TITLE: Chlorinated Hydrocarbons in the Upper Chesapeake Bay

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ABSTRACT

This presentation will summarize the levels of chlorinated hydrocarbons (CHC) found in the Upper Chesapeake Bay during a study performed in 1974-1975. In particular, the levels of PCB's, chlordane, and DDTR found in bottom sediments, suspended particulates, zooplankton, and shellfish will be summarized. The discussion will include the role of sediment deposits as traps for CHC's' suspended particulates as transport vehicles for CHC's; and movement of CHC's from the suspended particulate reservoir into the biological system.

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The Upper Bay Survey, carried out by the Westinghouse Ocean Research Laboratory, was a multidisciplinary study of the levels and transport of chlorinated hydrocarbons (polychlorinated biphenyls (PCB) and hard chlorinated pesticides) in the upper Chesapeake Bay. The study was funded during 1974 by the Maryland Department of Natural Resources to gain the environmental and resource management information essential to the local shellfish industry. This discussion will concentrate on the data resulting from the hydrocarbon analyses of bottom sediments, suspended sediments, zooplankton and shellfish.

Figure I shows the principal sampling stations throughout the upper bay. Bottom sediment grab samples were taken using either a Wildco Eckmon Bottom Sampler or a Ponar Grab Sampler. Suspended sediments were collected at three depths (surface, midwater and 0.5m from the bottom) by filtering through a glass fiber filter. Oblique tows with paired half-meter standard oceanographic nets were used to collect the zooplankton samples while a modified bottom trawl or Ponar Grab Sampler was used to obtain the shellfish.

All samples were extracted with 2:1 hexane:acetone using a Soxhlet extractor and then were subjected to a fuming sulfuric acid treatment. In addition, many of the extracts (bottom sediment, suspended sediment and zooplankton) required treatment with elemental mercury to remove sulfur which interfered with the chromatographic analysis.

All glassware used in the analysis was washed, soaked in Chromic Acid solution, rinsed with solvents, baked and checked by GLC before use. The glass fiber filters used to collect the suspended sediments were also washed with solvents and checked by GLC before use. The chlorinated hydrocarbons were identified and quantitated using multi-column, electron-capture, gas liquid chromatography. Peak relative retention times (to Aldrin) and peak heights or areas were compared to those of standard compounds. The amounts of PCB's and chlorinated pesticides were estimated by a manual subtraction procedure correcting for the overlapping peaks.

The polychlorinated byphenyl (PCB) residue pattern observed most often matched Aroclor* 1254 or a mixture of Aroclors 1254 and 1262, although Aroclors 1242 and 1248 were also found in many samples. For the purposes of this discussion, the PCB's will be discussed as total PCB.

*Registered trademark of Monsanto

Table I summarizes the total PCB, total chlordane (α and γ) and the total DDT (DDE, DDD, DDT) residues. The large standard deviations make it apparent that the range of chlorinated hydrocarbons found in any particular sample type is broad. The values fluctuate rapidly enough both temporarily and spacially that only unusually large events could be observed at enough points to describe a trend when sampling is limited to a fairly small number of samples as in this study. However, the multidisciplinary nature of the study enabled us to examine the interrelationships relevent to the understanding of the dynamics of the CHC movements.

One can see from Table I that both PCB and chlordane are 4 to 10 times higher on the suspended sediment (dry) samples than on the bottom sediment. A possible explanation - the average grain size of the suspended sediment is much smaller than that of the bottom sediments resulting in a greater surface area for absorption per unit weight. And, although the suspended sediments consist of primarily inorganic material, phytoplankton which were included in these samples could have bioconcentrated the CHC to some extent.

However, the total DDTR does not follow this pattern; in fact, the concentration of DDTR is the same in both suspended sediments and bottom sediments. This might be explained by the fact that all DDT uses were banned in the U.S. in 1972. If this ban had the effect of decreasing the DDT levels flowing into the Chesapeake Bay, the concentrations should be heavier in the bottom sediments which consist of materials deposited during many years while the suspended sediments consists of relatively new material. It does seem suspect, however, that both types of sediment had the same concentration. Further investigation is indicated.

