depth 21.5 feet

Current meter depth off the bottom:

2.0, 7.5 and 13.0 feet

Current meter time in:

8/23/77 at 1512

Current meter time out:

8/29/77 at 1545

Samples taken from top, mid, bottom, included
all parameters

Station 73.24 C - total depth 12.5 feet

Current meter depth off the bottom:

5 feet

Current meter time in:

8/23/77 at 1440

Current meter time out:

8/27/77 at 1600

Samples taken at mid depth, included all parameters,
except kepone

Station 87.67 sampled from 0900 8/24/77 to 1200 8/26/77

Station 87.67 A - total depth 33 feet

Current meter depth off the bottom:
0, 12.5 and 27 feet

Current meter time in:
8/22/77 at 1620 ..

Current meter time out:
8/29/77 at 1423

Samples taken at mid depth, included all parameters
except Kepone

Station 87.67 B - total depth 23.5 feet

Current meter depth off the bottom:
0, 9.5, and 16 feet

Current meter time in:
8/22/77 at 1705

Current meter time out:
8/29/77 at 1410

Samples taken at top, mid, bottom, included
all parameters

Station 87.67 C - total depth 13.5 feet

Current meter depth off the bottom:
3 feet

Current meter time in:
8/22/77 at 1730

Current meter time out:
8/29/77 at 1434

Samples taken at mid depth, included all parameters,
except Kepone

Station 111 - sampled from 8/24/77 at 0900 to 8/26/77 at 1200

Station 111 A - total depth 18 feet

Current meter depth off the bottom:
4 and 11 feet

Current meter time in:
8/22/77 at 1350

Current meter time out:
8/29/77 at 1215

Samples taken at mid depth, included all parameters
except kepone

Station 111 B - total depth 20 feet

Current meter depth off the bottom:
2, 7.5 and 13 feet

Current meter time in:
8/22/77 at 1140

Current meter time out:
8/29/77 at 1210

Samples taken at top, mid, and bottom depth, included
all parameters

Station 111 C - total depth 13 feet

Current meter depth off the bottom:
3 feet

Current meter time in:
8/22/77 at 1215

Current meter time out:
8/29/77 at 1225

Samples taken at mid depth, included all parameters,
except kepone

Tide gauges were installed in the following three locations. They were installed one week before the field intensive survey and pulled out one week after the intensive survey. Currently, all tide data are being sent to Fisher and Porter for reduction.

Tide gauge stations:

- 1) Wooden Pier at Ft. Eustis
- 2) Pier, Chickahominy Holiday Inn Campground
(off Rt. 5, near mouth of Chickahominy)
- 3) Westover, Va. Pier (near Hopewell)

II. Data Reduction

All hydrographical and sediment intensive data are currently being keypunched. Parameters include dissolved oxygen, temperature, conductivity, salinity, suspended solids and kelpene concentration. It is anticipated to finish keypunching and editing by the end of November, 1977.

Current meter films have been developed and are being prepared to be read. It is also planned to have the data reduction work done by the end of November, 1977.

PRELIMINARY ANALYSIS OF KEPONE DISTRIBUTION
IN THE JAMES RIVER

Donald J. O'Connor
Kevin J. Farley

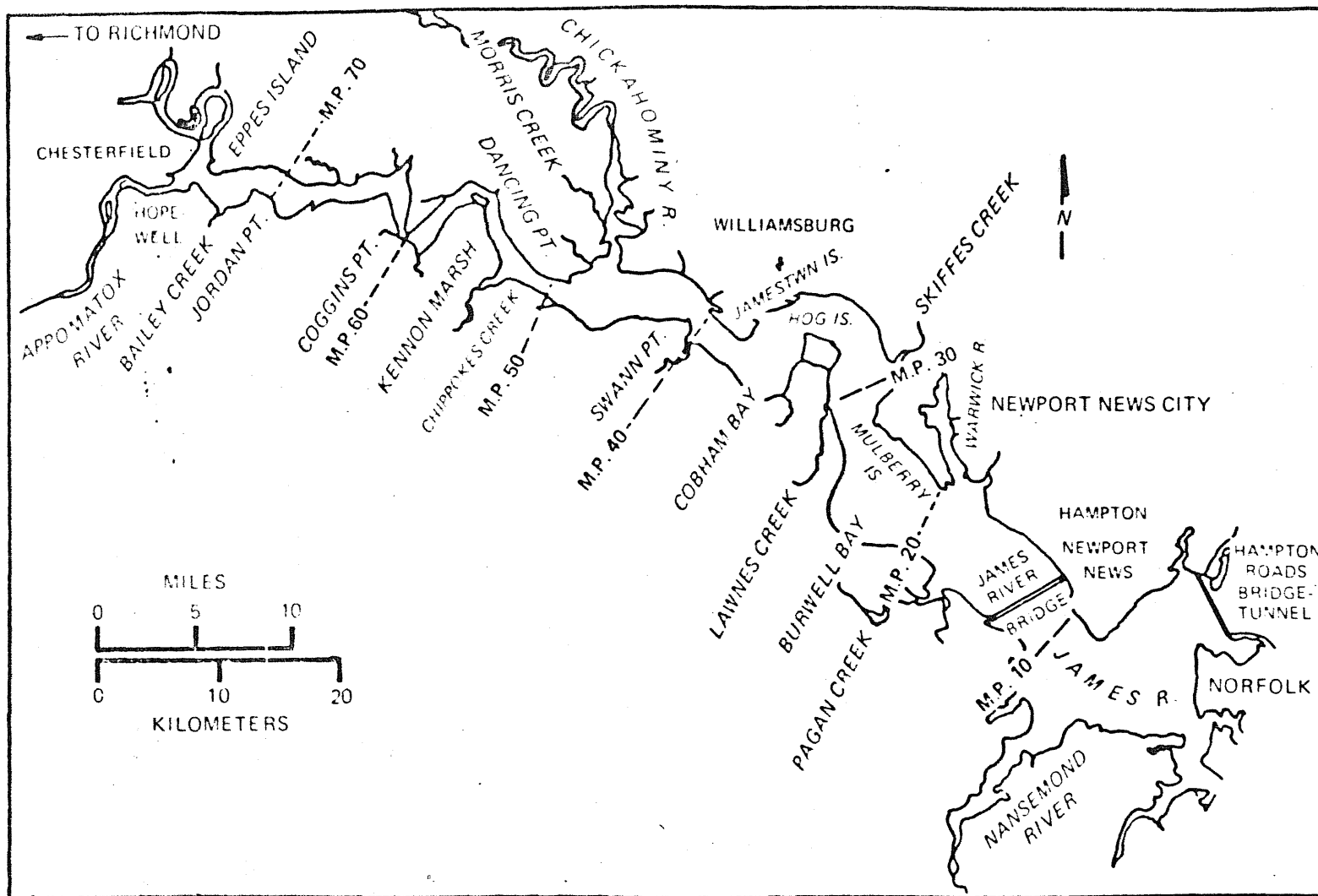
Environmental Engineering and Science Program
Manhattan College
Bronx, New York 10471

Introduction

The general purpose of this research project is to assess the effect of synthetic materials, such as pesticides, on the water quality and ecology of estuarine systems. The present phase of the project is being specifically directed to the analysis of the Kepone distribution in the James River estuary in the vicinity of and downstream from, Hopewell, Virginia. The ultimate goal is to provide a quantitative framework for evaluation of the time required to reduce the Kepone concentrations to acceptable levels.

