Trace Element Analysis of Seawater Samples from the 2002 Intergovernmental Oceanographic Committee (IOC) Intercalibration Cruise in the Northwestern Pacific Ocean

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Introduction

The Intergovernmental Oceanographic Committee (IOC; a subcommittee within UNESCO) has helped sponsor oceanographic research cruises to study the "baseline" distribution of trace elements and organic pollutants throughout the world's oceans. The latest of these cruises was in 2002, from Japan to Hawaii, and emphasized the impact of Asian dust and pollutants on the chemistry and biology of the northwestern Pacific Ocean. Seawater samples were collected using "clean" techniques and stored acidified for later analysis. Trace elements of interest include Al, Mn, Fe, Co, Ni, Cu, Zn, Cd, and Pb. Al and Pb are good tracers for aerosol input; Mn can indicate riverine input as well as input from organic-rich coastal sediments; Fe and the other elements are all affected by biological uptake and recycling, since they are required for phytoplankton photosynthesis. Combining the observed trace element distributions with models of physical water mass mixing, it is possible to estimate the rates of biological uptake and recycling. Those rates are important to quantify in order to validate more complicated general ocean circulation models that strive to simulate the oceanographic distributions of bio-active trace elements.

Experimental

Seawater samples were acidified to 0.024M HCl using ultrapure acid. An extraction scheme was developed to take advantage of the technique of isotope dilution analysis using the Finnigan Element-I in the Geochemistry group at the NHMFL. A 12mL subsample of acidified seawater is placed in a plastic tube and spiked with a mixture of isotopes of Fe, Ni, Cu, Zn, Cd, and Pb. For Al, Mn, and Co analysis, a set of 12 mL samples is spiked with 3 different levels of each element to generate standard additions calibration curves. The sample are allowed to equilibrate overnight, then buffered to pH 5.5 with 2M ammonium acetate and passed at 2mL/min over a 200 µL column of polymer-immobilized 8-hydroxyquinoline. This functional group is selective for transition elements and does not concentrate alkali or alkaline earth elements. The column is rinsed with 1 mL of ultrapure water, then eluted with 3 mL of 1.5M HNO3. The first 1mL of this eluent contains the majority of the eluted trace elements, and is collected preferentially in autosampler vials for ICPMS analysis.

Results and Discussion

Over 160 samples were analyzed from 9 vertical profiles and 50 surface transect samples. These data will be used in the PhD thesis of Peter Morton, a graduate student from Old Dominion University. Mr. Morton spent 8 weeks performing extractions in the FSU Oceanography Department and conducting analyses at the NHMFL. The data interpretation has just begun, and will continue for at least 6 months. We can already conclude that the data quality for Mn, Fe, Co, Ni, Cu, Cd, and Pb is excellent. Instrumental blanks interfere with the Al analysis, and Zn analysis is always a challenge due to ubiquitous contamination for Zn. The profiles for Fe, Co, Ni, Cu, Zn, and Cd show the well-known "nutrient-type" distributions due to phytoplankton uptake in surface waters and regeneration with depth. Pb shows a surface maximum due to the influence of atmospheric deposition of anthropogenic Pb, while Al shows a surface maximum due to mineral dust input. Mn shows influences of mid-depth lateral injection from continental shelf and slope sediments.

Conclusions

Our conclusions are still being developed, and several journal articles are anticipated after the data interpretation has been completed in 2007. The development of these extraction and ICPMS analytical techniques over the past three years has resulted in 4 additional NSF grants awarded to WML for research on trace element and isotope biogeochemistry in the oceans.

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