The bioconcentration of the CHC from the suspended sediment into the zooplankton can also be seen from Table I. If one assumes a 0.10 plankton dry to wet weight ratio the multiplication of the plankton wet values by 10 to converts these values to plankton dry. These can then be compared to the suspended sediment dry concentrations for the following bioconcentrations. PCB 5.4; chlordane 6.7; DDTR 28. The DDTR value becomes a more compatible 7.9 if two enormously high values are excluded.

The concentration ability of shellfish was determined by dividing the level accumulated in the shellfish tissue (wet weight) by the exposure concentration in the water. Using the values for CHC in the water column on the suspended sediments, the

shellfish concentrations were estimated at PCB 4,000; chlordane 30,000 and DDTR 45,000. These are, of necessity, only estimates as the water column CHC concentrations are not truely representative of those of the bottom sediment interface inhabited by the shellfish.

Although, the points are scattered, Figure 2 (a log-log plot) does indicate a positive relationship between the CHC concentration in the water column on the suspended sediment (ppt) vs. the concentration of suspended sediment in the water (mg/l). Despite the scattering caused by variations of CHC concentrations on the suspended sediments, the data does show that the bay water samples which had high suspended sediment concentrations also had high levels of CHC in the water on the suspended sediment.

A log-log plot (Figure 3) of total CHC in the water on zooplankton (ppt) vs. the zooplankton biomass in the water (mg/m^3) also indicates a positive relationship. As the zooplankton population in the water increases, the amount of CHC in the water on the zooplankton increases establishing the movement of CHC into the aquatic food chains which include the zooplankton community.

The bay water samples with high suspended sediment concentration also had high CHC concentrations in the water on the suspended sediments. This, coupled with the fact that the zooplankton population contains only a small fraction of the CHC present in the water column, indicates that the movement of CHC into the biological system is not influenced by changes in the concencentration of suspended sediment, but is regulated by whatever regulates the zooplankton concentration. Although an over simplification, one could visualize the suspended sediments in the water column as being a reservoir of CHC, which enters the biological system with zooplankton bloom.

Whatever the pathway, only a small percentage of the CHC in the water column is associated with the zooplankton (12 ppt PCB in the water column on suspended sediment vs. 0.042 on zooplankton). Although we did not have the data on the turnover rates in the plankton community, to quantify the rate of movement of CHC by this pathway, it can be assumed that a change in bay conditions which would increase the zooplankton population would also increase the flow of CHC from the suspended sediment reservoir into the biological system.

Sediment deposition is, most probably, the major route for the transport of CHC from the suspended sediment reservoir. The relationship between grain size and CHC concentration has already been demonstrated elsewhere* and as Baltimore Harbor is a trap for fine grain sediments in the upper Chesapeake Bay, it is not

surprising to find the harbor acting as a sink for CHC from the suspended sediment reservoir. Figure 4 shows that PCB concentration, for instance, was far higher in Baltimore Harbor than elsewhere in the bay.

A number of mechanisms exist for the movement of CHC out of these bottom sediment sinks, such as, resuspension of the material by tidal scows. Dredging and overboard discharge also could lead to a substantial resuspension.

Although the Urban-Industrial activities in and around Baltimore Harbor appear to generate locally high concentrations of PCB and DDT residues, the major source of these materials to the upper bay seems to be the Susquehanna River. Chlordane levels, however, do appear to come heavily from the harbor area. These aspects are discussed in more detail in the Biochemistry Section of the total Upper Bay Survey Report.

*H. D. Palmer and J. R. Schubel, "Chapter 4 = Estuarine Sedimentology, "Upper Bay Survey Final Report to the Maryland Department of Natural Resources, Volume II, T. O. Munson, D. K. Ela, and C. Rutledge and Westinghouse Ocean Division, Annapolis, Md. 1975.

In press.

