

DISTRIBUTION STATEMENT 2Approved for public release
Distribution Unlimited**FINAL REPORT****In -Situ Time Series Studies of Oceanic Trace Metal Variability**

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RESEARCH GOALS:

We aimed at improving our understanding of mechanisms controlling chemical fluxes of trace elements through the ocean, and to exploit this knowledge to improve our understanding of oceanic processes. In general, we used the distinctive properties of elements to contribute to a better-constrained model of ocean chemistry and its effects. Having observed short-term (days to weeks) temporal variability in near-surface trace element concentrations (see next section), we worked on ways to obtain high-resolution time-series data to understand this temporal variability. We developed a new moored trace element time-series sampler which we tested and are now deploying full-time in two key oceanic environments.

OBJECTIVES:

With the availability of our new in-situ time-series sampler, we now are able to explore temporal variability of metals at the level of detail necessary to determine the true spectrum of variability. We expect to determine just how rapidly episodes of trace metal enrichments in Bermuda surface waters occur and better correlate them atmospheric, oceanographic, and biological variability. We can examine the episodicity of upwelling and atmospheric infall.

APPROACH: In our in-situ sampler design, the collection of each sample is entirely independent. Since each sample is collected by an independent unit, the failure of any one component will affect only a single sample. Each sample unit has a microcontroller circuit which operates a DC motor which opens (and closes) 500 ml 1N HCl-filled polyethylene (or other composition) bottles by rotary motion. When the bottles are opened, the low-density acid exchanges with the surrounding seawater by passive density-driven flow. Since the acid and seawater mix during the exchange, the bottle is effectively flushed with several volumes of seawater, with additional flushing resulting from water motion relative to the sampler. The microcontroller circuit waits for a specified period (to allow the exchange to take place), and then reverses the motor, which closes the bottle and seals it until recovery. A small teflon vial inside each bottle has pinholes which allow for slow diffusive exchange. After the sample is collected, the hydrochloric acid diffuses out of the vial over a period of several hours to a day. This mechanism acidifies and stabilizes the sample. The microcontroller also takes note of the characteristics of opening and closing; if there is an indication of a stall, the motor circuit

voltage is temporarily doubled to start the system. The microcontroller circuit takes note of these characteristics and the actual time of sample collection, and saves these for interrogation upon return to the surface. The standard package consists of 12 units mounted within a thick protective frame which is secured onto a plastic-coated standard mooring pin made of stainless-steel. The electronics and motor are powered by 6 alkaline C-cells. The unit can also function as a "trace element rosette" allowing for the collection of an uncontaminated profile.

TASKS COMPLETED:

The design and construction of our revised unit was completed, and this unit was deployed on the "Testbed" mooring (T. Dickey et al.) off of Bermuda in April, 1995. The unit (now dubbed "MITESS") survived Hurricane Felix with no damage (despite the skepticism of the mooring pro from WHOI). The modules worked as expected at the point we deployed them, and we ended up with 6 good samples. The only problem we had was one which we learned about on deployment, which was that flickering sunlight can simulate 300 baud IR communications and open samples prematurely. Two bottles opened prematurely during deployment, three others during recovery, and one more as we examined the unit on the deck (the post-deployment units losing samples that had been collected and were otherwise good). This problem has now been solved (a password is required before control mode is activated). Other than that, the units worked well. They recorded their times of starting to open, full open, starting to close, and full close. The clocks functioned well and remained accurate. Fouling was minimal and posed no problem whatsoever in this environment. Although the batteries were replaced with new ones to ensure reliability, tests of the batteries (which had been used to power the electronics for 5 months and open and close the bottles) showed that they were nearly as good as new, indicated that our design could easily meet our design goal of 1-year or better deployment life (at least in warm waters). The unit was redeployed in August 1995. In November, 1995, the failure of a current meter above our sample dropped the entire mooring below it onto the seafloor. The mooring was recovered by dragging in March 1996. Although the electronics of some of the units were damaged by the catastrophic pressure increase, the unit was undamaged physically and was redeployed with new electronics at the end of the month. Late May, the acoustic release on the mooring was prematurely released by another scientist working nearby. The unit was recovered once moor with 100% success in sampling. It was then redeployed in early June 1996 in August and again redeployed. Recovery of the mooring expected in late November was canceled due to illness of a critical mooring tech. The unit was finally recovered in January 1997 and a doubled-up sampling unit (24 samples) redeployed in May 1997. In the May deployment at Bermuda, we also used one unit in profiling mode" to collect a 1000m-deep trace metal profile. Also in May of 1997, a doubled-up deployment of 24 units is being deployed at the HALE/ALOHA JGOFS mooring near Hawaii. In

