1979

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**Recommended Citation**

Bender, M. E.; Huggett, R. J.; and Hargis, W. J. Jr., "Kepone® Residues In Chesapeake Bay Biota" (1979).  
*VIMS Books and Book Chapters*. 21.  
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KEPONE® RESIDUES IN CHESAPEAKE BAY BIOTA

by

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ABSTRACT

Oysters from the James displayed variations in Kepone residue levels related to water temperature and their spawning cycle. Oyster depuration rates were related to temperature. In summer the "biological half-life" of Kepone in oysters was about one week, while during the winter about 40 days were required for residue levels to decline by 50 per cent. Residues in blue crabs varied as a function of sex, males having considerably higher residues than females. Fin fish levels from the James varied greatly, with residue levels being dependent on species and length of residence for migratory fishes. Average Kepone residues in freshwater fish species, which are resident their entire lives, varied from 0.04 to 2.4 µg/g. Long-term resident estuarine fin fish varied less than freshwater species, with mean concentrations between 0.6 and 2.7 µg/g. Short-term resident marine fish species, e.g., American shad and menhaden, exhibited low residues averaging less than 0.1 µg/g, while spot and croaker, which reside in the river for longer periods, had higher residues averaging 0.81 and 0.75 µg/g respectively.

In the Bay, croaker, spot, trout and flounder all exhibited similar residue patterns showing lower residue levels at stations further up-Bay from the Kepone source in the James River.

INTRODUCTION

Kepone, an insecticide whose use in the United States was restricted to an ingredient of ant and roach baits, was produced by two companies located in Hopewell, Virginia between 1963 and 1975. Allied Chemical produced about 1.5 million pounds of the chemical on an irregular schedule between 1966 and 1973. Life Science Products, Inc. made approximately 1.7 million pounds of the insecticide during 16 months of operation in 1974 and 1975. In July of 1975 the plant closed because of inadequate employee protection in the production of the toxic compound.

® Registered trademark for decachlorooctahydro-1,3,3-metheno-2H-cyclobuta (cd) pentalen-2 one. Allied Chemical Company, 40 Rector Street, New York, New York 10006.

Eflluents from the Life Science plant entered the Hopewell sewage treatment plant and caused its digesters to fail. Since the effluent from the sewage treatment plant was discharged to the upper tidal James River through Baileys Creek (Figure 1), the U.S. Environmental Protection Agency conducted a survey during the late summer of 1975 to determine if Kepone had contaminated the James River ecosystem. Their report (EPA, 1975) showed the pollutant to be in the air, soil and waters around Hopewell. Since that time extensive monitoring and research activities have been conducted by various state and federal agencies.

This manuscript discusses the results obtained during approximately eighteen months of monitoring Kepone residues in biota from the James River and lower Chesapeake Bay.

METHODS

To follow seasonal trends in Kepone residue levels, 12 oysters were taken monthly by the Virginia State Health Department and VIMS from each of the sampling stations shown in Figure 2. To determine depuration rates, oysters were taken from Wreck Shoals in the James River and transplanted to the York and Rappahannock rivers during January of 1975. A similar program was conducted during the early summer when oysters were transplanted to the York from five stations in the James River (Swash Hole, Ballard Marsh, James River Bridge, Pagan River and Nansemond Ridge).

Fin fish, blue crabs and other invertebrates were sampled by trawl over the entire tidal James at approximately 5 mile intervals. In the Chesapeake Bay fin fish collections were made from existing commercial pound nets located as shown in Figure 1. Collections at these stations for five species were made during April, June and September. All collections were either iced or frozen in the field prior to transport to the laboratory for processing.

Clams and oysters were opened at the hinge, drained, shucked, composited, and then blended to obtain a homogeneous mixture. Blue crabs were picked raw and the meats, excluding claw, were combined prior to blending. Fin fish tissues were ground in a meat grinder into hamburger consistency. These samples consisted of either whole fish or fillets (scaled, with skin). Whole fish
samples were utilized for small species (less than 30 grams of flesh). The small species included: spottail shiner, bay anchovy, Atlantic silverside, and hogchoker. Following blending or grinding, all samples were frozen at -5°C for 24 hours in order to rupture cells. After thawing, a mixture of anhydrous sodium sulfate and Quo®G-30 (precipitated silica, Philadelphia Quartz Co.) was added for desiccation. The proportions of sample to the desiccants were: 30 g mollusk tissue: 81 g Na₂SO₄: 9 g Quo; 30 g fish or crustacean tissue: 54 g Na₂SO₄: 6 g Quo. The samples were then mixed and refrozen to insure cell rupture. After thawing, the desiccated samples were ground with a blender to a powdery consistency and transferred to pre-extracted paper thimbles for Soxhlet extraction. Extraction was carried out using 1:1 ethyl ether-petroleum ether for 16 hours. Extracts were then concentrated by evaporation, under vacuum and heat, and cleaned by activated florisil column chromatography (EPA, 1975). The Kepone containing elutriate was analyzed by electron capture gas chromatography utilizing packed columns with one or
more of the following liquid phases: 4% SE-30 + 6% OV 210; 1.5% OV-17 + 1.95% QF-1 + 3% OV-1. On occasion, when concentrations and volume were sufficiently large to provide enough material for analysis, Kepone presence was confirmed by mass spectrometry.