Table 1. Average chlorinated hydrocarbons found in the upper Chesapeake Bay (Standard deviations are in parentheses)

Sample type	Number of samples	Total PCB	Total chlordane	Total DDT
Shellfish (wet,ppm)[a]	26	0.052(0.037)	0.016(0.017)	0.035(0.041)
Plankton (wet,ppm)	70	0.50(1.4)	0.041(0.032)	0.16(0.68)
Suspended sediment (dry,ppm)[b]	66	0.92(0.87)	0.061(0.086)	0.057(0.066)
Bottom sediment (dry,ppm)	54	0.28(0.57)	0.0052(0.014)	0.051(0.067)
Plankton (H_2O,ppt)[c]	69	0.042(0.164)	0.0038(0.0083)	0.010(0.035)
Suspended sediment (H_2O,ppt)	68	12(14)	0.53(0.88)	0.78(1.5)

[a]The values are expressed as µg CHC found per g wet weight of material extracted.

[b]The values are expressed as µg CHC found per g dry weight of material extracted.

[c]The values are expressed as ng of CHC found per l of water filtered to collect the material extracted.

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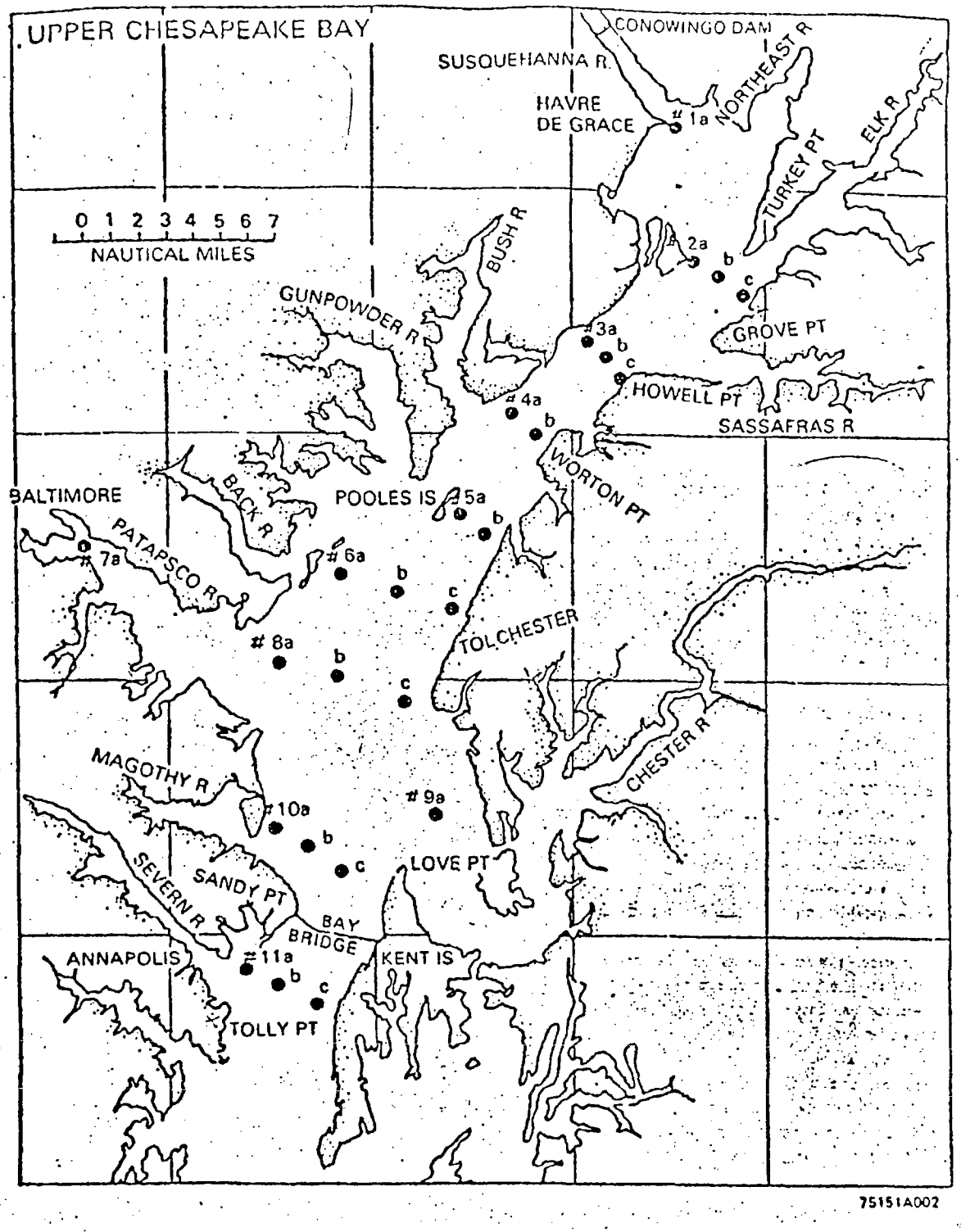

