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TRACING KEPONE CONTAMINATION IN JAMES ESTUARY SEDIMENTS

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The escape of Kepone into the James River estuary, Virginia, for more than nine years produced widespread contamination of the sediments with important ecological consequences. The pollutant extended seaward more than 100 km from its source and contaminated an estimated 31 million tonnes of sediment to depths of more than 60 cm. Kepone spread through the food chain and to every segment of the environment from marshes to the channel floor.

Kepone escaped mainly during high river inflow from a point source in freshwater tributaries. Near the source Kepone is associated with organic material but in the lower estuary it is adsorbed on fine-grained sediment. A bulk of the contaminated sediment is transported and trapped by the estuarine circulation. It accumulates in the turbidity maximum of the middle estuary far from the source. In this zone it is deposited in less energetic sites where sedimentation is relatively fast. Contamination extends downward > 60 cm; peak concentrations at 10 to 25 cm relate to high production in 1974. The Kepone inventory is now being buried by less contaminated sediment. "Recovery" is most rapid in the middle estuary where contamination was most intense.

INTRODUCTION

The careless manufacture and disposal of Kepone produced widespread contamination of sediments in James River estuary, Virginia. It contaminated an estimated 31 million tonnes of sediment (dry wt) and triggered an intensive investigation to determine its transport and fate in the estuary. The chief questions addressed were: (1) Where to? And how much? How far seaward does contamination extend at different concentrations? Where are the major Kepone sinks? (2) What are the transport routes? (3) What is the contamination history? How long will contamination persist?

This paper summarizes field and laboratory results directed toward these questions. It was first necessary, however, to determine the composition and sedimentologic association of the "new" pollutant. Furthermore, analytical techniques for processing large numbers of samples with low Kepone concentrations had to be developed.

WHAT IS KEPONE?

Kepone or chlordecone ($C_{10}Cl_{10}O$), is a polychlorinated hydrocarbon that degrades very slowly and resists destruction or decomposition. Because of its persistance and toxicity to insects, it was mainly exported and used on potato beetles, banana worms, and fire ants. When it reacts with phosphorus pentachloride, "Mirex" is produced. Kepone is highly toxic to animal life and a suspected carcinogen.

SOURCE AND SUPPLY

Kepone entered freshwater reaches of the estuary from a point source at production sites of Allied Chemical Corporation and Life Science Products in Hopewell, Virginia, U.S.A. Approximately 1·5 million kilograms, or 1650 tonnes, were produced between 1966 and 1975.

Kepone entered the estuary via waste water of a municipal sewage system and by leaching of contaminated soils and solid dump wastes in landfill. It seems likely that Kepone was flushed into the estuary through small tidal tributaries during times of run-off. However, the rates of supply are unknown.

Although Kepone escaped into the estuary undetected for nine years, archived sediment samples