Significant concentrations of Kepone are present in various phases of the estuarine system of the James River -- in solution, in suspension, in the sediment and in the food chain, particularly in various species of fish. The interrelationships, or more specifically, the transport, uptake and release of Kepone, as shown in Figure II, are thus affected by both physio-chemical mechanisms, as well as bio-ecological phenomena. The former of these includes the hydrodynamic transport through the estuarine system, adsorption to and desorption from the suspended and bed solids, and the settling and resuspension of these solids. The latter incorporates the assimilation and excretion routes through the various components of the food chain. Although less significant for Kepone, transfer to the atmosphere, photochemical oxidation and biological degradation are potentially significant transport and kinetic processes.

JAMES RIVER STUDY AREA



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FIGURE I
JAMES RIVER STUDY AREA

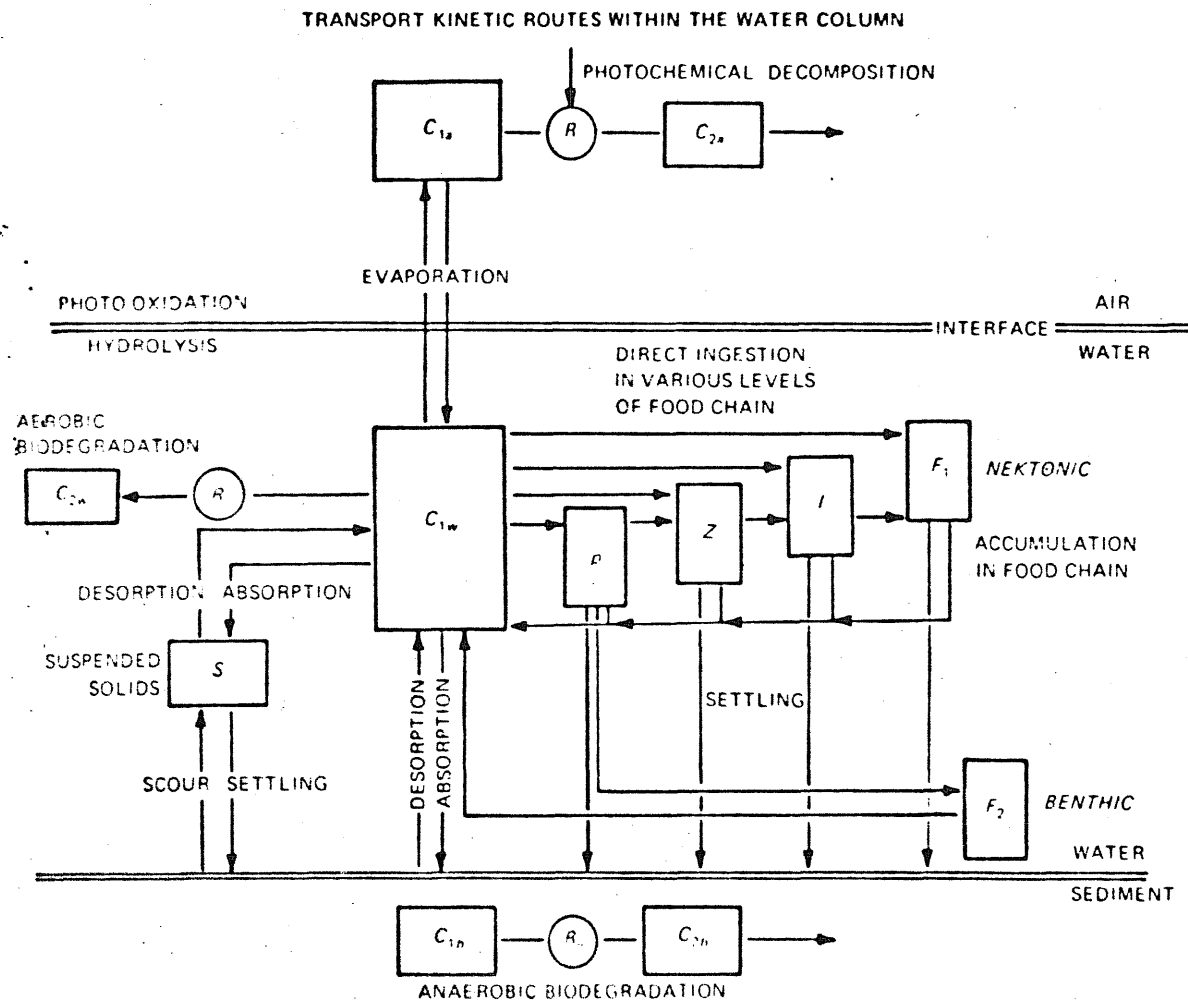


FIGURE II
TRANSPORT - KINETIC ROUTES WITHIN THE WATER COLUMN

The Distribution of Kepone on Solids

Natural clays of various types, and organic material, possess an adsorptive capacity. The rates of adsorptive reactions are being investigated experimentally under controlled laboratory conditions in order to provide realistic kinetic coefficients for the Kepone analysis. The desorptive characteristics of both the inorganic and organic fractions of the suspended solids are also being reviewed. This phenomena of adsorption-desorption is one of the important transfer routes in the ultimate transfer of Kepone from the system. Based on the Langmuir Isotherms, equations have been developed to predict the spatial and temporal distributions of Kepone in an advective-dispersive estuarine system. However, due to the preliminary nature of this work, the less complex, advective, steady state model was used for analysis. Equations governing the water column and estuarine bed for such a system are as follows:

1. Water

$$\text{Solids } U_1 \frac{\partial m_1}{\partial x} = -K_s m_1 + \alpha K_u m_2$$

$$\text{Dissolved } U_1 \frac{\partial C_1}{\partial x} = -K_o (r_c - r_1) m_1 C_1 + K_d r_1 m_1 - K_b (C_1 - C_2) - K_a C_1$$

$$\text{Particulate } U_1 \frac{\partial P_1}{\partial x} = +K_o (r_c - r_1) m_1 C_1 - K_d r_1 m_1 - K_s r_1 m_1 + \alpha K_u r_2 (m_2 - m_1)$$

2. Bed

$$\text{Solids } U_2 \frac{\partial m_2}{\partial x} = + \frac{K_s}{\alpha} m_1 - K_u m_2$$

$$\text{Dissolved } U_2 \frac{\partial C_2}{\partial x} = -K_o(r_c - r_2)m_2 C_2 + K_d r_2 m_2 + K_b(C_1 - C_2)$$

$$\text{Particulate } U_2 \frac{\partial P_2}{\partial x} = +K_o(r_c - r_2)m_2 C_2 - K_d r_2 m_2 + \frac{K_s}{\alpha} r_1 m_1 - K_u r_2 (m_2 - m_1)$$

where:

the subscripts 1 and 2 denote the water column and estuarine bed concentrations, respectively,

and where:

