



## Project Summary

# Chesapeake Bay Sediment Trace Elements

G. R. Helz, S. A. Sinex, G. H. Setlock, and A. Y. Cantillo

This report contains the results of analyses of bottom surface sediment samples and sediment vertical core samples from Chesapeake Bay, Baltimore Harbor, and the Elizabeth River. For the surface samples in the Bay, both the fine fraction and the unfractionated sediment were analyzed for chromium (Cr), manganese (Mn), iron (Fe), cobalt (Co), nickel (Ni), copper (Cu), zinc (Zn), cadmium (Cd), and lead (Pb), by atomic adsorption spectrometry. For the Bay cores, water content,  $^{210}\text{Pb}$ , carbon (C), nitrogen (N), aluminum (Al), silicon (Si), titanium (Ti), vanadium (V), chromium (Cr), manganese (Mn), iron (Fe), cobalt (Co), nickel (Ni), copper (Cu), zinc (Zn), and zirconium (Zr) were determined at various depths. Alpha spectrometry was used for  $^{210}\text{Pb}$ , and DC plasma emission spectrometry was used for all elements except C and N, which were determined by a CHN analyzer. More than 8,000 individual analyses are reported in Chesapeake Bay, making this the first comprehensive survey of trace element chemistry in the Bay. Baltimore Harbor and the Elizabeth River were sampled to represent areas of high contamination. Samples of the bottom surface sediments and vertical sediment samples were also taken to provide comparison of these contaminated areas with those of the Bay.

*This Project Summary was developed by EPA's Chesapeake Bay Program, Annapolis, Maryland to announce key findings of the research project that is fully documented in a separate report of the same title (see Project Report ordering information at back).*

## Introduction

A number of previous investigations of toxic substances have been made in various parts of Chesapeake Bay. In all cases, however, the analytical work was conducted as part of isolated projects, and the methods used were generally not comparable from one project to another. Thus, it has not been possible to make a regional synthesis that would allow different parts of the Bay to be compared and changes with time in the condition of the Bay to be convincingly documented. The Environmental Protection Agency's Chesapeake Bay Program provided the first opportunity to examine the question of contamination in the Bay on a regional scale. Samples were collected throughout the Bay and were analyzed for a particular class of toxic substances by a single laboratory using consistent, clearly described procedures.

This report is about trace elements in the sediments of Chesapeake Bay. In high concentrations, certain of the trace elements studied are known to be toxic to a large variety of organisms. In low concentrations, however, they may be essential micro-nutrients. Knowledge of the distribution of trace metals is important not only because of their potential impact on the ecosystem but also because they might serve as tracers for other anthropogenic substances which are themselves much more difficult to detect in the environment.

This study consisted of three components. The concentration of nine elements was determined in 246 surface sediment samples in order to establish the current geographic distribution of these elements. Vertical profiles were determined in 45 cores to investigate the

possibility of historical changes. Finally, the  $^{210}\text{Pb}$  and  $^{226}\text{Ra}$  activity in certain cores was measured in order to determine deposition rates and provide a scale for any historical changes observed.

### Procedure/Methodology

Both surface grab samples and vertical core samples were collected. All surface samples were collected between April, 1977 and June, 1981. The sampling stations were located along 25 transects running roughly in an east-west direction and extending from the mouth of Chesapeake Bay to the Susquehanna River as well as along two special transects into Baltimore Harbor and the Elizabeth River. A Ponar grab was used for sampling, and variable-range radar triangulation was used for navigating. An unfractionated sub-sample and a  $<63\ \mu\text{m}$  sub-sample were measured in most cases. Whereas the unfractionated sediment samples were found to be reasonably reproducible in muddy terrain, the data obtained from sandy environments are limited by the chemical heterogeneities inherent in sands.

Most of the core samples were obtained during the November, 1978, May to June, 1979, and May to June, 1981 cruises. Sampling reducibility studies were not attempted with the core samples.