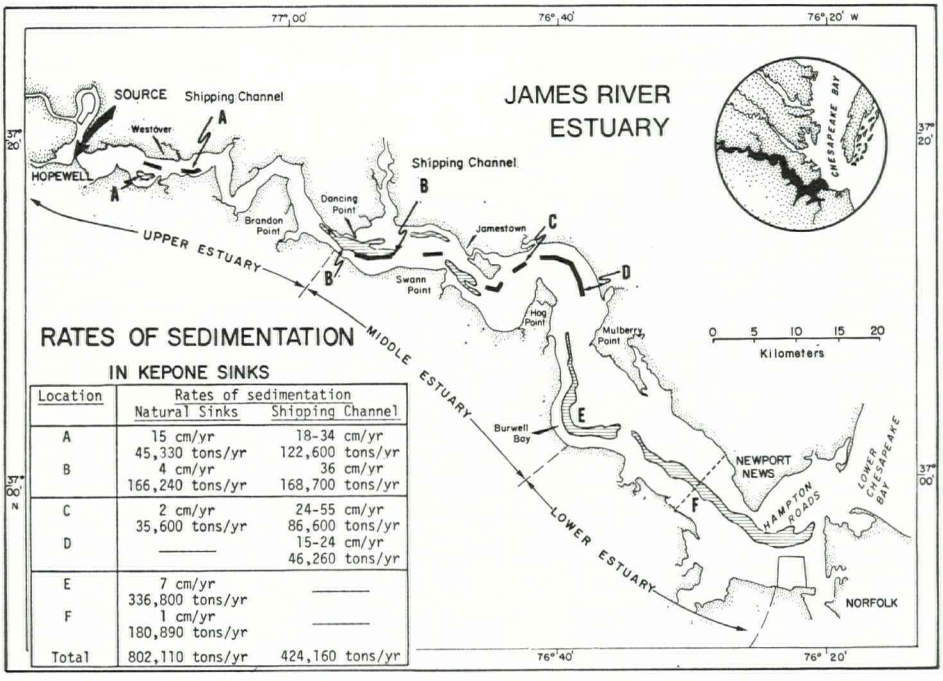

Figure 68. Location of the James River estuary in the southern Chesapeake Bay region, upper right. Zones of deposition, major Kepone sinks, and natural channel, hachured; shipping channel, solid. Rates from radionuclide analyses and from maintenance dredging surveys of the Corps of Engineers, 1965 to 1977.

collected from the middle estuary revealed that Kepone first appeared in July 1966 and substantial amounts were present in May 1967. Therefore, contamination of the middle estuary began within 6 to 12 months after production started and spanned more than nine years.

THE ESTUARY

The James River estuary is a transition zone between fresh water in the river and the marine environment of lower Chesapeake Bay (Fig. 68). Salinity ranges from nearly zero at Jamestown to $19^{0}/_{00}$ on the average, at the mouth. Tidal amplitude is less than 51 cm but tidal energy is sufficient to promote haline mixing and substantial resuspension of fine-grained bed sediments.

Sediments accumulating in the James River are predominately silty clay with mean particle size ranging from 1·4 μ to 20 μ. Organic matter is about 1·4 to 7·0 per cent by dry weight. Most organic-rich fine sediment accumulates in the middle estuary, mainly in less energetic parts of the zone as marginal embayments, and on the channel floor (Fig. 68). These are sites of relatively fast accumulation and thus potential sinks for contaminated sediment.

FIELD OBSERVATIONS

The top one cm of bed sediment was obtained repetitively every three to nine months, from more than 40 stations from December 1976 to September 1979, a time after the main supply of Kepone had been halted. Distribution of Kepone at depth was determined from 25 gravity cores and 24 box cores. Suspended sediments were sampled in contamination zones simultaneously with current measurements during periods of: (1) low river inflow, well-mixed salinity structure and spring tide, (2) high river inflow, partly-stratified structure and spring tide. Collections were made by submersible pump and centrifuging from 3 to 4 depth intervals, over 2 to 4 tidal cycles and at 4 to 6 anchor stations. The samples were analysed for total suspended concentrations, Kepone content, total carbon and combustible organic content. Procedural details are given in Trotman and Nichols (1978).

LABORATORY ANALYSIS

Kepone concentrations in the sediment were quantified by gas-liquid chromatography with electron capture detectors. The basic extraction procedures involved drying the samples with anhydrous sodium sulfate

and soxhlet extraction of the Kepone with 1:1 (v/v) ethyl:petroleum ether (16 hrs). Following extraction, interfering compounds were removed by column chromatography utilizing activated florisil. To check the extraction efficiency of this method, samples were fortified with known amounts of Kepone, extracted and analysed. Extraction efficiencies are given in Huggett et al. (1980).

For estimating time scales of sediment contamination, subsamples from cores taken in December 1978 were analysed for gamma-emitting radionuclides using a lithium-drifted germanium detector coupled to a computer-based multichannel analyser system. Particular attention was given to the artificial radionuclides ^{137}Cs, ^{134}Cs, and ^{60}Co.

KEPONE BEHAVIOR

WHAT STATE?

All major components of the estuary were contaminated with detectable concentrations of Kepone; i.e. water, sediments, and biota (Table 21). Highest residues, averaging 4·8 $\mu g \cdot g^{-1}$ were found in zooplankton while phytoplankton averaged 1·3 $\mu g \cdot g^{-1}$. Bed sediments averaged 0·11 $\mu g \cdot g^{-1}$ in August 1977, a content slightly higher than that in total suspended material which averaged 0·09 $\mu g \cdot g^{-1}$. The sediments not only contained 9000 times more Kepone than estimated in solution, but the total mass of Kepone in bed sediments, an estimated 10 tonnes, exceeds that of all other reservoirs combined.