Residue concentrations are reported as µg/g (ppm) wet weight.

RESULTS AND DISCUSSION

To detect whether differences in residue levels in oysters existed due to sampling location, a one-way analysis of variance was performed on data from 8 stations sampled over a period of 13 months. The overall mean residue level was 0.16 µg/g for this period. Differences between stations were not detected at the 0.05% level (F = 1.70, 7/95 d.f.). Seasonal differences in residue levels were tested by comparing the monthly results from all sampling stations. The F ratio obtained was significant at the 0.01% level (6.48 with 14/101 d.f.). Moving averages were used to construct Figure 3 which depicts the seasonal variation of Kepone residues in James River oysters. Each point in this figure represents the average of the preceding, present and subsequent months.

FIGURE 3 Seasonal Trends in James River Oyster Residues

In bodies of water contaminated by Kepone, residue levels decline during the colder months, when the oysters are relatively inactive. As feeding increases during the spring, residues increase. A decline in Kepone level occurs after spawning in the late summer and then residues increase briefly until the weather cools when they again decline.

The major value of the oyster beds in the James River is their production of seed oysters which are transplanted to growing areas throughout the entire Chesapeake Bay. Because of this practice and the importance of this seafood to the economy, it was essential to know the rate at which oysters depurated Kepone. Consequently, depuration experiments were conducted.

The results of the depuration experiments are summarized graphically in Figure 4. The loss rate shown during the winter represents the pooled data from oysters depurated in both the York and Rappahannock rivers. These oysters originated from the same stock and were held at locations of similar salinity.

FIGURE 4 Oyster Depuration Rates

Oysters from five locations in the James were depurated in the York during the summer. The average initial Kepone concentration for these animals was 0.107 µg/g, with a standard error of 0.0023. After 16 days of depuration, the average Kepone concentration for these oysters was 0.018 µg/g with a standard error of 0.0018.

As might be expected, temperature had a dramatic effect upon the rate at which Kepone was depurated by the oysters. In summer the “biological half-life” of Kepone was about one week, while during the winter about 40 days were required for residue levels to decline.

Average Kepone residues for the major species collected in the James River are shown in Table 1. Kepone levels in migratory species, e.g. croaker, spot, bluefish, and shad, increased as they stayed longer in the estuary; therefore, the residue levels for these species reported in the table are averaged over their period of residence. Residue levels in long-term residents, e.g. hogchoker, white perch and catfish, did not fluctuate seasonally. Although the data are limited, no trends in residue levels in the James River could be detected as a function of distance from the Kepone source at Hopewell, either for estuarine species or for the freshwater residents.

Considerable variation in Kepone residue occurs between species (Table 1). Freshwater species, which are resident their entire lives, vary in average Kepone residues from 0.04 µg/g to 2.4 µg/g. Of the two species of catfish of major commercial importance in the river, the
TABLE 1 James River-Kepone Residues (µg/g)