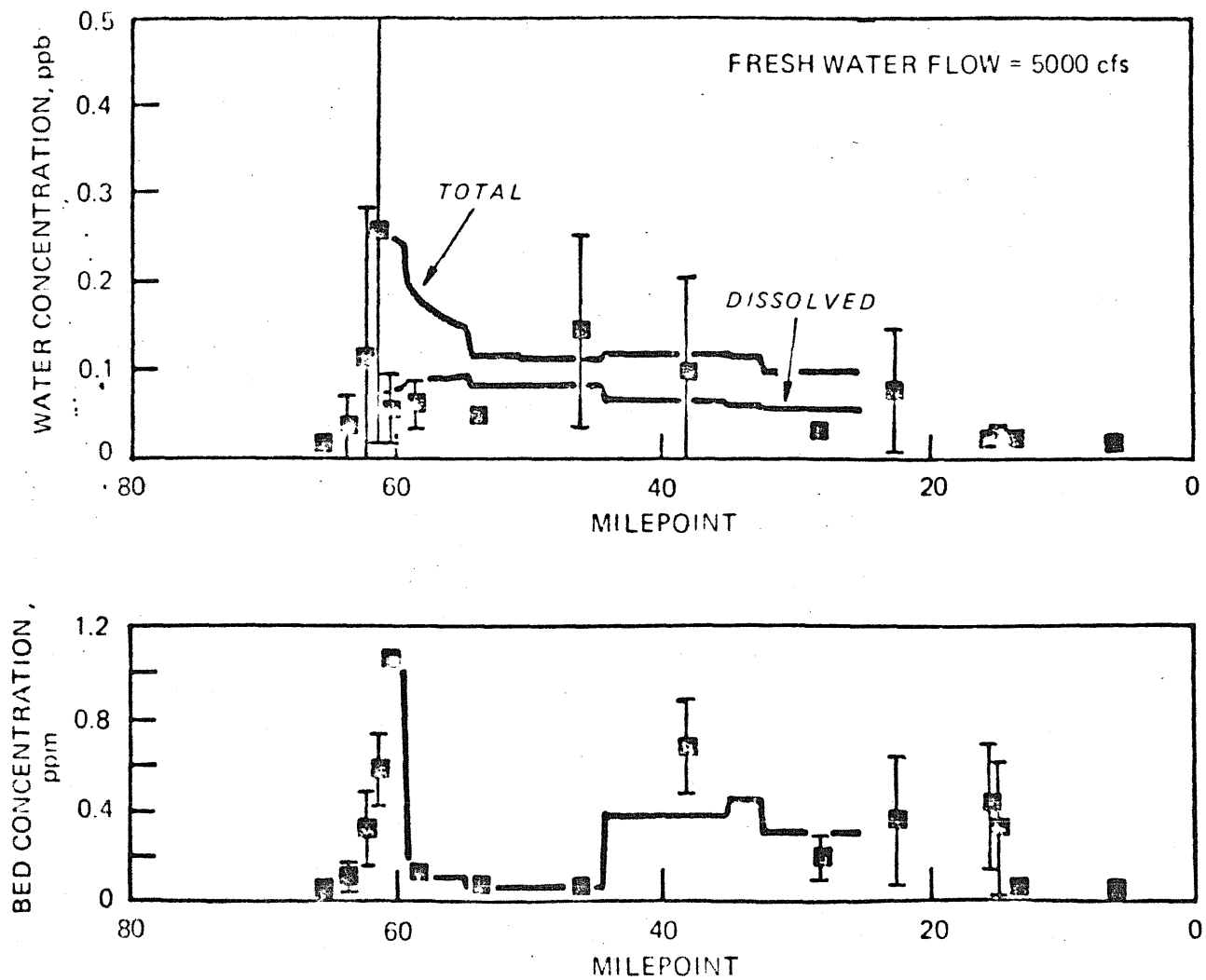
U	- horizontal velocity	[m/sec]
C	- dissolved Kepone concentration	[$\mu\text{g}/\ell$]
x	- longitudinal distance	[meters]
K_o	- adsorption coefficient	[1/($\mu\text{g}/\ell$ -day)]
r_c	- solids adsorptive capacity	[$\mu\text{g}/\text{g}$]
r	- Kepone concentration on the solids	[$\mu\text{g}/\text{g}$]
m	- solids concentration	[g/ ℓ]
K_d	- desorption coefficient	[1/day]
K_b	- bed diffusion coefficient	[1/day]
K_a	- aeration coefficient	[1/day]
P	- solids Kepone concentration	[$\mu\text{g}/\text{g}$]
K_s	- solids settling coefficient	[1/day]
α	- the ratio of bed volume to water column volume	[dimensionless]
K_u	- solids scour coefficient	[1/day]

As a first step, this preliminary analysis was simplified by various assumptions - subject to verification by the ongoing field and laboratory studies. The first of these assumptions - solids being in equilibrium i.e. $\frac{\partial m_1}{\partial x}$ and $\frac{\partial m_2}{\partial x} = 0$, appears to be a safe assumption for the non-saline portion of the estuary. In addition, the bed solids concentration, m_2 , was said to be much greater than the suspended solids concentration, m_1 ; the aeration term, K_a , was taken to be negligible; and the solids adsorptive capacity, r_c , was assumed to be much greater than either of the Kepone concentrations on the solids, r_1 and r_2 . The kinetic coefficients - K_o , K_d , K_s , and K_u , were assigned from the limited data available. Finally, for this "first-cut" model, the Kepone concentrations on the bed solids, r_2 , were assigned from data; these concentrations were in turn utilized in predicting the Kepone water column concentrations.

Based on these assignments of coefficients, the longitudinal distribution of total and dissolved Kepone in the water column is presented in Figure III along with the State Water Control Board 1976 Kepone data. The line of total Kepone concentration fits the data quite well and although the dissolved fraction of Kepone is high, this concentration is merely a function of Kepone kinetic coefficients, K_o and K_d - values which were obtained from a minimal amount of sketchy data. Further analysis is presently being performed which will predict both the water column and the bed concentrations of Kepone.

The above analysis will be further complicated as the

JAMES RIVER, STATE WATER CONTROL BOARD 1976 KEPONE DATA



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FIGURE III
KEPONE CALCULATION FOR THE JAMES RIVER ESTUARY (1976)

saline portion of the estuary is approached. As the lighter clay particles which are maintained in suspension in the non-saline area encounter the saline region of the estuary, flocculation and agglomeration may occur, increasing the size and possibly the density of the particles. These factors result in further deposition, which is enhanced by virtue of their occurrence in the null zone of the estuary. There are, therefore, a variety of significant factors which may account for the accumulation of solids and Kepone in the estuarine bed at the fresh water-saline interface. These factors, along with the inability to assume solids equilibrium in the saline region, have lead to a detailed investigation of solid material in the estuary.

Hydrodynamic Transport

Since the concentration of suspended solids is an important factor as an accumulation site for Kepone, the temporal and spatial distribution of the solids within the estuarine system is a necessary element in the analysis. The distribution is determined by the hydraulic transport through the estuarine system. A two-dimensional (longitudinal-vertical) analysis has been developed, based on the fundamental principles of momentum, continuity and state.