In laboratory experiments Huggett et al. (1980) tried to extract Kepone from contaminated bed sediment using estuary water of varying pH and salinity, e.g., 7 to 8 pH, and fresh water to 19·5 $^0/_{00}$. Thirty-six separate extractions were analysed with fractions in the range $\mu g \cdot kg^{-1}$, and the resulting Kepone content of the water was compared with that of the exposed sediment. Results showed no apparent effect of either pH or salinity on extraction of Kepone from the sediments. It was concluded that Kepone supplied in solution is strongly sorbed by suspended solids. It is unlikely, therefore, that Kepone is "extracted" by estuarine water or mobilized as it is transported seaward. Instead, Kepone provides a good tag for dispersal of river-borne sediment.

ASSOCIATION WITH SEDIMENTS

The association of adsorbed Kepone with sedimentary materials is revealed by natural distributions in bed sediments and by settling experiments (Trotman and Nichols, 1978). Scatter plots of Kepone content versus mean particle size and per cent clay throughout the estuary show no relationship. However, there is a general trend for Kepone content to increase with increasing organic content. In the laboratory, bulk bed sediment from different parts of the estuary was allowed to settle in carboys and analysed for particle size and total carbon content. Results showed that samples from near the source and the middle estuary contain a high Kepone content in coarse sediment size fractions (> 63 μ). These fractions also contain a relatively high carbon content. By contrast, samples from the lower estuary have a high Kepone content in fine size fractions (< 63 μ) of relatively low carbon content. Consequently, the association of Kepone in the sediments seems to shift from predominately organic material near the source to fine-grained sediment in seaward zones.

Table 21. Average Kepone concentrations and the estimated Kepone mass in various components of the James River estuary; mass expressed as wet weight

Component	Kepone content (μg/g)	Kepone mass (kg)
Zooplankton	4·80	25
Freshwater fishes	2·50	18
Migratory fishes	0·40	87
Phytoplankton	1·30	1
Organic detritus	0·70	–
Benthic fauna (molluscs)	1·50	6
Bed sediments	0·11	9 300*
Suspended material (Total solids)	0·09	5
Estuary water	< 0·00001	–

* Equivalent dry wt mass in 2600 kg.

SEDIMENT DISTRIBUTION

WHERE TO?

Kepone contaminated nearly every segment of the estuary including tributary creeks, marshes, shoals, and the channel floor. However, patterns of contamination vary widely across the estuary and with distance seaward along its length. Contamination of bed sediment extends from 11 km above the Kepone source at Hopewell seaward to Hampton Roads, a distance of 130 km. Average concentrations in surface sediments along the main channel range from less than 20 ppb to 193 ppb (Fig. 69). Although sediments near the source are locally enriched to 4540 ppb, muddy sediments from the middle estuary are the most widely contaminated. Major sinks form in the middle estuary, the Jamestown–Dancing Point reach, and in Burwell Bay (Fig. 68). These zones lie in the turbidity maximum at average river inflow; they are sites of relatively fast sediment accumulation (Nichols, 1972). Instead of concentrations decreasing with distance

away from the source, Kepone content is higher in the middle estuary than elsewhere. The "ultimate" Kepone sinks are located far from the source. Consequently, the distribution of contaminated bed sediment is not controlled by supply from a point source but mainly by the estuarine accumulation and depositional regime.

WHAT ROUTES?

Kepone is transported from its source to its sink along two pathways: (1) a bioecological route, and (2) a hydrodynamic sedimentologic route (O'Connor and Farley, 1977). Although the hydrodynamic route is very complex, an attempt is made to trace transport routes from: (1) short-term field observations of contaminated suspended material, and (2) bed sediment contamination patterns in relation to the Kepone source.

Suspended sediment provides a vehicle for dispersal and accumulation of Kepone. It can be supplied directly by erosion of contaminated soils or creek sediments; alternately, it may serve as a depot for adsorption of Kepone introduced in solution.

At relatively low river inflow, a time when sediment influx is low and the salt intrusion head is close to the source (station 111, Fig. 70), the Kepone content of suspended material tends to increase with distance toward the source. This trend partly reflects low dilution of contaminates by mainstream influx; for another part, it can reflect resuspension of contaminated bed sediments (Fig. 70B, C). This is confirmed by temporal measurements of Kepone in suspended material over several tidal cycles that tend to go up and down with the suspended concentrations and with the current strength. When the net transport of Kepone is calculated over four tidal cycles, the magnitude of transport as well as the direction vary widely from station to station along the estuary. Transport is affected more by local variations in bed sediment resuspension rather than by advection from source to sink.

