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Bioavailability and Biogeochemical Processes of Trace Metals in the Surface Ocean

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Introduction

Natural, or anthropogenic, forces on climate change and global elemental cycles could have significant influences on the atmospheric deposition of aerosols, including essential trace elements such as iron, to the surface ocean. As a result, induced changes in the structures of primary production, and the marine plankton food web, may affect the distribution of carbon between the atmosphere and ocean, as well as the production of the biogenic gases such as DMS, which lead to the feedback reaction to the global climate (Jickells *et al.* 2005). An elucidation of the stimulation effects of biological activity by the trace elements in aerosols is a key for a better understanding of a series of these processes.

In the subarctic western North Pacific, a deficiency of iron, and other trace metals, in seawater has been shown to be an important limiting factor for a phytoplankton growth, and controls primary production (Takeda and Tsuda 2005). In addition, a temporal increase in the primary productivity, after the deposition event of Asian dust, was reported in the

subtropical North Pacific (Young *et al.* 1991). However, the dissolution process of trace metals in atmospheric aerosols such as the Asian dust, which is a main supply process of micronutrients to the surface seawater, has not been fully elucidated. Biologically-important trace metals, such as iron, zinc and copper, are known to exist mostly in the form of an organic complex with natural organic ligands in seawater, and thus their biological availability, as well as their chemical reactivity, may dynamically change by the photochemical processes and biochemical reduction in the surface water (Morel and Price 2003). Therefore, in order to understand the chemical reactivity of trace metals which are released from the atmospheric aerosols to the surface seawater, the biological uptake of these elements by microbes, and the scavenging processes of these elements within the water column, it is necessary to conduct a study that considers interactions between the chemical speciation of trace elements and the biological processes.

In the context of the foregoing scientific background, the Surface Ocean-Lower Atmosphere Study (SOLAS) has

been established as one of the core projects under the International Geosphere Biosphere Programme (IGBP), and the elucidation of the dissolution process of trace elements derived from atmospheric aerosols to the seawater, and its biological utilization in the pelagic ecosystem, is one of the important topics. In contrast to recent activities investigating the influence of dust, derived from the Sahara, on marine biogeochemical cycles in the Atlantic Ocean, the promotion of an integrated study, based on the latest knowledge of atmospheric chemistry, chemical oceanography and biological oceanography, was strongly needed in the western North Pacific, where a large quantity of atmospheric deposition occurs by Asian dust events.

In this study, we have investigated the biogeochemical processes of trace metals, which are supplied through the deposition of atmospheric aerosols such as Asian dust, and its bioavailability for phytoplankton growth in the surface waters of the western North Pacific Ocean, from the viewpoint of the following three questions for the purpose of clarifying how essential trace elements, such as iron, are supplied in a form available for phytoplankton from the aerosols which are deposited in the western North Pacific:

(1) What is the major factor controlling the solubility of trace elements in the aerosols?

(2) What is the dominant chemical form of trace elements that are released from the aerosols into the seawater?

(3) What kind of chemical form of the trace elements can the phytoplankton use for their growth in the surface ocean?

The purpose of this study has been to quantitatively evaluate the relationship between the supply of trace elements from the atmosphere and changes in the biological productivity in the surface waters, considering not only the supply flux, but also the physical and chemical speciation of trace elements in the seawater. New knowledge

obtained by this study could make a significant contribution to a better understanding of the elemental cycles and the roles of the biological carbon pump in the ocean, and, consequently, the prediction of the response of the marine ecosystem to future climate change.

Methods

In addition to the oceanographic observations in the subarctic and subtropical western North Pacific, on-board culture experiments, and atmospheric sampling on land stations, were conducted together with aerosol dissolution experiments and phytoplankton culture experiments in the laboratory.

Solubility of trace elements in aerosols

Total deposition samples were collected at three stations (Hedo in Okinawa, Kushiro in Hokkaido and Otsuchi in Iwate) in Japan during the high dust season, when Chinese Loess (Kosa) frequently reaches Japan. We determined the total and soluble fractions of trace elements in the total deposition samples and the solubility by using a high-resolution inductively-coupled plasma (ICP) mass spectrometer (Finnigan Element2, Thermo Electron Co.), and investigated the effects of anthropogenic substances on the solubility.