In this analysis, under steady state, tidally averaged conditions, the longitudinal momentum equation for a laterally homogeneous estuary is:

$$0 = \frac{1}{\rho} \frac{\partial p}{\partial x} + N \frac{\partial^2 u}{\partial z^2} \quad (1)$$

where ρ = density; p = pressure; N = vertical eddy viscosity; and u = horizontal velocity. The coordinates for Eq. 1 are shown in Fig. IV in which the longitudinal x -axis is positive toward the ocean and the vertical z -axis is positive toward the bed of the estuary channel. Boundary conditions compatible with Eq. 1 are,

$$\frac{\partial u}{\partial z} = 0 \quad \text{at } z = -n \quad (2)$$

$$-N \frac{\partial u}{\partial z} = C_d / u_b / u_b \quad \text{at } z = h \quad (3)$$

in which $-n$ = surface elevation and h = average depth; C_d = dimensionless friction coefficient; and u_b = velocity at the bed. The vertical component of the momentum equation is simply the hydrostatic pressure equation:

$$\frac{1}{\rho} \frac{\partial p}{\partial z} = -g \quad (4)$$

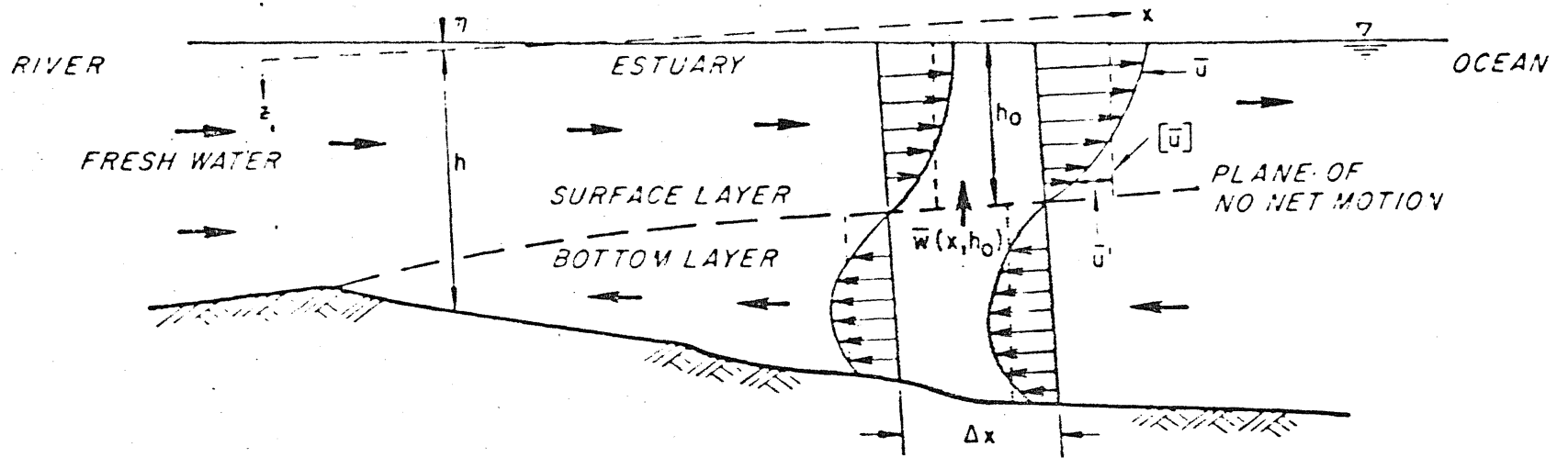


FIGURE IV
SCHEMATIC DIAGRAM OF TWO-DIMENSIONAL ESTUARINE CIRCULATION

In order to solve Eq. 1, the hydrostatic pressure, Eq. 4, is expressed in terms of the horizontal and vertical distribution of salinity. The equation of state which specifies the density as a function of salinity is given by:

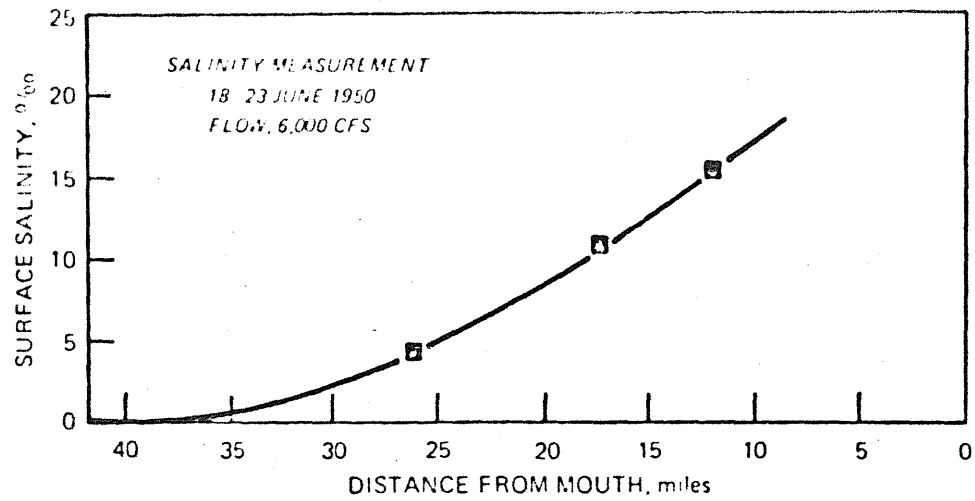
$$\rho = \rho_f(1 + \alpha\bar{C}) \quad (5)$$

in which ρ_f = the density at zero salt content and $\alpha = 0.000757$ (parts per thousand)⁻¹. The components of the pressure force are then evaluated in terms of the observed vertical and longitudinal salinity gradients and freshwater flow, which are assumed known from measurement.

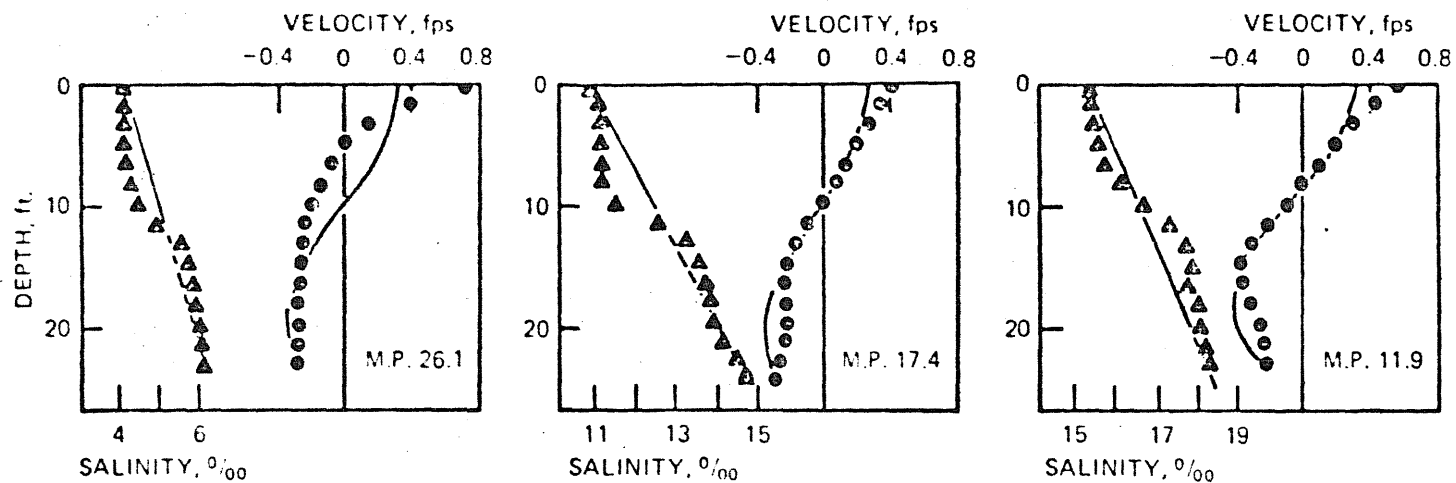
The solution of the above equations indicates that local rather than boundary conditions control the magnitude and gradient of horizontal velocity at a particular location. Because of local control, the velocity at one location is relatively independent of those at other locations. This condition occurs as a result of decoupling the equations of motion and salt transport.