With the experience gained from these multiple deployments, minor adjustments to the electronics boards and programs were made and a new batch of 27 modules was completed late in 1997. We now have a total of 51 modules with spare electronics so that we can collect 24 samples per deployment at two sites (Bermuda and Hawaii).

The samples from the deployments April 1995-November 1996 have been analyzed for lead and iron variability, providing the most detailed time series in existence for these elements. The current deployments will improve on that series by a factor of

two, with weekly sampling. The contributions of this device to the Bermuda Testbed Mooring program have been described in two manuscripts, one published and one in press (Dickey et al., 1997a; Dickey et al., 1997b).

Major progress in oceanic trace metal analyses has been made by postdoctoral fellow Jingfeng Wu. We have developed new methods for the analysis of Pb, Cu, Cd, and Fe in small-volume (1-10 ml) seawater samples using $\text{NH}_3\text{-Mg}(\text{OH})_2$ coprecipitation and ICPMS isotope-dilution analysis. Using this method makes analyses for these very rapid and simple, and we have analyzed for Pb, not only the above-mentioned moored time series samples, but also hundreds of surface and profile samples from cruises from previous years. A paper on one of these data sets has been written and will be submitted shortly (Wu, Boyle, and Measures, 1997).

The Bermuda Pb time series through the end of 1996 is in press (Wu and Boyle, 1997a); we see a decline in surface Pb from ~160 picomoles/kilogram in 1979 to ~60 pmol/kg in 1990, and then a leveling out at about 40 pmol/kg since. We suggest that the decline was due to the phasing out of leaded gasoline, and that with the near termination of the use of leaded gasoline in the United States, lead is now supplied by eolian delivery of Pb emitted during high-temperature industrial processes.

The new analytical methods have been written up in two manuscripts, one in press (Wu and Boyle, 1997b) and one just submitted (Wu and Boyle, 1997c).

On another front, collaboration with Lex van Geen (LDEO), has traced the high metal plume observed in our earlier ONR work to acid mine effluent from the Rio Tinto in southwestern Spain. This single small river is a major source of trace metals to the Mediterranean via the Gibraltar inflow. van Geen has confirmed that metal levels were astoundingly high in this acid-mine-drainage-influenced river. This work is now published (van Geen et al., 1997). A preliminary qualitative analysis of the Tinto water and showed that it also contains high levels of As, Co, Pb, and Te. Master's student Janice Vatland completed her Master's Thesis analyzing the continental shelf waters to see how far downstream the signature of these other elements can be followed, and determined that this river is a major source of Pb, Co, and particulate Fe to the Mediterranean Sea. We have also continued working on our data interpretation of trace element samples collected from the Eastern Mediterranean Sea, South Atlantic sector of the Southern Ocean and analyzed for Cd and other trace metals.

SCIENTIFIC ACCOMPLISHMENTS:

We deployed our "MITESS" moored in-situ trace metal serial sampler four times and have shown that it is a rugged and reliable trace metal serial-sampling device. It survived three episodes of hurricane-force winds on the surface mooring and returned the first automatically-collected time-series trace metal samples ever published. Analyses of these samples for Pb and Fe have provided the most detailed-ever time series for these elements.

Our analytical developments have made the analysis of Pb, Cu, Cd, and Fe in seawater reliable, fast, and simple for very small samples.

Our work on the Rio Tinto has now revealed that other trace elements can be expected to show anomalously high metal levels in the Atlantic inflow into the Mediterranean Sea.