Speciation of trace elements derived from aerosol in seawater

We have established a sensitive method of determining Fe(II) in seawater, and we have investigated the distributions of Fe(II) in surface seawater. To understand the scavenging processes of trace metals in seawater by biogenic particles, produced during phytoplankton blooms, biogeochemical cycles of rare earth elements in surface waters were investigated during the iron fertilization experiment in the western subarctic North Pacific (SEEDS-II).

Chemical form of trace element used for phytoplankton growth

On-board culture experiments were conducted using surface waters with a natural phytoplankton assemblage in the subarctic and subtropical western North Pacific by adding atmospheric dry/wet deposition samples collected at the Japanese coast and the sea. Increases in phytoplankton biomass and changes in dominant phytoplankton groups were examined during the incubation. In addition, laboratory culture experiments were carried out using a diatom culture strain isolated from the subarctic western North Pacific to evaluate the biologically-available fraction of iron included in the atmospheric deposition samples.

Based on the results obtained from these studies, the atmospheric deposition fluxes of trace elements, in a form available for phytoplankton growth, were estimated, and a main process that controls the bioavailability of trace elements originating from atmospheric deposition, was extracted to evaluate the role of trace elements in the interaction of the atmosphere and ocean.

Results and Discussion

What is the major factor controlling the solubility of trace elements in the aerosols? (1) Dissolution process of iron from the Asian dust particle

The dissolution of iron from the Asian dust standard particle (CJ-2) was examined by a dissolution experiment using a flow-through system with artificial seawater. Iron concentration in the eluted seawater showed two peaks just after the initiation of the seawater permeate and after seven hours (Fig. 1). This result suggests that the dissolution of highly-reactive iron occurred at the surface of the dust particles, and also the flush out of small colloidal iron occurred during the initial phase of the contact of seawater with the CJ-2 par-

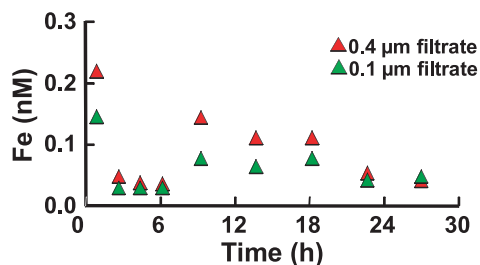


Fig. 1. Changes in the iron concentration in the artificial seawater eluted from the Asian dust standard particle (CJ-2).

ticles. Less reactive iron was then slowly released in the dissolved and colloidal fractions from the CJ-2 particles. Oooki *et al.* (2009) reported that the dissolution rate of iron in the Asian dust strongly depended on the particle size, and, therefore, further study is needed to elucidate the magnitude and time-scale of changes in the particle size of Asian dust after deposition into the surface seawater.

The addition of the model iron-complexing organic ligand, DFB, to the seawater did not stimulate the dissolution of iron from the Asian dust particles within 24 hours, and there was no clear difference in the solubility of dust iron between the artificial seawater and the filtered surface seawater, which contained natural organic ligands, collected from the subarctic western North Pacific. Therefore, the existence of iron-complexing organic ligands at concentrations usually observed in the surface water (a few nM) may not strongly accelerate the dissolution of iron from the dust particles within a timescale of a few days. However, considering the residence time of dust particles in the surface mixed layer, which had been estimated to be several weeks, it cannot be excluded that the iron-complexing organic ligands are playing an important role in maintaining the iron in a dissolved form after the release from dust particles on a longer timescale.