Results of this analysis are presented for Pritchard's June 1950 survey and Nichols' March 1965 survey of the James River in Figure V and VII respectively. In addition, the solution also indicates the depth at which the net horizontal velocity is zero. Defining this depth at a number of stations and interpolating for others delineates the plane of no net motion for the saline intrusion zone of the estuary, Figures VI and VIII. At the tail of the salinity intrusion, this plane meets the bed of

VELOCITY CALCULATION R JAMES RIVER ESTUARY (JUNE, 1950)



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NOTE: SALINITY AND VELOCITY MEASUREMENTS BY THE CHESAPEAKE BAY INSTITUTE

FIGURE \bar{V}
VELOCITY CALCULATION FOR JAMES RIVER ESTUARY (JUNE, 1950)

SALINITY CALCULATION FOR JAMES RIVER ESTUARY
(JUNE, 1950)

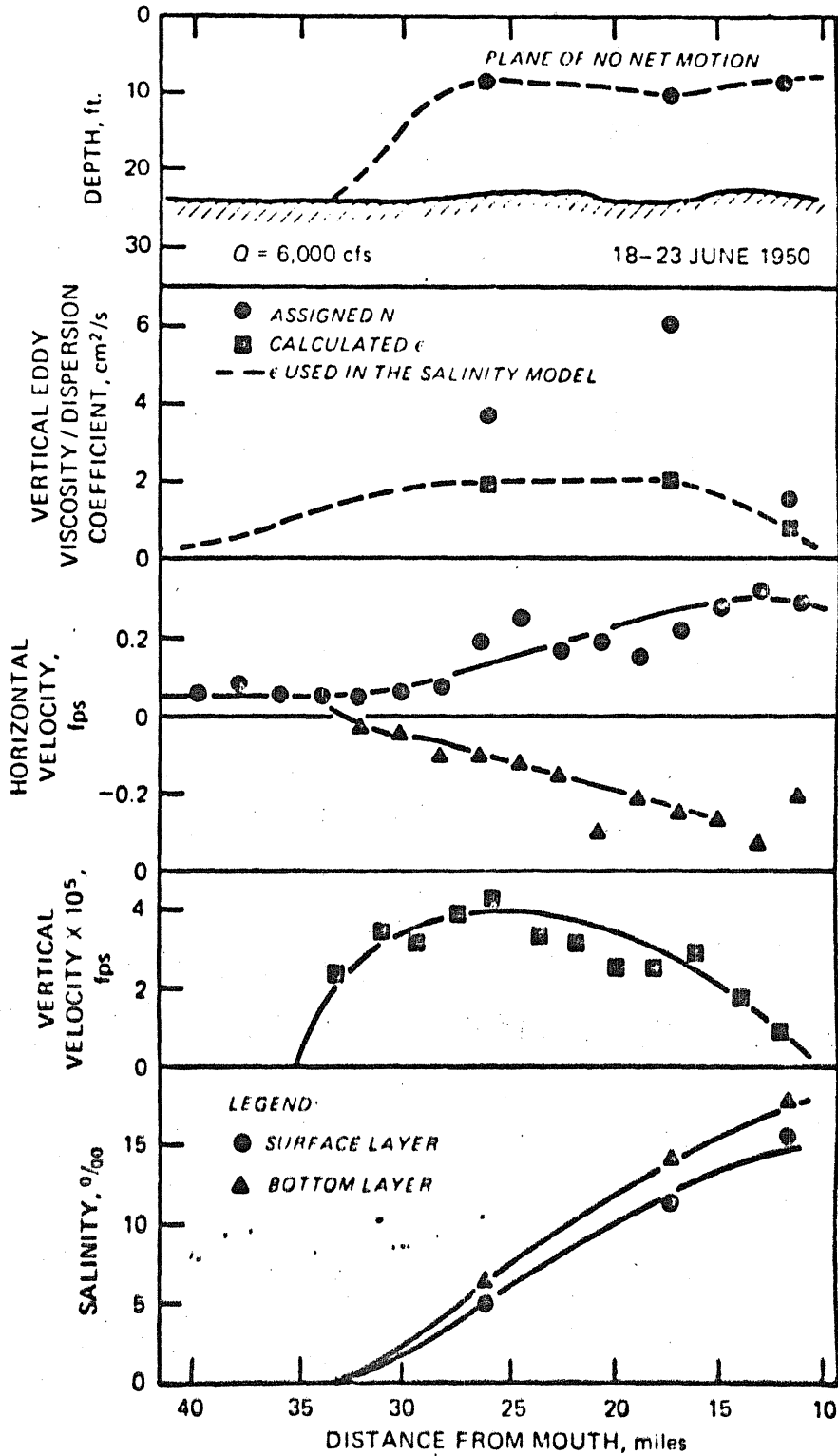
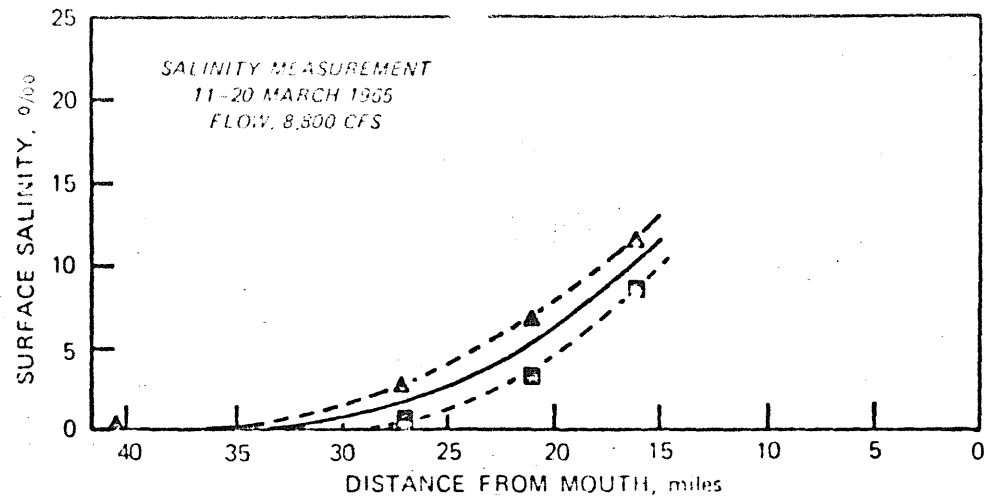