At relatively high river inflow, a time of substantial sediment influx, both the salt intrusion and the landward near-bottom flow are restricted to the lower estuary (station 28, Fig. 70). The distribution of Kepone content in suspended material tends to increase in the zone of the turbidity maximum (Fig. 70B). Since the turbidity maximum forms in a near-bottom convergence of residual river flow and estuarine flow (Kuo et al., 1978), Kepone transport must follow the estuarine circulation of a partly-stratified system, i.e.: (1) seaward through tributary creeks and freshwater reaches, (2) partial entrapment in the turbidity maximum of middle reaches, (3) partial seaward escape through the upper estuarine layer, and (4) landward transport through the lower estuarine layer and settling into sinks. By following these routes, contaminated suspended material that is very fine grained or organic can escape the estuary through the upper layer. However, the bulk of the sediment load that is carried near the bed is mainly trapped in the estuary. Once deposited, Kepone may be ingested by benthic animals and thus transferred to bioecological pathways.

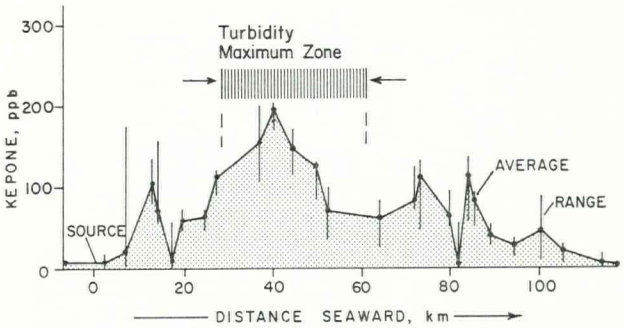

Figure 69. Distribution of Kepone concentrations in bed sediments with distance seaward along the estuary. Based on an average of three sample sets collected from channel stations (> 4 m depth) between December 1976 and July 1977.

KEPONE RECORD

A time scale for evaluating the contamination history was developed from radionuclide distributions. Worldwide fall-out from atmospheric weapons tests deposited ^{137}Cs in the James River watershed with peak deposition in 1963. This radionuclide binds strongly to illitic soil minerals (Tamura, 1964) and is transported into the estuary with erodable soil particles. In addition, all three man-made radionuclides, ^{137}Cs, ^{134}Cs, and ^{60}Co are released into the middle estuary via discharge from a nuclear power plant at Hog Point (Fig. 70A). These radionuclides also became sorbed to the sediments and deposited in the estuary. Records of the power plant releases (Phillips and Gruhlke, 1977) indicate several "spikes" or pulse inputs rather than a constant rate of release. The largest spike is 10 Ci of ^{137}Cs released in June 1975 together with approximately 2 Ci of ^{134}Cs and 0·4 Ci of ^{60}Co (decay corrected to December 1978). For ^{60}Co other spikes occurred in March 1976 and January 1977. When high concentrations of these radionuclides are found at depth in cores, they provide a time marker for Kepone contamination. In turn, both the radionuclide and the Kepone distributions provide a time tag to determine rates of sedimentation.