Figure 1. The principal stations at which samples and measurements were taken in the Upper Bay Survey.

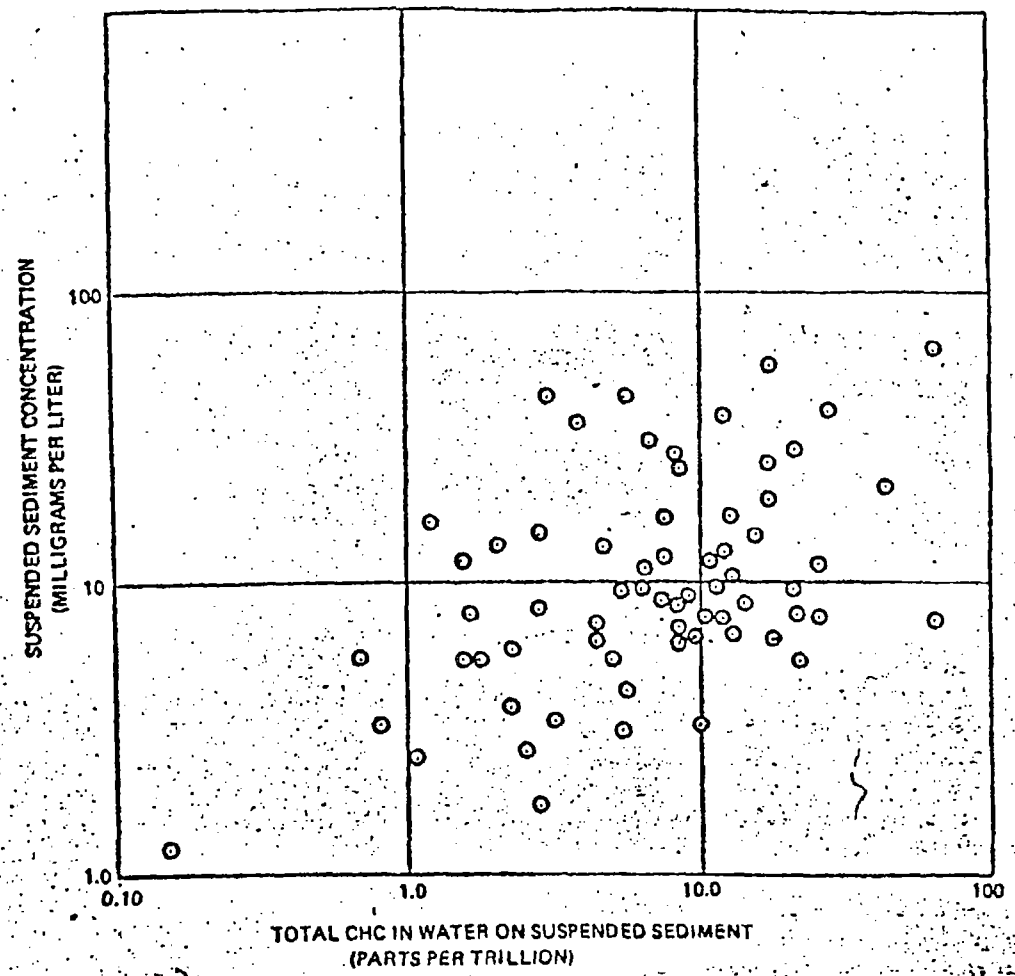

Figure 3. A plot of the log of the suspended sediment concentration in the water (milligrams per liter) versus the log of the total CHC concentration in the water associated with the suspended sediment (parts per trillion).