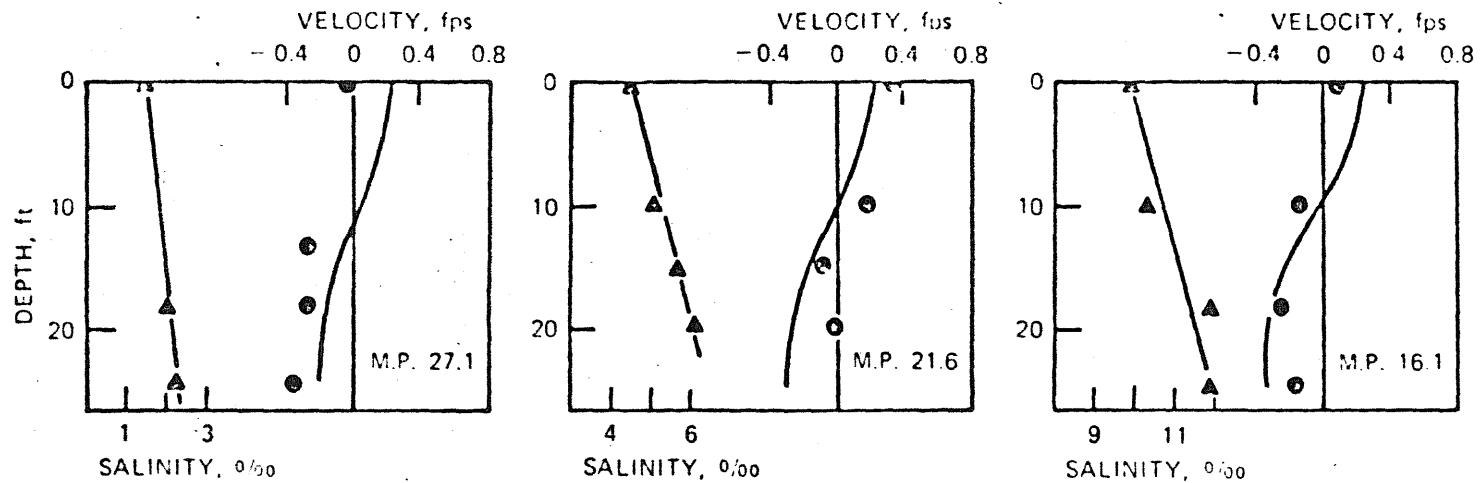
FIGURE VI

SALINITY CALCULATION FOR JAMES RIVER ESTUARY (JUNE, 1950)

VELOCITY CALCULATION FOR JAMES RIVER ESTUARY (MARCH, 1965)



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NOTE: SALINITY AND VELOCITY MEASUREMENTS BY THE VIRGINIA INSTITUTE OF MARINE SCIENCE

FIGURE VII

VELOCITY CALCULATION FOR JAMES RIVER ESTUARY (MARCH, 1965)

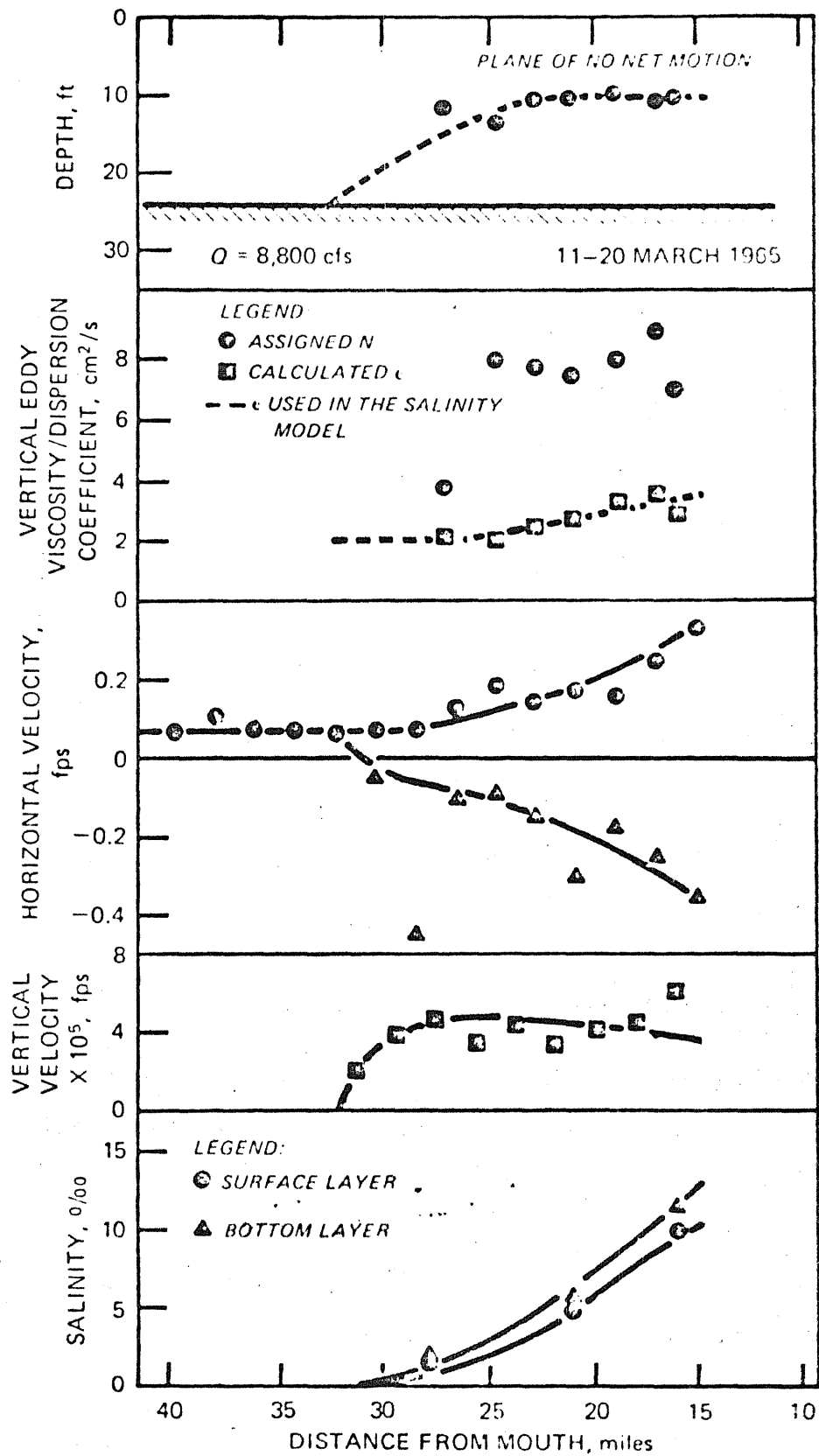


FIGURE VIII

SALINITY CALCULATION FOR JAMES RIVER ESTUARY (MARCH, 1965)

the estuary. Upstream of this area, the horizontal velocity in the whole water column is in the seaward direction.

The estuary is then segmented horizontally and the horizontal flow in the surface layer at each vertical cross section is first calculated. Horizontal flow difference between two adjacent vertical planes gives the vertical flow between the surface and bottom layer, from which the vertical velocity is obtained by dividing by the average width of the segment. This procedure is obviously a solution of the hydraulic continuity.

The vertical flux of salt due to dispersion between the surface and bottom layers is described by the dispersion coefficient, ϵ , obtained from the vertical eddy viscosity through an empirical relationship,

$$\epsilon = N(1 + R_i)^{-1} \quad (6)$$

where R_i (Richardson number) is defined as:

$$R_i = \frac{g \frac{\partial \rho}{\partial z}}{\rho \left(\frac{\partial \bar{u}}{\partial z} \right)^2} \quad (7)$$

Equation 6 indicates the relationship between the two coefficients, whose general validity has been shown by field data, as presented by Officer.