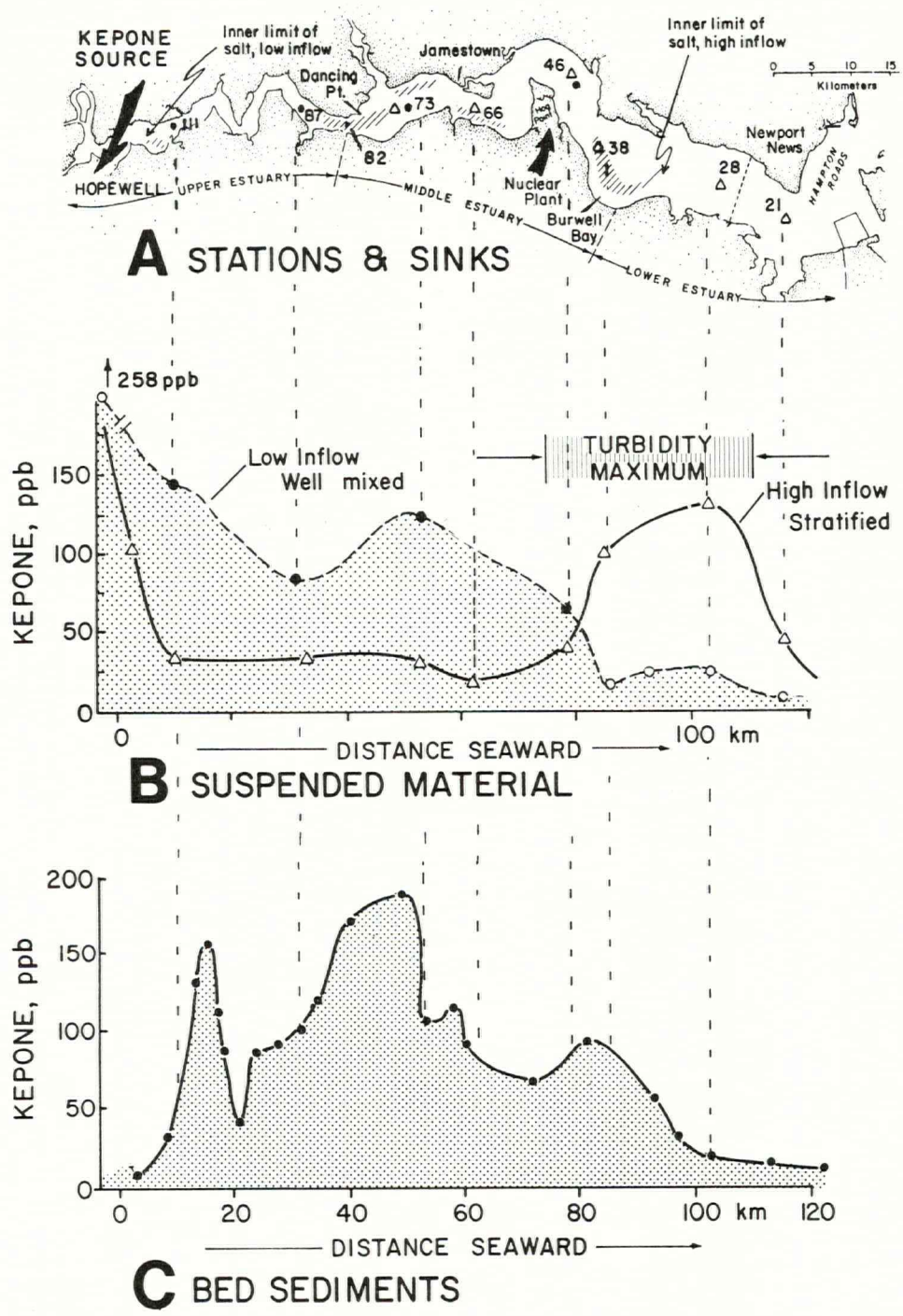

Figure 70. A. Location of anchor stations or suspended sediment and current measurements; hachured, location of major Kepone sinks. B. Longitudinal distribution of Kepone content in total suspended material, average of surface and near-bottom concentrations at low river inflow, August 1977; and high river inflow, April–May 1979. C. Longitudinal distribution of Kepone content in bed sediments from the channel, July 1977.

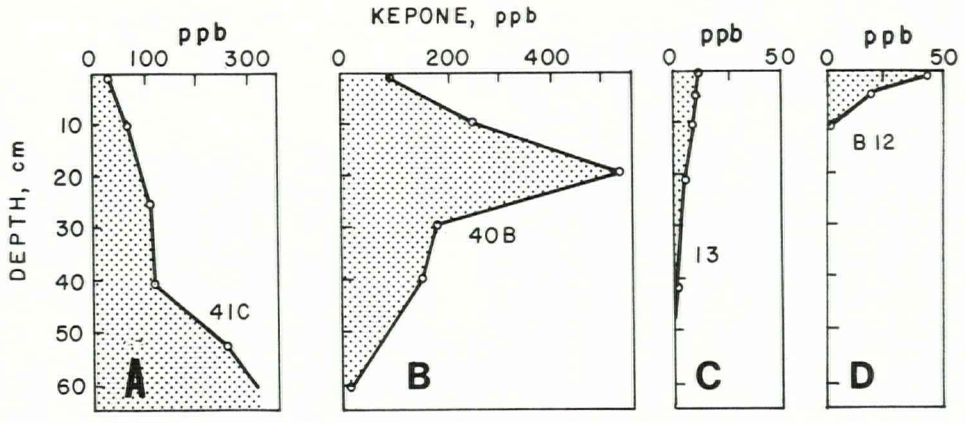

Figure 71. Vertical profiles of Kepone content in cores from different sedimentation zones. A, relatively fast sedimentation in shipping channel; B, intermediate sedimentation, natural channel; C, lower estuary; D, slow sedimentation, middle estuary shoal.