Papers published in refereed journals (ONR-project related only):

Orians, K.J. and E.A. Boyle. 1993. The determination of picomolar concentrations of titanium, gallium, and indium in seawater by inductively coupled plasma mass spectrometry (ICPMS) following an 8-hydroxyquinoline chelating resin preconcentration, *Anal. Chim. Acta.* 282:63-74.

Colodner, D.C, E.A. Boyle, and J.M. Edmond. 1993. Determination of rhenium and platinum in natural waters and sediments, and iridium in sediments by flow injection isotope dilution inductively coupled plasma mass spectrometry, *Anal. Chem.* 65:1419-1425.

Colodner, D.C., G. Ravizza, J. Sachs, K. Turekian, J. Edmond, E. Boyle. 1993. The geochemical cycle of rhenium: a reconnaissance, *Earth. Planet. Sci. Lett.* 117:205-221.

Boyle, E.A. (1994) A comparison of carbon isotopes and cadmium in the modern and glacial maximum ocean: can we account for the discrepancies?, in *Carbon Cycling in the Glacial Ocean: Constraints on the Ocean's Role in Global Change* (eds. R. Zahn, T.F. Pedersen, M.A. Kaminski, and L. Labeyrie), NATO ASI Series, Vol. 17, Springer- Verlag, Berlin, p. 167-194.

Boyle, E.A., R. A. Sherrell, and M.P. Bacon (1994) Lead variability in the western North Atlantic and Central Greenland: implications for the search for decadal trends in anthropogenic emissions, *Geochim. Cosmochim. Acta* 58:3227-3238

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van Geen, A., J.F. Adkins, E.A. Boyle, C.H. Nelson, A. Palanques. 1997. A 120 year record of metal contamination on an unprecedented scale from mining of the Iberian Pyrite Belt, *Geology* 25:291-294.

Wu, J.F. and E.A. Boyle. 1997a (in press). Lead in the western North Atlantic Ocean: completed response to leaded gasoline phaseout, *Geochimica Cosmochimica Acta*.

Wu, J. and E.A. Boyle. 1997b (in press). Low blank preconcentration technique for the determination of lead, copper and cadmium in small-volume samples by isotope dilution ICPMS, *Anal. Chem.*

Dickey, T., D. Frye, H. Jannash, E. Boyle, D. Manov, D. Sigurdson, J. McNeil, M. Stramska, A. Michaels, N. Nelson, D. Siegel, G. Chang, J. Wu. 1997b (in review). Preliminary results from the Bermuda Testbed Mooring Program, submitted to Deep-Sea Research.

Wu, J. and E.A. Boyle. 1997c (draft). Low Blank Preconcentration Technique for the Determination of Lead, Copper and Cadmium in Small-Volume Seawater Samples by Isotope Dilution ICPMS

Wu, J., E.A. Boyle, C. Measures. 1997 (draft). Iron, Lead and Aluminum in the surface waters of northwest Atlantic ocean.

Papers in other literature:

Dickey, T.D., D. Frye, H.W. Jannasch, E. Boyle, A.H. Knap. 1997a. Bermuda Sensor System Testbed, Sea Technology, April, p. 81-86.

Invited Conference Presentations:

Bell, J., J. Betts, and E.A. Boyle. 1994. A new moored in-situ automated trace element sampling device. American Society of Limnology and Oceanography meeting.

Contributed Conference Presentations

Bell, J., J. Betts, and E.A. Boyle. 1994. A New Moored In-situ Automated Trace Element Sampling Device, Ocean Sciences Meeting.

Dickey, T., D. Frye, M. Stramska, H. Jannash, E. Boyle, D. Manov, D. Sigurdson, and A. Michaels 1995. The Bermuda Testbed Mooring Program, Ocean Sciences Meeting (San Diego).

Number of post-docs supported part time: 2

Number of female post-docs supported part time: 1.

Number of other technical personnel supported part time: 2

Number of female graduate students: 1

Listing of honors:

- (1) Fellow, American Geophysical Union (1994)
- (2) Huntsman Award (1994) (Bedford Institute of Oceanography)