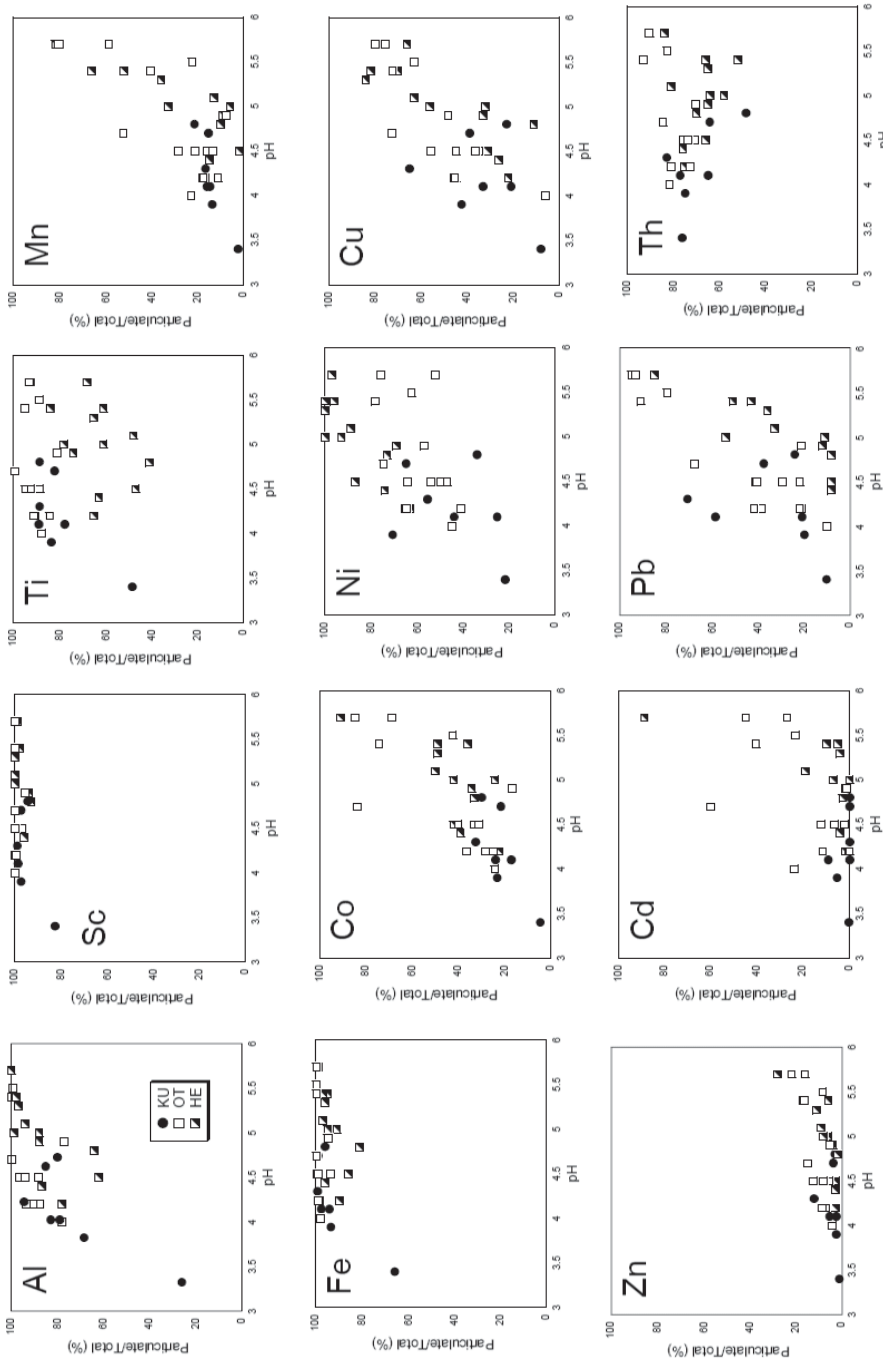


Fig. 2. Relationship between particulate/total (%) of trace metals and pH values at each station, Cape Hedo (HE), Kushiro (KU), and Otsuchi (OT).

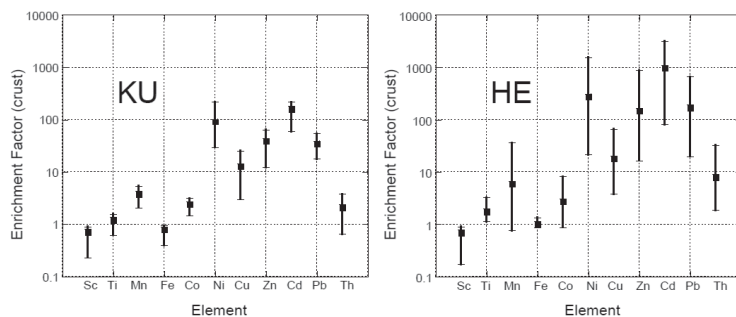


Fig. 3. Al-normalized enrichment factors of trace metals at KU and HE stations.