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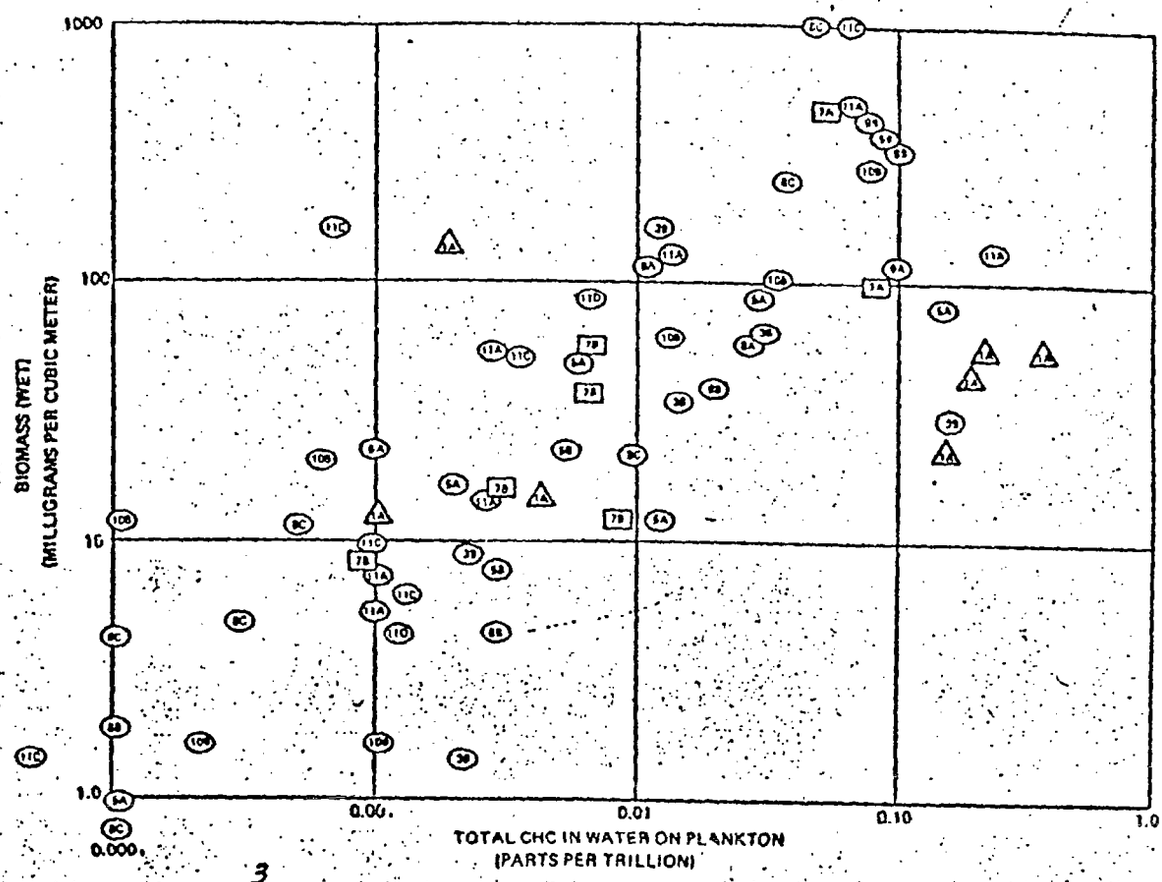

Figure 3. A plot of the log of zooplankton biomass (milligrams weight per cubic meter) versus the log of the total CHC in the water associated with the zooplankton (parts per trillion).