Surface sediments from the main stem of Chesapeake Bay were extracted with nitric and hydrochloric acids. Sample extracts were analyzed by atomic absorption spectroscopy under conditions recommended by the manufacturers. In order to determine a larger group of elements in the core samples and in the surface samples from Baltimore Harbor and the Elizabeth River and to have an independent method with which to check the atomic absorption data, another method was developed which involved fusing the samples with lithium metaborate, dissolving the resulting glass in nitric acid, and using direct current argon plasma emission spectroscopy (DCP) to determine the metal content of the solutions. Deposition rates in the cores were determined by  $^{210}\text{Pb}$  assays using the alpha-spectrophotometric measurement of daughter polonium-210.

### Results/Conclusions

The frequency distributions for all elements in the unfractionated samples were approximately log-normal. Some elements displayed a bimodal

distribution. Factor analysis of Bay samples showed that either one factor was involved in the control of trace elements in the sediments, or, more likely, there were coalescent multiple factors.

Analysis of the data indicates that the elements in the  $<63\ \mu\text{m}$  fraction decrease seaward, probably reflecting the distance from the Susquehanna River, which delivers relatively metal-rich sediment to the Bay. In some places, the metals also decrease eastward across the Bay, suggesting that either seaward transport of Susquehanna-derived sediments is more effective on the western side due to the Coriolis effect or that the western side is enriched due to sediment derived from the Piedmont tributaries. The results for the unfractionated sediments are similar to those for the  $<63\ \mu\text{m}$  fraction but contain additional variation due to grain size.

Chromium concentrations tend to decrease down the Bay with high concentrations (up to 135 ppm) in both the unfractionated and  $<63\ \mu\text{m}$  fractionated samples occurring in and around Baltimore Harbor and the Elizabeth River.

Manganese concentrations range from 74 to 6900 ppm in the  $<63\ \mu\text{m}$  fraction and also decrease seaward. Elevated levels have been found just north of Baltimore Harbor in the area of the Gunpowder River, as well as in the Harbor itself. Elevated levels are also found in the Elizabeth River.

The distribution of iron shows the typical decrease seaward, with elevated levels occurring around Baltimore Harbor and Annapolis. The Baltimore enrichment is thought to be due more to local accumulation of fine-grained, iron-rich particles than to industrial activity, because the Fe/Al ratio is not particularly anomalous in this region. However, large discharges of iron-rich waste have historically occurred in the Harbor. Slightly elevated levels at the mouth of the Rappahannock River also may be caused by the high clay content in this area.

Cobalt and nickel closely resemble manganese in distribution. In addition to the causes of enrichment already mentioned, the discharge of Back River, which contains both industrial and municipal wastewater from Baltimore, may contribute to the enrichment.

Copper, lead and zinc also display the typical southward decrease, with each showing a strong source from Baltimore Harbor. Copper and zinc levels are elevated just north of the Harbor, and all

three are enriched at the mouth of the Rappahannock. These elements are generally enriched in the upper rather than the lower parts of cores, suggesting regional contamination that is presumed to be increasing with time.

Sedimentation rates were also calculated and range from 0.7 to 42.6 m per year. The highest rates were calculated for Susquehanna River cores and several cores collected near the mouth of the Potomac River. Most of the core samples from the upper and lower portions of the Bay were in the range of several millimeters per year accumulation rate.

The levels of metals in the sediments of Baltimore Harbor and the Elizabeth River area are high compared to those in the surrounding Bay sediments. However, both areas are composed of fine-grained sediment and part of the elevated levels may be due to this fine fraction. The Elizabeth River area shows consistent anthropogenic enrichment only for Zn, whereas Baltimore Harbor is enriched in Co, Cr, and Zn with minimal V enrichment.

Baltimore Harbor is working as an effective trap for fine-grained sediments. Most of the deposition is occurring in the inner reaches of the Harbor. The zone of contamination is over three meters in thickness. The zone wedges out in a seaward direction and seems to show only minor signs of appearing in the Bay proper.

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*Duane Wilding is the EPA Project Officer (see below).*

*The complete report, entitled "Chesapeake Bay Sediment Trace Elements," (Order No. PB 83-207 621; Cost: \$19.00, subject to change) will be available only from:*

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