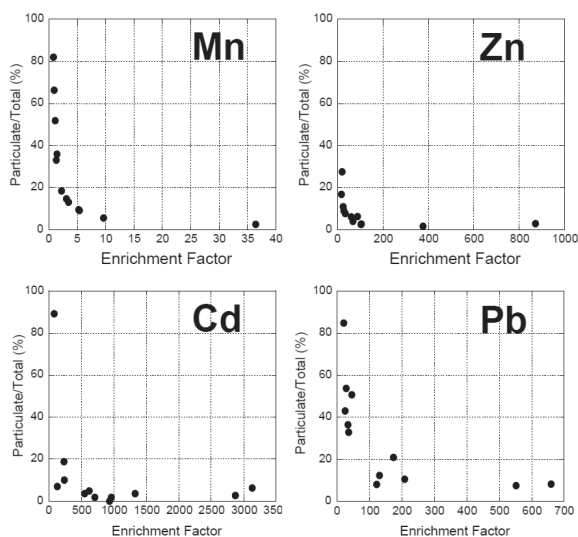


Fig. 4. Relationship between particulate/total (%) and enrichment factor values for Mn, Zn, Cd, and Pb at HE station.

(2) Solubility and origin of trace metals in atmospheric deposition samples

The averaged atmospheric deposition of Al was the highest among the trace metals at Cape Hedo (Okinawa), Kushiro (Hokkaido) and Otsuchi (Iwate) in 2008, which was consistent with the crustal abundance. The total deposition flux of iron was $194 \mu\text{g}/\text{m}^2/\text{day}$ in Kushiro.

The percentages of particulate fractions to total fractions were higher for scandium, aluminum and iron, than those for manga-

nese, cobalt, copper, zinc, cadmium and lead. The percentages were lower at lower pH conditions for most trace metals (Fig. 2). The enrichment factors, calculated from aluminum concentrations, indicated that iron, titanium and scandium were derived from the crust, but others were influenced by human activities (Fig. 3). For example, Mn, Co and Th, which showed relatively-high enrichment factors, were highly correlated with other components other than the crustal component, which probably