<table>
<thead>
<tr>
<th>Long-term Residents</th>
<th>X</th>
<th>N</th>
<th>Std. Error of X</th>
</tr>
</thead>
<tbody>
<tr>
<td>Spottail shiner (Notropis hudsonius)</td>
<td>0.08</td>
<td>6</td>
<td>0.02</td>
</tr>
<tr>
<td>Channel catfish (Ictalurus punctatus)</td>
<td>0.04</td>
<td>45</td>
<td>0.004</td>
</tr>
<tr>
<td>White catfish (Ictalurus catus)</td>
<td>0.25</td>
<td>14</td>
<td>0.03</td>
</tr>
<tr>
<td>American eel (Anguilla rostrata)</td>
<td>0.64</td>
<td>15</td>
<td>0.55</td>
</tr>
<tr>
<td>Black crappie (Pomoxis nigromaculatus)</td>
<td>1.0</td>
<td>10</td>
<td>0.13</td>
</tr>
<tr>
<td>Largemouth bass (Micropterus salmoides)</td>
<td>2.4</td>
<td>14</td>
<td>0.54</td>
</tr>
<tr>
<td>White perch (Roccus americanus)</td>
<td>2.7</td>
<td>20</td>
<td>0.39</td>
</tr>
<tr>
<td>Bay anchovy (Anchoa mitchilli)</td>
<td>0.65</td>
<td>13</td>
<td>0.15</td>
</tr>
<tr>
<td>Atlantic silverside (Menidia menidia)</td>
<td>1.6</td>
<td>15</td>
<td>0.43</td>
</tr>
<tr>
<td>Hogchoker (Tricheutes maculatus)</td>
<td>0.94</td>
<td>22</td>
<td>0.13</td>
</tr>
<tr>
<td>Grass shrimp (Palaemonetes pugio)</td>
<td>0.60</td>
<td>8</td>
<td>0.15</td>
</tr>
<tr>
<td>Sand shrimp (Crangon septemspinosus)</td>
<td>2.0</td>
<td>3</td>
<td>0.09</td>
</tr>
<tr>
<td>Xanthid crabs</td>
<td>0.27</td>
<td>3</td>
<td>0.03</td>
</tr>
<tr>
<td>Blue crab (Callinectes sapidus)</td>
<td>0.19</td>
<td>180</td>
<td>0.02</td>
</tr>
<tr>
<td>Blue crab (Callinectes sapidus)</td>
<td>0.81</td>
<td>43</td>
<td>0.07</td>
</tr>
<tr>
<td>Oyster (Crassostrea virginica)</td>
<td>0.16</td>
<td>140</td>
<td>0.01</td>
</tr>
<tr>
<td>Hard clam (Mercenaria mercenaria)</td>
<td>0.09</td>
<td>121</td>
<td>0.009</td>
</tr>
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</table>

<table>
<thead>
<tr>
<th>Short-term Residents</th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>American shad (Alosa sapidissima)</td>
<td>0.03</td>
<td>50</td>
<td>0.004</td>
</tr>
<tr>
<td>Atlantic menhaden (Brevoortia tyrannus)</td>
<td>0.05</td>
<td>8</td>
<td>0.02</td>
</tr>
<tr>
<td>Spot (Leiostomus xanthurus)</td>
<td>0.81</td>
<td>40</td>
<td>0.13</td>
</tr>
<tr>
<td>Croaker (Micropogon undulatus)</td>
<td>0.75</td>
<td>60</td>
<td>0.16</td>
</tr>
<tr>
<td>Bluefish (Pomatomus saltatrix)</td>
<td>0.29</td>
<td>30</td>
<td>0.20</td>
</tr>
</tbody>
</table>

1 Blends of 12 individuals.

channel catfish, Ictalurus punctatus, and the white catfish, Ictalurus catus, the former exhibited lower levels by almost an order of magnitude. We have investigated the total lipid content of these two species (Bligh and Dyer, 1959) as a possible explanation for the residue differences observed and find virtually no difference between the two species in lipid content. The average lipid content of flesh for white catfish was 9.6 mg/g (S.D. 2.3) and 10.7 mg/g (S.D. 2.1) for the channel catfish.

Other possibilities to explain the species differences include either different uptake mechanisms or possibly the existence of metabolic mechanisms for Kepone breakdown and/or elimination in channel catfish which white catfish do not possess.

Long-term resident estuarine (brackish water) fin fish varied less than the freshwater species in their Kepone residues, with average levels between 0.6 and 2.6 µg/g.

Short-term marine fish species, e.g. American shad and menhaden, exhibited low levels of Kepone averaging less than 0.1 µg/g, while spot and croaker, which usually reside in the river for somewhat longer periods, had residues averaging 0.81 and 0.75 µg/g respectively.

Blue crab residues averaged 0.19 µg/g for females and 0.81 µg/g for males. The male crabs spend a greater proportion of their lives in the river system than do the females; this habit probably accounts for the observed difference in Kepone body burdens.

Residue levels for other chlorinated hydrocarbon pesticides, e.g. DDT, have been shown to vary as a function of size for a given fish species (Reinhart and Bergman, 1974). We have tested four species of fish (croaker, bluefish, hogchoker and channel catfish) to evaluate whether a similar relationship exists with Kepone. An example of the type of relationship found between Kepone and fish size is shown in Figure 5. Hogchokers, croaker, and bluefish exhibited similar relationships, indicating that Kepone body burdens are not related to the size of the individuals.