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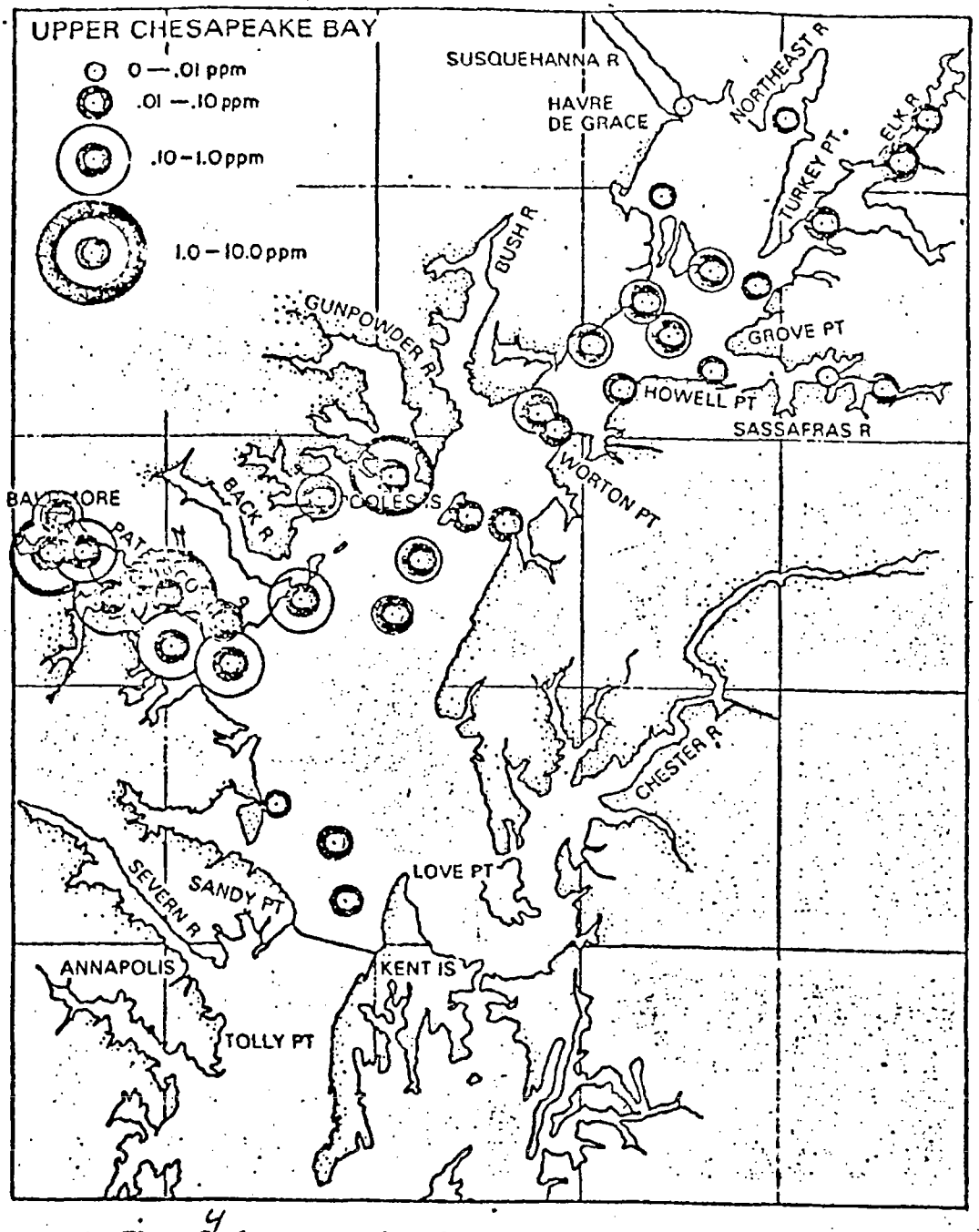

Figure 6. A representation of the concentration of PCB's in bottom sediments samples from the upper Chesapeake Bay.