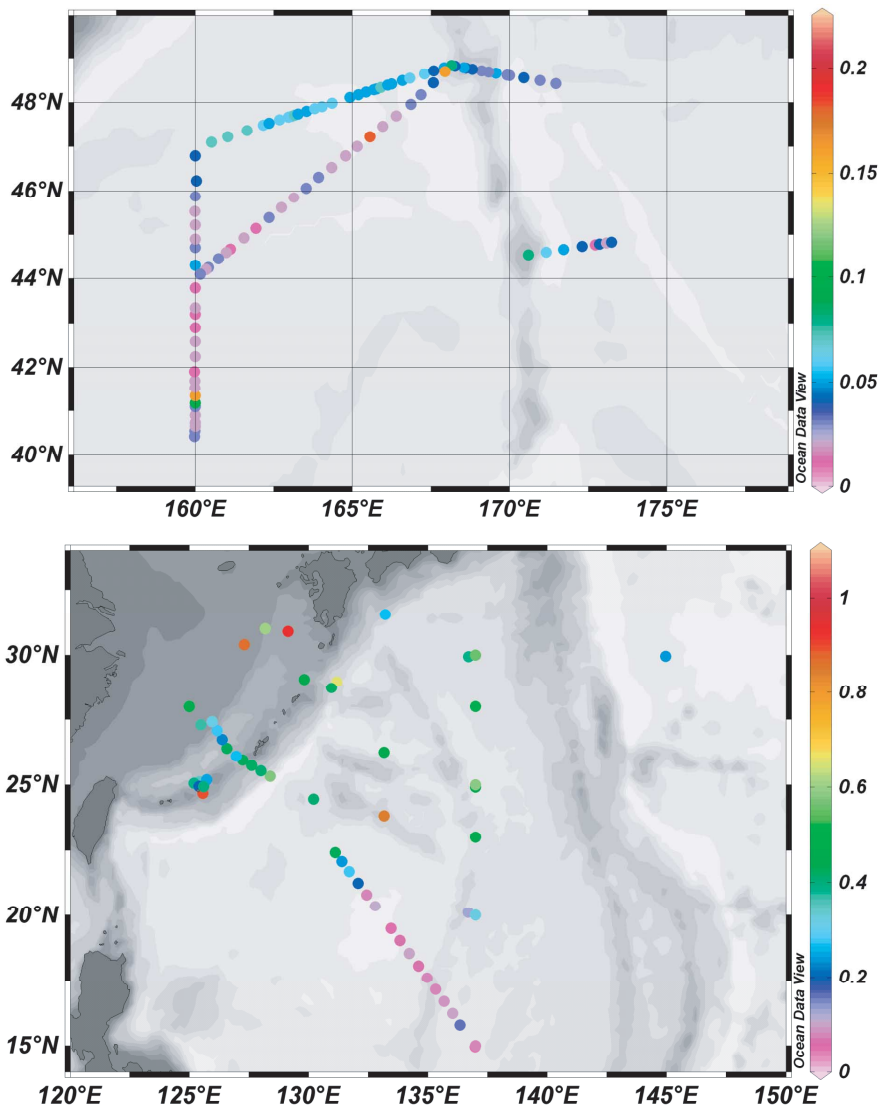


Fig. 5. Horizontal distribution of dissolved iron (nM) in the surface water observed in the subarctic (top) and the subtropical (bottom) western North Pacific Ocean.

indicates the effect of anthropogenic emissions. However, Al in the total deposition samples collected in Cape Hedo might be partially derived from anthropogenic substances. We noted that scandium is more representative for crustal substances than is aluminum in this case.

Generally, trace metals in the total deposition samples, influenced by anthro-

pogenic substances, were more easily dissolved than those in the samples collected at the Kosa event (Fig. 4). The soluble fractions of iron were about 6% collected in Cape Hedo, which was 4 times higher than those at the Kosa event. The anthropogenic substances largely affect the solubility of trace metals by lowering the pH of aerosol (Hsu *et al.* 2010), which is an impor-

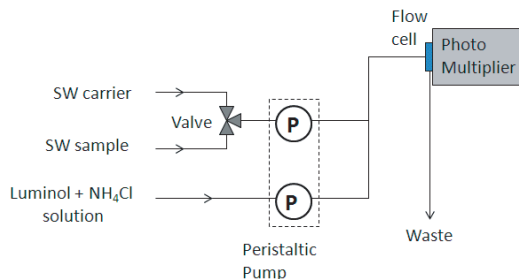


Fig. 6. Conceptual diagram of the analytical system for detecting Fe(II) in seawater.

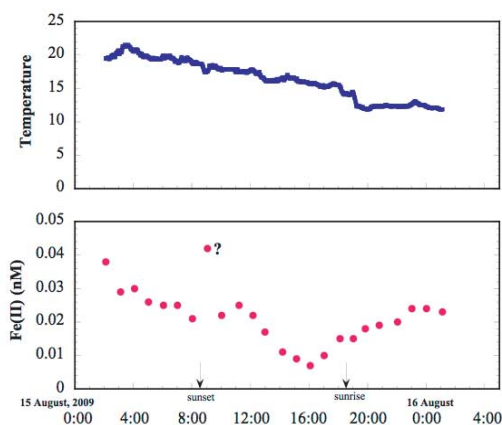


Fig. 7. Time variation of temperature and Fe(II) in surface waters of the western subarctic North Pacific.

tant process for the supply of dissolved fractions of trace metals to the sea surfaces.

What is the dominant chemical form of trace elements that are released from the aerosols into the seawater?