The effect of length of residence in the lower James on residue levels can be seen in Figure 6, where a long-term resident, hogchoker, and a migrant, croaker, are compared. Residues in croakers increase as their length of residence increases beginning in January when they first move into the estuary, and increasing linearly throughout the summer. Hogchokers, on the other hand, being permanent residents of the estuary, appear to be at equilibrium with Kepone sources in the river system.

FIGURE 5 Length vs. Kepone Residues for Channel Catfish From the James River
Stations in Chesapeake Bay were sampled for five fin fish species during April, June and September. Our most complete set of data is for 21 June 1976 sampling period, when at least 10 fish of each species were obtained. The results of this survey are shown in Figure 7. Croaker, spot, trout and flounder all exhibit similar residue patterns showing declining residues as one moves up-Bay from the Kepone source in the James River.

FIGURE 6 Seasonal Residue Patterns in James River Croakers and Hogchokers

FIGURE 7 Kepone Residue Patterns in Chesapeake Bay Fishes, 21 June 1976

Those species in the James River which have body burdens of the pesticide over the established “action levels” may not be harvested. Action levels are established by the Food and Drug Administration when food products are inadvertently contaminated with harmful materials. Since people consume different quantities of various foods, different action levels for different foods are established. The higher action level is assigned to those foods which are eaten in smaller quantities. Present action levels for fisheries products for Kepone are: 0.3 µg/g for fin fish, 0.3 µg/g for oysters and clams and 0.4 µg/g for crabs.

The presence of Kepone residues in aquatic resources of the James River has limited the harvest of certain species and created a situation which may result in damage to the resources through either acute or chronic toxic effects.

FIGURE 8 Frequency Distribution of Kepone Residues in Chesapeake Bay Bluefish, 21 June 1976

Bluefish, however, did not exhibit this pattern—their residues were essentially the same regardless of sampling location. The bluefish, being highly mobile, may move into the James for a time and then migrate to other areas of the Bay mixing with populations which have not stayed in the lower James River for an extended period of time. As a consequence, the resulting population sampled at a given station would be comprised of fishes with both high and low residue levels. Therefore the average residue level does not reflect dilution of the Kepone source, whether food and/or water, as is shown for the other species. Support for this theory is presented in Figure 8 which shows the distribution of Kepone residues in bluefish taken during the late June sampling. As can be seen in the figure, a biomodal distribution pattern exists, supporting our conclusions that those individuals with high residues spent more time in the James, where Kepone occurs, than the somewhat larger group having residues below 0.1 µg/g.

The factors which determine whether a particular species will concentrate Kepone above the “action level” are not well known. However, we do know that the crustaceans, fishes, and shellfish closer to the source, i.e. in the James River, have much higher residues than those found outside the James.

All commercial fin fish in the James River, with the exception of catfish, shad and herring, exceed the action level of 0.3 µg/g. Male blue crabs in the James generally have levels in excess of 0.4 µg/g, while females caught at the same location have lower residues.

At present we do not have any direct evidence that toxic effects due to Kepone exposure are occurring in the biota of the James River. However, laboratory studies to determine the potential impact of Kepone contamination on some estuarine organisms have been conducted. Hansen et al. (1977) have shown that the growth of mysid shrimp and sheepshead minnows was
reduced by exposure to 0.07 µg/l and 0.08 µg/l respectively. Blue crab mortality was observed by Schimmel and Bahner (1977) during a 28 day feeding experiment when the animals were fed food contaminated with Kepone at levels of 0.15 and 1.9 µg/g. Dupuy (1976) found setting success of larvae produced by Kepone-contaminated oysters taken from the James and spawned in the laboratory to be equal to control groups. Additional studies are in progress to further assess the potential effects of Kepone on other estuarine and freshwater organisms.

The results of two of these studies indicate that effects on populations of some species may be occurring in the James River. The strong probability that blue crab mortalities are related to ingestion of Kepone is indicated by the fact that Kepone residues in most James River fish, a primary food of the crab, are equal to or exceed those which produced mortality in the laboratory. In addition, Kepone residues in James River fish are frequently higher than those reached by laboratory fish populations which were deleteriously affected by Kepone exposures (Hansen et al., 1977).

The rapid accumulation of Kepone by fishes such as spot and croakers during their spring migrations has demonstrated the continuing availability of Kepone in the system. Although we cannot project future conditions on the basis of scarcely more than a year’s data, there is no indication of a significant decline of residue levels in James River animals. Furthermore Kepone is a long-lived chemical species. We must conclude, therefore, that unless the reservoir of Kepone available in the system is somehow reduced, present conditions will continue for many years.

REFERENCES


