



Project Summary

The Characterization of the Chesapeake Bay: A Systematic Analysis of Toxic Trace Elements

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As part of a multidisciplinary study of Chesapeake Bay, the National Bureau of Standards (NBS) was asked to develop the techniques and procedures necessary to measure trace and toxic element concentrations within the water column throughout the length of Chesapeake Bay. The Inorganic Analytical Research Division of the Center for Analytical Chemistry at NBS has completed the analysis for selected elements (Cd, Ce, Co, Cr, Cu, Fe, Mn, Mo, Ni, Pb, Sc, Sn, Th, U, and Zn), including some elements at concentrations consistently below one picogram per milliliter (part per trillion). The characterization of Chesapeake Bay can be divided into five major phases. The first included the development and construction of a sampling system for the trace metallic elements dissolved in water and a filtration system for collecting the particulate elemental component.

The second phase consisted of sampling chemical stabilization by acidification and storage of the samples in the field. The total complement of 102 samples was obtained, filtered, acidified and stabilized. There were also 51 replicate bottom samples obtained and frozen for archival use. A series of over 30 blanks was also prepared and integrated with the 102 water samples to be analyzed.

The third major phase of activity consisted of the chemical separation and preparation of samples for the analytical instrumental methods. The chemical separation/sample preparation stage of this work has been described in the literature for both instrumental techniques.

The fourth major phase consisted of the instrumental analysis of the samples for the trace elements. The total number of elemental concentrations resulting from the analyses of the contracted elements exceeded 3000 and involved several thousand more unreported analyses totaling over 5000 separate determinations.

The fifth major phase involved data reduction and evaluation of the statistical significance of the blank. The blanks were statistically modeled for each element, and the blank and uncertainty of the blanks were applied to the data. The concentrations were adjusted uniformly to at least the 95 percent confidence limit.

This Project Summary was developed by EPA's Chesapeake Bay Program, Annapolis, MD, 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

This report describes the National Bureau of Standards' (NBS) efforts in a multidisciplinary study of Chesapeake Bay coordinated by the U.S. EPA's Chesapeake Bay Program. The NBS used the best available technology to determine the trace and toxic element concentrations in the water column. As part of this program, the NBS has collected and analyzed both the dissolved and suspended particulate fractions of 102 water samples covering the entire length of Chesapeake Bay. The elements of interest include Cd, Ce, Co, Cr, Cu, Fe, Mn, Mo, Ni, Pb, Sc, Sn, Th, U, and Zn. These analyses were accomplished using specific chemical preconcentration, separations and manipulations to prepare the samples for analysis by Neutron Activation Analysis (NAA) and Graphite Furnace Atomic Absorption Spectrometry (GFAAS).

Except for neutron activation analysis and anodic stripping voltammetry, no analytical techniques are currently available for the untreated sample determination of trace elements in seawater at concentrations below five $\mu\text{g L}^{-1}$. Usually it is necessary to preconcentrate the trace elements from a large volume and separate the transition elements from the alkali and alkaline earth elements. In such sample preparations, the efficiency of concentration, completeness of separation, and total analytical blank become critical to the final instrumental method.

A more recent separation procedure utilizing Chelex resin produced a sample devoid of alkali, alkaline earth, and halogen elements, and left a dilute nitric acid/ammonium nitrate matrix containing only the trace elements of the seawater sample. This procedure was used in conjunction with GFAAS to analyze Chesapeake Bay estuarine samples.

Procedure/Methodology

The method of preparation described for solid samples from 100 mL of estuarine or seawater uses Chelex 100 resin, followed by the determination of 12 trace elements by NAA. This procedure has been used to analyze NBS SRM 1643a, as well as high salinity water samples collected near the mouth of Chesapeake Bay.