(1) Horizontal distribution of trace metals in the oceanic surface waters

Continuous sampling of the surface water along several transects were conducted in the subarctic and the subtropical western North Pacific using a trace-metal clean Fish sampling system (Fig. 5). Regardless of some variations in the phytoplankton abundance, the dissolved

iron concentration was extremely low throughout the observation area in the subarctic waters. It seems that the rapid uptake of dissolved iron by a phytoplankton assemblage under conditions of iron deficiency can suppress possible changes in the dissolved iron concentration by the atmospheric deposition of mineral dust or anthropogenic aerosols. On the other hand, there was a west-east gradient in the dissolved iron concentration in accordance with the change in the deposition flux of Asian dust in the subtropical waters from the East China Sea to the western North Pacific. Observed high dissolved

iron concentrations in the western regions suggest that dissolved iron in the surface water was mostly complexed by natural organic ligands.

(2) *Fe(II)* in surface waters

In seawater, trace metals exist in various chemical forms, such as organic complexes, and inorganic forms. Availability of the trace metals in seawater by phytoplankton depends on the chemical forms of the trace metals. For Fe, Fe(II) is an important inorganic form in seawater because Fe(II) is an easily-available form for marine phytoplankton.

We have investigated a sensitive analytical method of detecting Fe(II) in seawater based on an existing chemiluminescence method (Hansard and Landing 2009). The conceptual diagram of the flow analytical system is shown in Fig. 6.

Using this system, the detection limit of Fe(II) in seawater was 5–13 pM onboard the ship. In the western subarctic North Pacific, the Fe(II) concentrations in surface waters were 5~43 pM (Fig. 7), which was almost the same level as reported in a previous study (Roy *et al.* 2008).

Based on previous studies, Fe(II) is produced, as expected, by photoreduction in surface waters. However, we could not observe a clear relationship between Fe(II) and the light intensity. For more than 12 hours, about 20 pM of Fe(II) was kept in surface waters. In polar regions, it is known that oxidation rates of Fe(II) become slower at a lower temperature (Croot *et al.* 2001). Also in the western subarctic North Pacific, Fe(II), produced by photoreduction, might be kept for a relatively long time. We performed UV-irradiation experiments to decompose naturally-occurring organic matter in seawater. After the UV-irradiation, the oxidation rates of Fe(II) become faster, which indicates that the naturally-occurring organic matter in seawater affects the oxidation rate of Fe(II) in seawater.

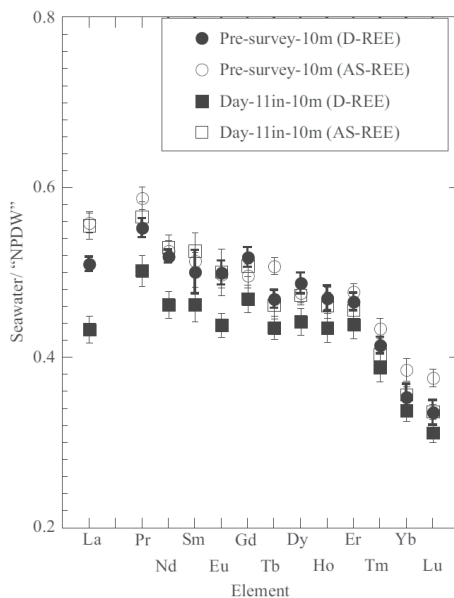


Fig. 8. North-Pacific-Deep-Water normalized patterns of REE in surface waters during the Fe fertilization experiment (SEEDS-II). D-REE: REE concentrations in dissolved fraction (0.2- μ m pore size); AS-REE: REE concentrations in acid-soluble fraction.

(3) Rare earth elements in seawater during the phytoplankton bloom induced by an iron fertilization experiment

During the iron fertilization experiment in the western subarctic North Pacific (SEEDS-II), we investigated rare earth elements (REE) in seawater. After the phytoplankton bloom, dissolved REE rapidly decreased, though total REE concentrations (including particulate fractions) were almost constant in seawater (Fig. 8). Decreases of light REE were more remarkable than those of heavy REE. Light REE are more easily complexed with organic ligands on the surface of biogenic particles (Sholkovitz *et al.* 1994), which is consistent with the observed trend of REE during the phytoplankton bloom. The scav-

