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Behaviors of dissolved and particulate Co, Ni, Cu, Zn, Cd and Pb during a mesoscale Fe-enrichment experiment (SEEDS II) in the western North Pacific

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ABSTRACT

During mesoscale Fe enrichment (SEEDS II) in the western North Pacific ocean, we investigated dissolved and particulate Co, Ni, Cu, Zn, Cd and Pb in seawater from both field observation and shipboard bottle incubation of a natural phytoplankton assemblage with Fe addition. Before the Fe enrichment, strong correlations between dissolved trace metals (Ni, Zn and Cd) and PO_4^{3-}, and between particulate trace metals (Ni, Zn and Cd) and chlorophyll-*a* were obtained, suggesting that biogeochemical cycles mainly control the distributions of Ni, Zn and Cd in the study area. Average concentrations of dissolved Co, Ni, Cu, Zn, Cd and Pb in the surface mixed layer (0–20 m) were 70 pM, 4.9, 2.1, 1.6, 0.48 nM and 52 pM, respectively, and those for the particulate species were 1.7 pM, 0.052, 0.094, 0.46, 0.037 nM and 5.2 pM, respectively. After Fe enrichment, chlorophyll-*a* increased 3 fold (up to 3 $\mu g\,L^{-1}$) during developing phases of the bloom (<12 days). Mesozooplankton biomass also increased. Particulate Co, Ni, Cu and Cd inside the patch hinted at an increase in the concentrations, but there were no analytically significant differences between concentrations inside and outside the patch. The bottle incubation with Fe addition (1 nM) showed an increase in chlorophyll-*a* (8.9 $\mu g\,L^{-1}$) and raised the particulate fraction up to 3–45% for all the metals, accompanying changes in Si/P, Zn/P and Cd/P. These results suggest that Fe addition lead to changes in biogeochemical cycling of trace metals. The comparison between the mesoscale Fe enrichment and the bottle incubation experiment suggests that although Fe was a limiting factor for the growth of phytoplankton, the enhanced biomass of mesozooplankton also limited the growth of phytoplankton and the transformation of trace metal speciation during the mesoscale Fe enrichment. Sediment trap data and the elemental ratios taken up by phytoplankton suggest that export loss was another reason that no detectable change in the concentrations of particulate trace metals was observed during the mesoscale Fe enrichment.

1. Introduction

The subarctic North Pacific, equatorial Pacific and Southern Oceans are classified into high-nitrate low-chlorophyll (HNLC) regions, where Fe has been suggested as a prime micronutrient controlling the growth and biomass of phytoplankton. This finding was confirmed by mesoscale Fe enrichments in these regions (Coale et al., 1996, 2004; Martin et al., 1994; Tsuda et al., 2003).

In addition to Fe, various trace metals are essential to marine organisms, often as co-factors in enzymes and as structural elements in biomolecules (Morel and Price, 2003). Co is well known as a central metal in a corrin ring core of vitamin B_{12} and is an essential micronutrient for *Prochlorococcus* (Saito et al., 2002). Ni is a co-factor in urease. Cu is a co-factor in Cytochrome *c* oxidase (da Silva and Williams, 2001), and in enzymes, such as multicopper oxidase (La Fontaine et al., 2002), and proteins, such as plastocyanin (Peers and Price, 2006), recently identified to be important in eukaryotic phytoplankton. Zn is present in a large number of enzymes including alkaline phosphatase and carbonic anhydrase (Morel and Price, 2003). Cd is also contained in Cd-specific carbonic anhydrase in diatom *Thalassiosira weissflogii* (Cullen et al., 1999; Lane et al., 2005). It is also suggested that substitution of an essential metal for another is common in marine phytoplankton (Morel and Price, 2003). Moreover, recent studies suggest that Fe availability is likely to affect the elemental stoichiometry of Co, Ni, Zn and Cd in phytoplankton (Cullen et al., 2003; Twining et al., 2004).

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Biogeochemical cycles are thought to be a major factor controlling the distribution and partition of dissolved and particulate trace metals in seawater. However, it is difficult to observe directly the effect of biological activities on the distribution and partition of trace metals, especially in the open sea. Recently, some data have been reported on the interaction between organisms and trace metals during the mesoscale Fe-enrichment experiments (Gordon et al., 1998; Frew et al., 2001; Kinugasa et al., 2005). The results were very different among the experiments. The concentrations of dissolved and particulate trace metals (Al, Cd, Co, Cu, Mn, Ni and Zn) did not change significantly during IronEx I in the eastern equatorial Pacific Ocean (Gordon et al., 1998). During SOIREE in the Southern Ocean, there were no significant variations for dissolved Ni, Cu and Zn concentrations, while 70% of initial dissolved Cd was partitioned into particulate matter due to biological utilization by algae (Frew et al., 2001). In contrast, Kinugasa et al. (2005) found significant decreases in dissolved concentrations of Co, Ni, Cu, Zn and Cd during SEEDS I in the western North Pacific. They suggested that the dissolved trace metals were taken up by algae and incorporated into particulate species. According to their dissolved and acid-dissolvable data, the particulate trace metals remained in the mixed layer during SEEDS I. These mesoscale Fe enrichments mainly focused on the development phase of the bloom over less than 13 days.