The record of Kepone contamination is revealed by vertical profiles of Kepone content as a function of depth in the sediments (Fig. 71). Character of the profiles varies widely according to the relative rates of deposition. A nearly complete record of contamination is exhibited in cores from zones where sedimentation is intermediate, i.e. 3 to 10 cm per year. Such zones consist of tributary creek mouths, natural channels, and margins of shoals. These profiles consist of peak Kepone concentrations at 10 to 20 cm below the surface with generally decreasing concentrations upward and downward (e.g. Figs. 71B, 72). As shown in Figure 72, the contamination peak follows peak Kepone production in 1974. A secondary maximum at 25 to 30 cm approximately corresponds to relatively high production during 1971 to 1972.

In zones where sedimentation is relatively fast, e.g. the shipping channel floor, and major Kepone sinks as Burwell Bay, Kepone concentrations decrease upward (Fig. 71A). This trend represents decreasing contamination from 1975 to 1978 following a halt in production. By contrast, where sedimentation is relatively slow or the upper record missing, Kepone content increases upward (Fig. 71D). Contamination extends to greater depths in zones of fast sedimentation than in zones of slow sedimentation.

Cores from the lower estuary, e.g. 13, Figure 71C, exhibit an increase in Kepone content upward. One interpretation of this trend is that Kepone content is increasing in the lower estuary as concentrations decrease in the middle and upper estuary. However, the Kepone content is very low and X-ray radiographs indicate extensive bioturbation. Most cores from the middle and upper estuary, however, are free of bioturbation and physical reworking. Despite two major floods and frequent coastal storms, the sedimentary record of Kepone contamination is well preserved.

HOW LONG?

The record of contamination indicates that the Kepone inventory is being progressively buried and diluted by an influx of less contaminated sediment. "Recovery" began shortly after peak production was halted in July 1975. It started in the middle estuary, a zone of high Kepone content and relatively fast sedimentation, e.g. the Dancing Point–Jamestown sink (Fig. 70A). The vertical profiles show that recovery was relatively fast at first, in 1976, and then more gradual after 1977 (Figs. 71A, 72). Recovery has been aided by frequent and abnormally high river inflow with consequent high sediment influx. Relatively uniform concentrations in the upper 5 to 10 cm of a few cores suggest a continued "residual" supply of Kepone either from secondary non-point sources as plankton and resuspended sediment within the estuary, or from the original source area.

The trend of recovery recorded in cores is confirmed by repetitive sampling of surface sediments along the estuary channel from September 1976 to September 1979. As shown in Figure 73, concentrations decreased most in the middle estuary between September 1976 and July 1977. Although upper and lower estuary stations exhibit local variations and reversals in the trend depending on the density of stations and possible scour, the main trend of recovery compares favorably with upper parts of cores.

Recovery is also indicated by average concentrations in surface sediments with time in the two main