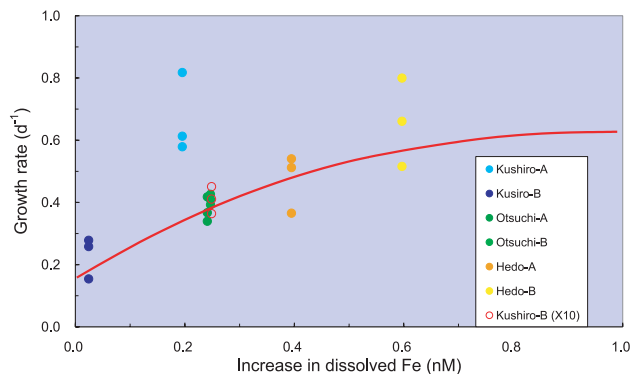


Fig. 9. Relationship between the dissolved iron concentration increased by the addition of atmospheric dust samples, and the specific growth rate of the diatom culture strain. Atmospheric dust samples collected in Hedo, Otsuchi or Kushiro was added to the culture media to obtain the same final concentration of total iron at 5 nM. The red line in the figure indicates the growth rate of the diatom cultured with iron sulfate spiked at the corresponding dissolved iron concentration.

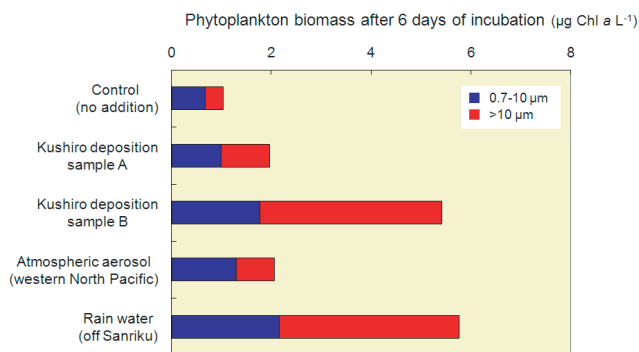


Fig. 10. Increase reply of the phytoplankton crowd of the North Pacific subarctic zone area to addition of an atmosphere descent thing and the rainwater.

enging process of REE could be applicable for other trace metals, indicating that the REE are suitable tracers for particle-reactive trace metals in seawater.

What kind of chemical form of trace elements can the phytoplankton use for their growth in the surface ocean?

(1) Biological availability of iron released from the Asian dust

On-board culture experiments were conducted using surface waters collected

from the subarctic Oyashio waters by adding the Asian dust standard particle (CJ-2) or inorganic iron sulfate, and the growth response of the phytoplankton assemblage were monitored for 5 days. Although significant growth stimulation of diatoms, such as *Chaetoceros* spp., by inorganic iron addition suggested that the phytoplankton were under iron stress, the observed growth response to the CJ-2 addition was relatively small. The biological availability of iron in the atmospheric