The second Fe-enrichment experiment in the western North Pacific (SEEDS II) was carried out in summer 2004 (Tsuda et al., 2007). We observed variations in dissolved and particulate Co, Ni, Cu, Zn, Cd and Pb inside and outside the Fe patch for 26 days to cover the developing and declining phases of the bloom. We also conducted bottle incubation experiments with Fe addition on board the vessel using surface seawater, from which mesozooplankton had been removed, and followed the changes in trace metals. We report different behaviors of the trace metals between the mesoscale Fe enrichment and the bottle incubation experiments, and discuss the fate of trace metals.

2. Methods

2.1. Reagents and materials

Ultra-high purity HCl, HF, HNO_3, HOAc, NH_3 (TAMAPURE-AA-10 and 100, Tama Chemicals) were used for cleaning of materials, sample preservation and preconcentration. Standard solutions of elements were prepared from commercially available standard solutions (NACALAI TESQUE). All solutions were stored in low-density polyethylene (LDPE, Nalge Nunc International) bottles, which were cleaned according to the methods of Kinugasa et al. (2005). Polycarbonate nucleopore filters (0.2 μm pore size, 47 mm diameter; Nuclepore, Costar) were cleaned according to methods described in Nakatsuka et al. (2007) and stored in MQW (Milli-Q Gradient-A-10 system, Millipore). A closed filtration system was constructed with PFA materials and LDPE bottles. The interior of the filtration system was cleaned successively with 6 M HF (TAMAPURE-AA-100), 0.1 M HCl (TAMAPURE-AA-10) and MQW. The cleaning of materials and preparation of solutions were carried out in a clean laminar flow hood while wearing polyethylene gloves.

2.2. Fe enrichment and patch observation during SEEDS II

The observation during SEEDS II was performed using the R/V *Hakuho Maru* (HK) and R/V *Kilo Moana* (KM) from 13 July to 27 August 2004. The Fe enrichment and observation during the first 2 weeks (days 0–12) and the last 4 days (days 23–26) were carried out using HK. The observation between days 13 and 22 was conducted using KM. The experimental site was located at 48.5°N, 165°E in the northwest subarctic gyre. Prior to the Fe enrichment, a preliminary survey of surface water confirmed that the area was HNLC ($NO_3^- > 18\,\mu M$ and chlorophyll-$a < 1\,\mu g\,L^{-1}$) and that the dissolved Fe concentration was low (~0.02 nM; Nishioka et al., 2009).

$FeSO_4 \cdot 7H_2O$ (1860 kg) and sulfur hexafluoride (SF_6) were dissolved in seawater on board and injected into surface water in an area of 64 km^2 on 20 July (days 0–1). Since the enriched Fe was rapidly lost from the patch until day 2 (<0.5 nM for total dissolved concentration), the second Fe enrichment ($FeSO_4 \cdot 7H_2O$, 950 kg) was executed in an area of 168 km^2 inside the patch between days 5–6. SF_6 was available to trace the Fe patch for the first 12 days. Since pCO_2 in the patch decreased significantly, it was used to trace the patch between days 13 and 26. General methods and results of SEEDS II were detailed in Tsuda et al. (2007) and references therein. Nishioka et al. (2009) have described the method of Fe enrichment and the distribution of Fe during SEEDS II.

2.3. Seawater sampling

Discrete seawater samples were collected from upper 150 m depths with two types of clean sampling devices during the HK cruise. Twelve liters of Niskin-X samplers attached to an epoxy-coated aluminum frame of a CTD-carousel system (Sea Bird Electronics) were used inside the patch. 10 L Niskin-X samplers were attached to a Kevlar hydro-wire and tripped with Teflon messengers outside the patch. The drain cock of the sampler was replaced with a Teflon one. The interior of the sampler was coated with Teflon and cleaned with detergent and HCl.

Seawater samples were subdivided into LDPE bottles. Immediately after collection, seawater (500 mL) was filtered through a Nuclepore filter using the closed filtration system in a shipboard Class 1000 clean room. The filtrate was acidified to pH 2.2 with 20% w/w HCl (TAMAPURE AA-10, 190 μL/100 mL of the filtrate) and stored until the determination of dissolved trace metals on land. The filter and particulate matter were taken in an acid-cleaned Petri dish and frozen until analysis on land.

During the KM cruise, seawater sampling was preformed by using Teflon coated Niskin-X samplers and Teflon messengers deployed on Kevlar hydro-wire. Filtration was carried out with an acid-cleaned 0.22-μm Durapore membrane filter (Cartridge type-Millipak 100, Millipore) in a clean hood on the deck. The filtrate was acidified to pH 2.2 with HCl as done during the HK cruise. No particulate sample was collected during the KM cruise.

2.4. Bottle incubation with Fe addition

Seawater for the bottle incubation experiment was collected using three Niskin bottles from 10 m depth outside the patch (47°N, 165°E) on day 24. The seawater was characterized by ~0.3 $\mu g\,L^{-1}$ of chlorophyll-a, >15 μM of NO_3^- and <0.1 nM of dissolved Fe. The seawater was homogenized in an acid-cleaned 25-L polycarbonate tank and filtered through a 202-μm mesh in order to remove mesozooplankton. The seawater was divided into 10-L fractions. One fraction was added with $FeCl_3$ stock solution to achieve a final Fe concentration of 1 nM (+Fe) and subdivided into 10 polycarbonate bottles (1 L). The other fraction was used as control seawater. This fraction was also subdivided into 10 other bottles. The cap of each bottle was sealed with parafilm and nylon tape. Each bottle was covered with a polyethylene bag and a shade cloth that reduced the light irradiance to ~35% of an ambient