

Clean sampling technique for analysis of trace metals in seawater

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Introduction

Some trace metals, like iron, copper and zinc, in seawater are now known to be essential nutrients for phytoplankton growth in the ocean. The roles of trace metals in marine ecosystem have been recognized, but their biogeochemical cycles have not been understood fully yet. Recent progress of analytical chemistry enables us to reveal the isotopic composition and speciation of the trace metals in seawater, which will provide us with strong tools for the biogeochemical studies of trace metals in seawater. To apply the state-of-the-art analytical techniques for the trace metals in seawater, we need to collect the samples without any contamination. Especially for contamination-prone trace metals, such as iron and zinc, we must be very careful during seawater samplings. We have examined some sampling methods in Japanese GEOTRACES programs to establish the clean sampling technique for trace metals in seawater.

Methods

Research cruise: This study was carried out during the KH-12-4 research cruise (23 August to 5 October, 2012) of R. V. Hakuho-maru under Japanese GEOTRACES program. We occupied at the sampling stations in the western and central subarctic North Pacific.

Sampling methods: Seawater samples were collected with Teflon-coated Niskin-X samplers. The samplers were deployed onto CTD-CMS, which was connected to titanium-armored cable. The samplers were also attached to titanium wire and Kevlar wire. After recovering the samplers, seawater was filtered with 0.2 micrometer-pore size capsule filter directly from the sampler. The filtered samples were collected in each sample bottle in class-100 air space in the laboratory of R.V. Hakuho-maru.

Onboard analytical methods: Seawater samples were acidified with hydrochloric acid to < pH 1.8. Zinc was determined with cathodic stripping voltammetry (van den Berg, 1984) by using ammonium-pyrrolidine dithiocarbamate (ADPC) onboard the clean laboratory of Hakuho-maru. For the voltammetric analyses, interfering organic substances in the samples were decomposed by UV-irradiation. The samples were readjusted to pH 7.0 with aqueous ammonia and buffer solution, and then analyzed. The detection limit was 0.03 nM. Iron was determined with chelating resin preconcentration and chemiluminescence detection method (Obata et al., 1993) in the same laboratory. The samples were readjusted to pH 3.2 with aqueous ammonia and buffer solution, and then analyzed. The detection limit was 0.03 nM. All the analyses were performed in the No. 4 clean laboratory of R. V. Hakuho-maru.

Results and Discussion

We have determined iron and zinc in seawaters collected with the three different sampling methods. Iron concentrations in the seawater samples collected with three different methods were identical. On the other hand, we obtained higher zinc concentrations in seawater samples collected with Niskin-X attached to Kevlar wire than those with other methods. Because we used the same Niskin-X bottles during titanium wire and Kevlar wire samplings, the contamination was caused during the sampling operation. Many sacrifice Zn anodes were used in the research vessel, especially around the propellers of the Hakuho-maru. By minimizing the influence from the propellers, we obtained the identical Zn concentrations from the seawater samples collected with three different methods. To collect the seawater samples without contamination, we need to know the detailed structure of the research vessel.

Keywords: ocean, trace metal, clean technique, sampling technique