The extremely low trace concentrations in these estuarine waters caused the procedural blank to be of paramount

importance. The integrity of the sample can be compromised by just a brief exposure to normal laboratory air or less than exhaustively cleaned container materials, etc. In addition, the extremely high concentrations of alkali, alkaline earth, and halogen elements in the marine water matrix make direct analysis difficult or impossible for most analytical techniques.

To circumvent these problems, special chemical and instrumental procedures were developed and chemical separation/preconcentration procedures based on the chelating resin Chelex-100 were applied prior to NAA and GFAAS analysis. The elimination of the matrix elements allowed the determination of many elements that could not otherwise be analyzed and enhanced the sensitivity of other elements of interest. The control of the blank in this procedure has enabled its contribution to be low enough not to limit the measurement of most elements in pristine samples.

To ensure sample integrity and accurate analytical blank determinations, 30 dissolved and particulate blanks were prepared during the sample collection. The blanks were then carried through all manipulations and analyses as additional samples interspersed throughout the analyses, with a minimum of three per set.

Evaluations were made using computer-assisted statistical comparisons with data of known statistical reliability. The analysis, blank contribution, corrections, and mathematical manipulation of the data in this report have resulted in 58 data sets which are of known statistical reliability. These data sets contain the sample numbers arranged in a numerical sequence approximating the geological arrangement of Chesapeake Bay, from Susquehanna River to, and including, the Atlantic Ocean. The concentrations are given as a best value, and a maximum and minimum value which represent at least the 95 percent confidence limit of the concentration. The significant figures of each concentration are determined by the range of the maximum and minimum value.

The potential information in the particulate elemental concentration data is even more difficult to understand. Although it may appear initially to be uncertain in interpretive value, a technique long used in the study of atmospheric particulate material is applicable. The comparison of elemen-

tal ratios for different samples instead of the absolute concentration is informative. By normalizing the concentration of each element to a crustal element, such as Sc, problems caused by differing amounts of bottom sediment suspended in water (loading effects) are eliminated.

Scandium was chosen for this purpose because it has relatively few anthropogenic uses. Since it is not used in a refined form in industry and is refractory in nature, it is not expected to be introduced into the environment in an enriched state or in significant quantities. When these ratios are divided by ratios of average crustal material, a crustal enrichment factor (EF) results. This is done for convenience and to allow a crude comparison with naturally occurring material.

In these data the concentrations from Wedepohls' compilation for crustal elements has been used. Similar though not identical results could be obtained using other compilations. Additionally, the computation of EFs relative to average soils and average sedimentary rocks would be of value to see how the suspended sediments of Chesapeake Bay differ from those natural materials.

Ideally, the EFs for each element will remain constant if the sources contributing to the suspended sediment remain the same. Although the concentration of the various elements may fluctuate several orders of magnitude from sampling to sampling, the EFs should be constant if the sources are constant as they are not effected by mass loading.

Conclusions

Uses of these EFs to produce an interpretive model for evaluating and concluding elemental relationship and origins can be postulated. However, actual conclusions cannot be drawn until a rigorous scrutiny of the statistical significance of the individual sets of enrichment factors has been completed. Because this technique has not been used for water particulates previously, many cross references between elements and geological positioning, as well as within set limits, must be evaluated.

In this report, the enrichment factors normalized to the Wedepohl crustal numbers have been given without interpretation to at least the 90 percent confidence limit.

These data are of sufficiently well known reliability that statistical com-

parison can be performed resulting in significant trends of known reliability. This work has not been included in this report and is of a sufficiently complex nature to comprise a separate effort, which has been recently initiated.

References

1. Wedepohl, K.H. 1966, "Origin and Distribution of the Elements." L.H. Aherns, ed. Pergamon Press, London. pp 999-1016.

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Duane Wilding was the EPA Project Officer (for information, see below).

The complete report, entitled "The Characterization of the Chesapeake Bay: A Systematic Analysis of Toxic Trace Elements," (Order No. PB 82-265 265; Cost: \$18.00, subject to change) will be available only from:

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