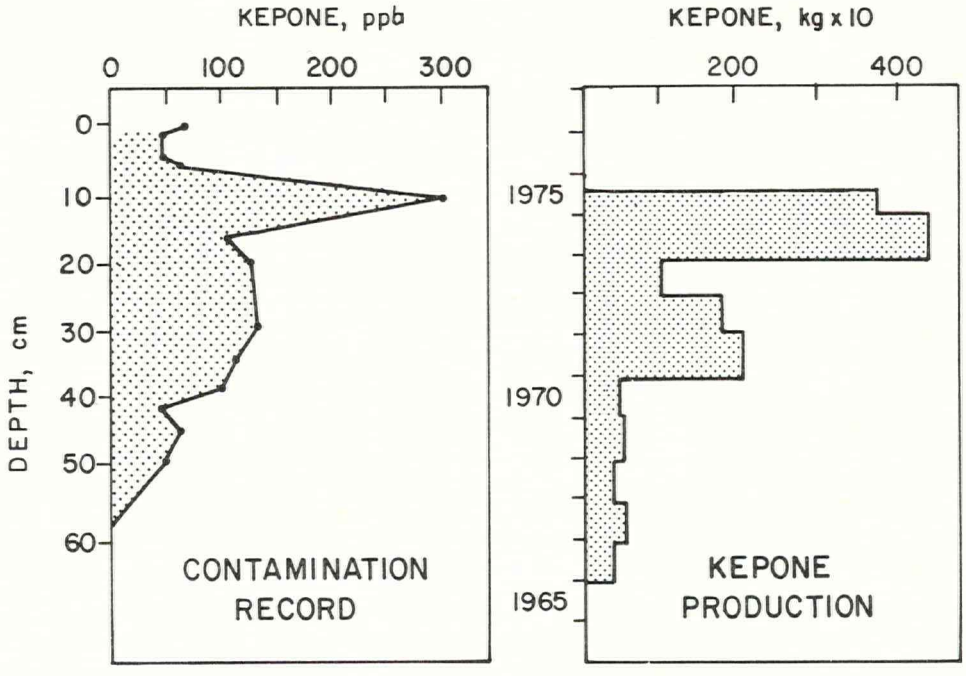

Figure 72. Vertical profile of a nearly complete contamination record, core 82 (Fig. 70A), in relation to Kepone production from sales records, 1966 to 1975.

sinks (Fig. 74). These show more rapid recovery in the landward sink than in the seaward sink, i.e. the Dancing Point–Jamestown sink, which contains higher concentrations and mass of Kepone, an estimated 2·6 tonnes (dry wt). Fortunately, zones where contamination is most intense have more rapid burial and recovery.

Despite the reduced concentrations of Kepone to low levels in the sediments, relatively high contamination persists in plankton and fish throughout the estuary. This trend suggests that Kepone can persist in biological components long after major reductions in the original source input. It remains to determine if the sediment sinks represent terminal deposition of Kepone or if they simply act as temporary storage reservoirs from which remobilization can occur.

WHAT NOW?

The lessons learned from Kepone pollution point out gaps in our knowledge that require attention for developing future studies elsewhere.

1. Undetected for nine years, Kepone is an example of but one out of thousands of potentially new toxic substances being manufactured every year. Such substances should be identified by groups and their association with the sediments determined.
2. Sources of substances, point and non-point sources, need to be assessed and if possible, their input loadings determined. Each input could be considered a natural experiment and monitored or utilized for study.
3. Many substances have been widely dispersed from their source, yet have found their way into distant zones of sediment accumulation. Entrapping processes need attention, particularly those leading to enrichment of organic material and very fine sediment, and those that induce rapid sedimentation in deeper water areas. Such sites are the most sensitive indicators of contamination.
4. Fate of contaminates in sinks should be studied through: a, characterization of physical, chemical, and biological processes operating in the sediments after deposition; and b, assessment of the rates of those processes. Significant processes include resuspension and exchange with overlying water, at times caused by storms, in addition to biological processing and chemical diagenesis. Attention should be given to degradation of the contaminates in the sediment and biological availability of sedimentary material.

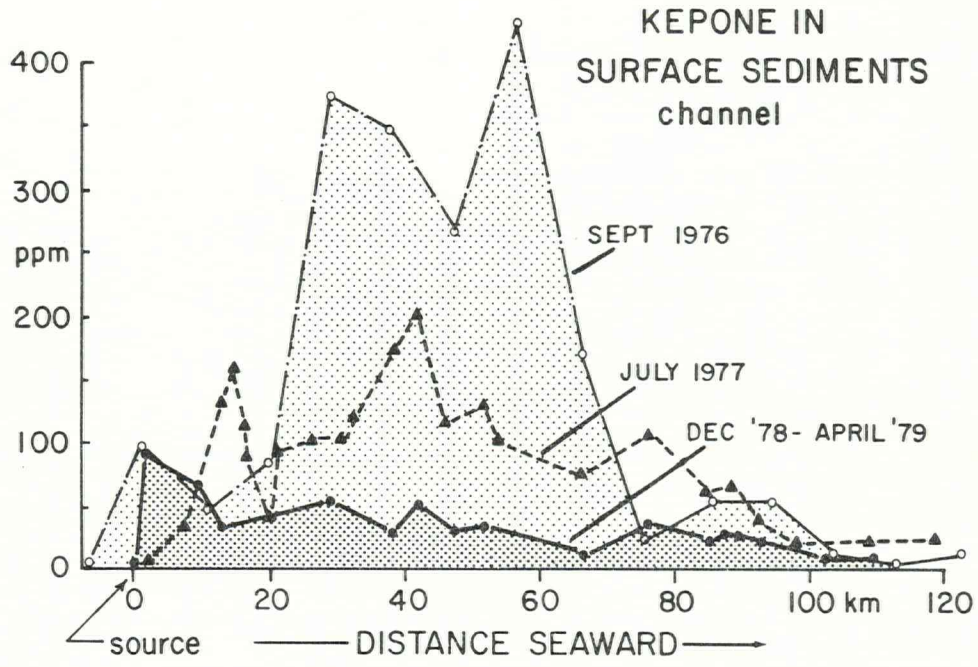

Figure 73. Longitudinal distribution of Kepone in surface sediments at different times, September 1976, July 1977, December 1978 to April 1979. Decreasing concentrations indicate gradual "recovery" in the middle estuary.