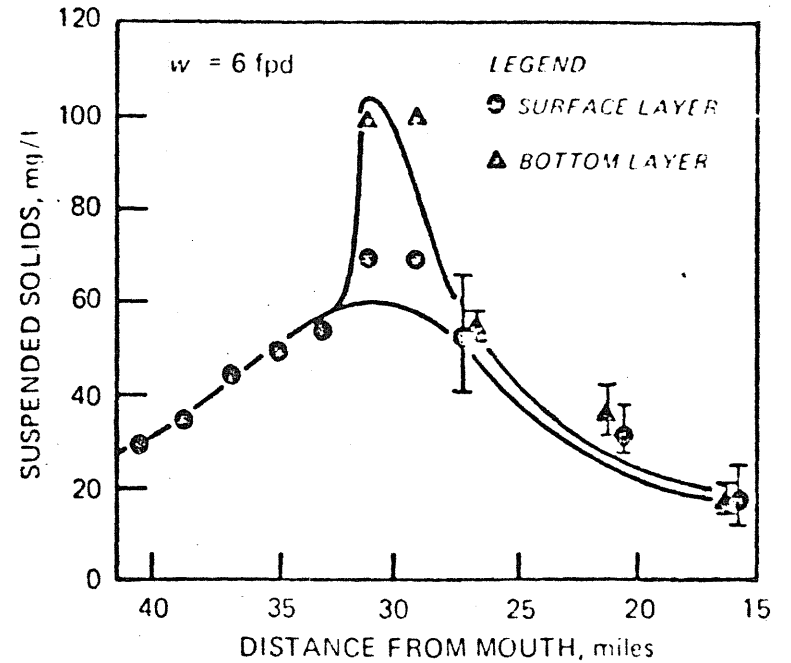
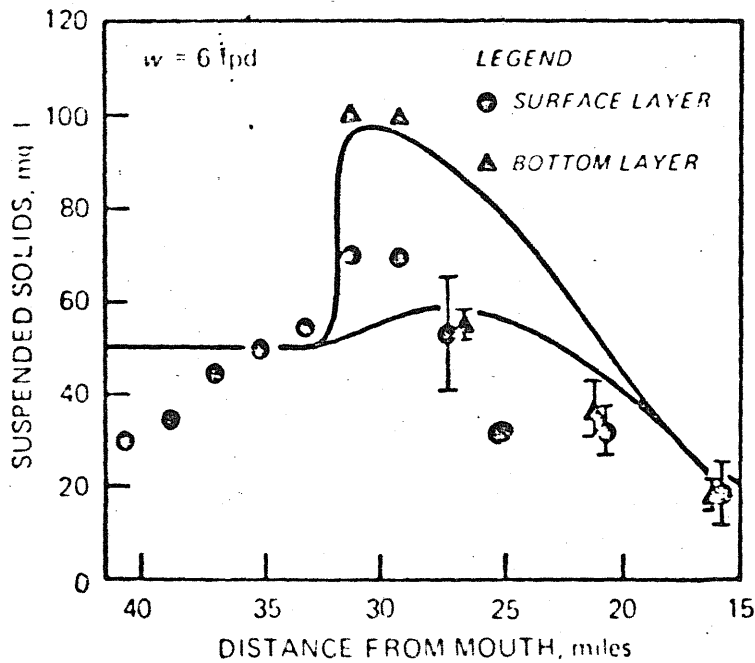
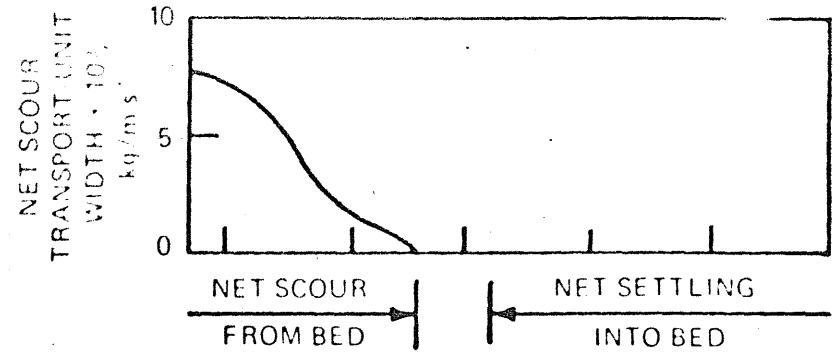
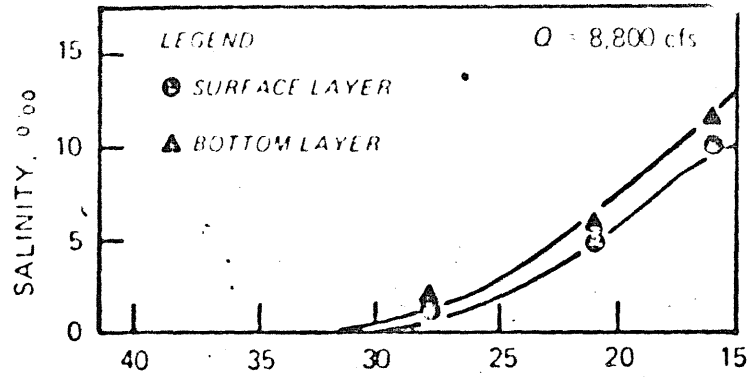
The tidal diffusion and velocity shear contributions, which can be envisioned collectively as a longitudinal dispersion across a vertical section following the classical one-dimensional estuarine analysis, did not exhibit themselves in the portion of the

estuary that our models were concerned.

The distribution of salinity was used to test the validity of the hydrodynamic model - bottom panels of Figures VI and VIII. Based on these validations of the hydrodynamic model, an analysis of suspended solids followed by incorporating the settling and scour rates with the hydrodynamic transport to determine the distribution of solids. Settling rates, for the present, were assumed constant down the length of the estuary and this rate was obtained from the average particle size, using a modification of Stokes' Law. Since little work has yet been performed on scouring rates in estuaries, these rates were assigned merely to show that a good fit can be obtained. Results of this solids modeling, with and without the assigned scouring rates, are presented in Figure IX.

ASSIMILATION AND DEPURATION OF KEPONE IN THE FOOD CHAIN

The transfer of Kepone from its initial discharge at Hopewell to its accumulation in the fishery stock may occur in a number of ways. It may be ingested directly from that which is dissolved or suspended in the water; it may be assimilated by the phytoplankton-zooplankton; and it may be taken in by bottom feeders from the material which has settled in the channel bed. The predominant sites for settling appear to be downstream from Hopewell, in the region of the fresh water-saline interface, and in various dead zones in the fresh and saline regions. Experiments involving assimilation and depuration of Kepone by various species are being conducted. The rates of accumulation and



NOTE SUSPENDED SOLIDS MEASUREMENTS BY THE VIRGINIA INSTITUTE OF MARINE SCIENCE

FIGURE IX
SUSPENDED SOLIDS CALCULATION FOR JAMES RIVER ESTUARY (MARCH, 1965)

excretion, equilibrium conditions and concentrations, lethal and chronic - are being analyzed in order to incorporate these kinetic factors in a food chain analysis.

Preliminary analysis has been made in evaluating the assimilation and depuration kinetics on various species of fish. Data from experimental studies performed at EPA's Gulf Breeze Laboratory are used to evaluate the relevant coefficients. The equation utilized in this analysis - similar to the Langmuir kinetic equation for the adsorption to and desorption from suspended solids, is as follows:

$$\frac{\partial(rm)}{\partial t} = K_o(r_c - r)m(t)C - K_d rm(t)$$

where

r	- Kepone concentration in the biomass	[µg/g]
m	- biomass concentration	[g/ℓ]
t	- time	[days]
K _o	- assimilation coefficient	[1/day]
r _c	- biomass assimilation capacity	[µg/g]
C	- dissolved Kepone concentration	[µg/ℓ]
K _d	- depuration coefficient	[1/day]

The only assumption made in this analysis was that the biomass assimilation capacity, r_c, was taken to be much greater than the Kepone concentration in the biomass, r. Results of this analysis for oysters (*Crassostrea, virginica*) are presented in Figure X.

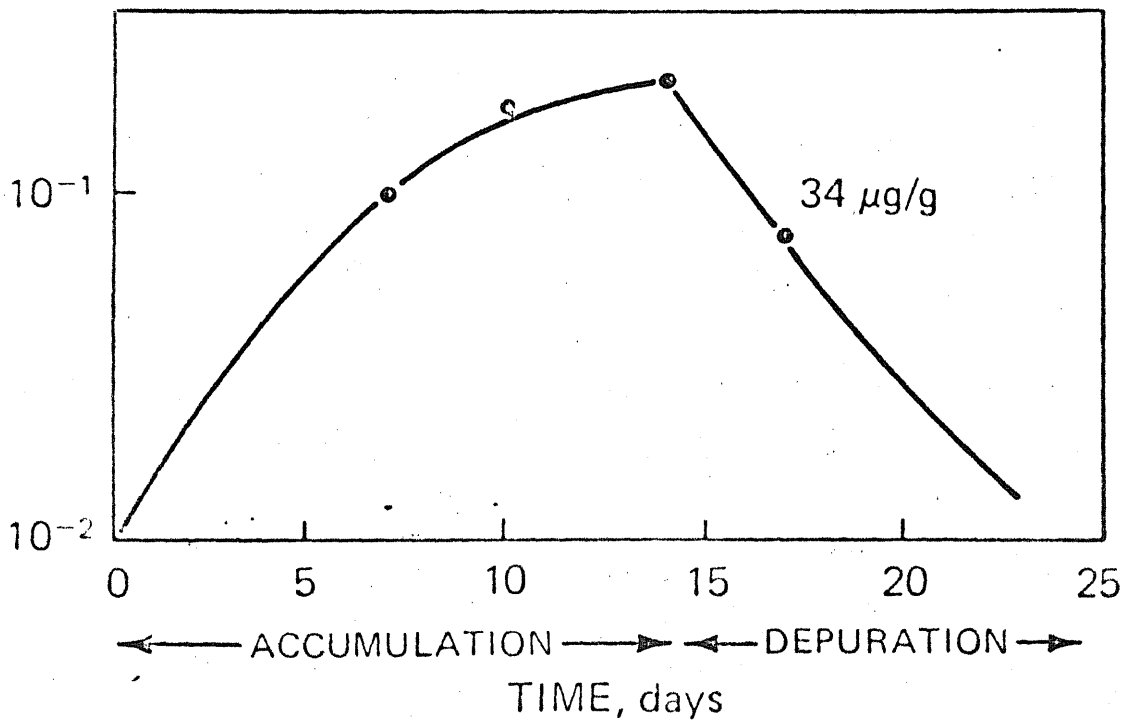
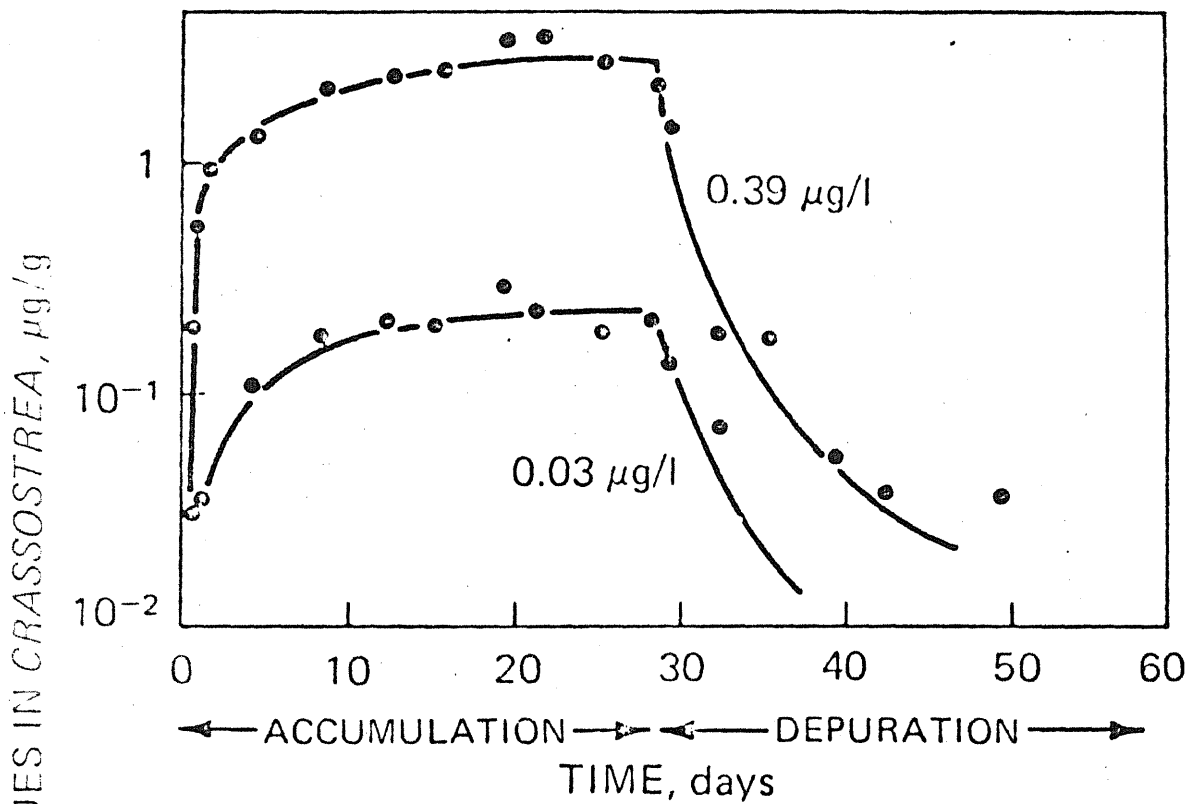


FIGURE \bar{X}

CALCULATION FOR THE ASSIMILATION AND DEPURATION OF KEPONE IN OYSTERS

From these results, it can be shown that the bio-ecological phenomena of assimilation and depuration can be modeled utilizing Langmuir kinetics if data for the evaluation of the relevant coefficients is available.

CONCLUSION

The equations presented in this report appear to be sufficiently realistic as a first approximation in representing the various phenomena under consideration. At the present time, the analysis is being extended to treat the ecological system as a continuum using trophic length as a metric. Given the inputs from the sources in the vicinity of Bailey's Bay, the transport in the non-saline and saline regions of the James estuary and the distribution of suspended solids and Kepone, the food chain model is being enlarged to include the uptake and excretion of Kepone in the various trophic levels and the predation and feeding associated with these levels. At this time, the saline and non-saline regions of the estuary are being combined into one continuous solution. Steady state conditions, which represent average conditions during various seasons of the year, are being assumed for these preliminary steps of the analysis.

ACKNOWLEDGEMENTS

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Schnoor is acknowledged. Various phases of the computations were performed by Cherng-Ju Kim and George A. Leahy, research assistants in the Environmental Engineering and Science Program at Manhattan College.