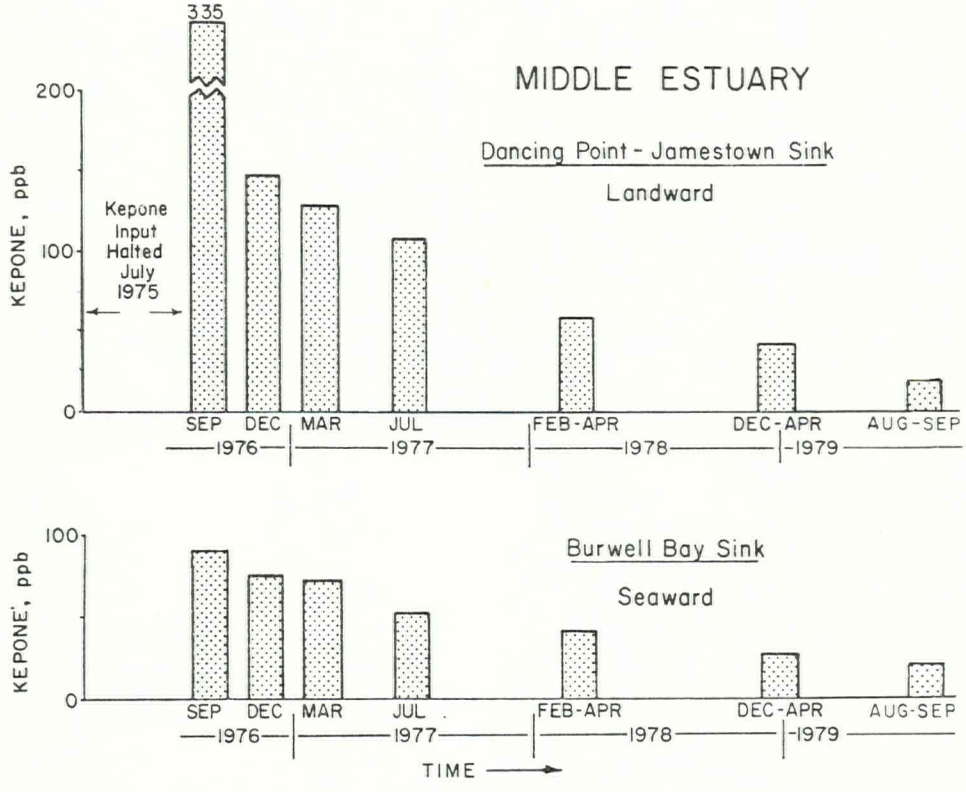

Figure 74. Time trends in average Kepone content of surface sediments from major sinks of the middle estuary between September 1976 and August–September 1979.

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REFERENCES

Huggett, R. J., Nichols, M., and Bender, M. E. 1980. Kepone contamination of the James River Estuary. *In* Am. Chem. Soc. Contaminants and sediments, Vol. 1, pp. 33–52. Ed. by R. A. Baker. Ann. Arbor Science Publishers Inc., Ann Arbor, Michigan.

Kuo, A., Nichols, M., and Lewis, J. 1978. Modeling sediment movement in the turbidity maximum of an estuary. Va. Water Resources Center, Bull. 111, 76 pp.

Nichols, M. 1972. Sediments of the James River Estuary, Virginia. *In* Geol. Soc. Am. Memoir, 133: 196–211. Ed. by B. Nelson.

O'Connor, D. J., and Farley, K. 1977. Preliminary analysis of Kepone distribution in the James River. Report to the Environmental Protection Agency, Environmental Research Lab, Gulf Breeze, Fla., 22 pp.

Phillips, J. Wynn, and Gruhlke, J. 1977. Summary of radioactivity released in effluents from nuclear power plants from 1973 through 1976. U.S. Environmental Protection Agency, EPA-520/3-77-012.

Tamura, T. 1964. Selective sorption reaction of cesium with mineral soil. Nucl. Safety, 5: 262–268.

Trotman, R. and Nichols, M. 1978. Kepone in bed sediments of the James Estuary. Virginia Institute of Marine Science, Spec. Sci. Rept., 91: 24 pp.