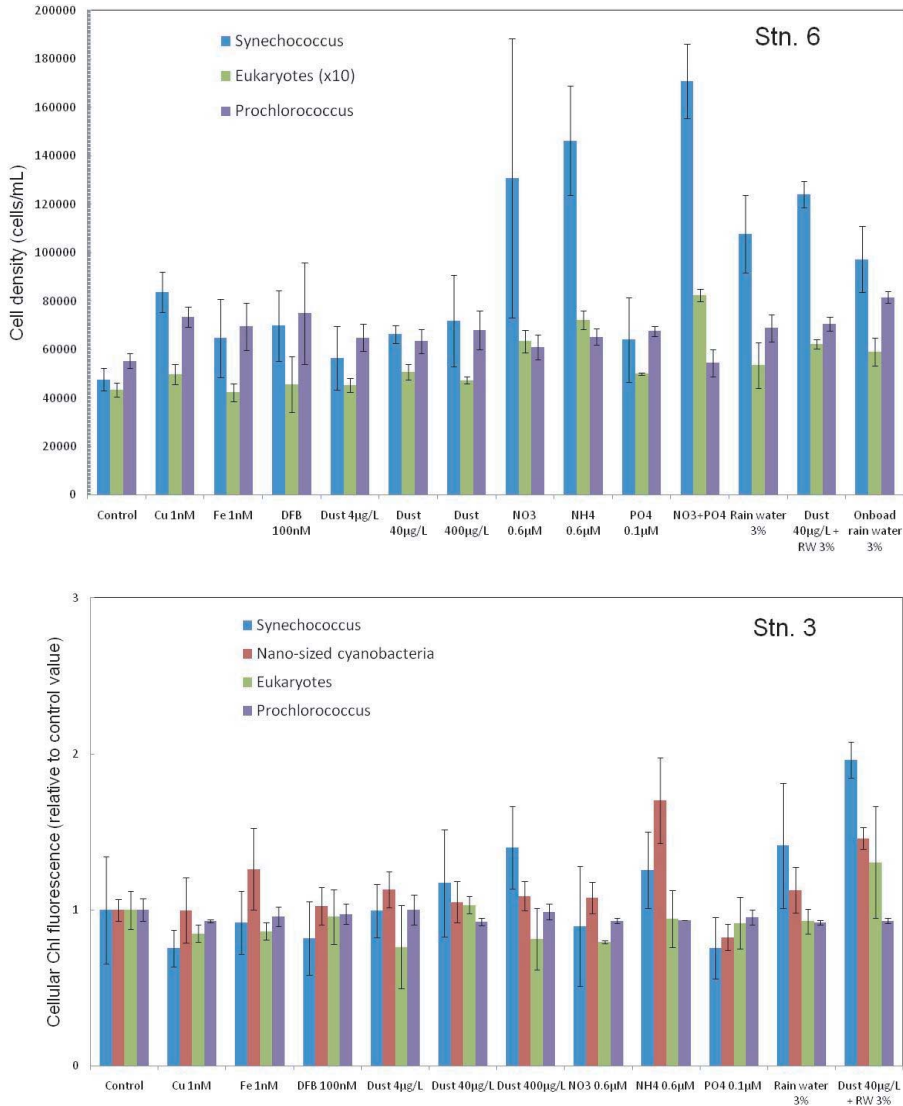


Fig. 11. Cell density (top) and relative intensity of cellular chlorophyll fluorescence (bottom) of each phytoplankton group observed after 24 hours during enrichment experiments conducted in the East China Sea (top) and the subtropical western North Pacific (bottom). Additions to the surface water were made with 1 nM CuSO_4 , 1 nM FeSO_4 , 100 nM iron-complexing organic ligand (DFB), 4, 40 and 400 $\mu\text{g/L}$ Asian dust collected in Nagasaki, 0.6 μM NaNO_3 , 0.6 μM NH_4Cl , 0.1 μM NaH_2PO_4 , or 3% (v/v) rain water collected at the western North Pacific during the cruise.

deposition samples collected at the coastal areas in Japan was examined by laboratory culture experiments using a diatom culture strain isolated from the subarctic North

Pacific. The growth rate of iron-limited diatom cells showed a clear correlation with iron concentration in the dissolved phase (Fig. 9), suggesting that most of the

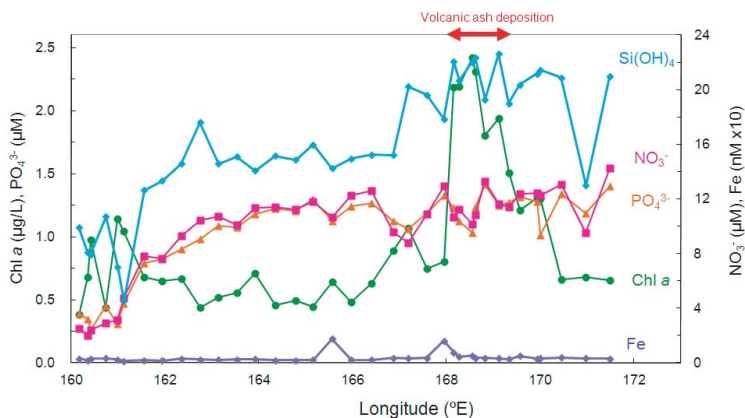


Fig. 12. Changes in dissolved iron, chlorophyll a and nutrient concentrations in the surface water along the E-W cruise track at 48°N in the subarctic western North Pacific. The area of the volcanic ash deposition is indicated by a red arrow.

iron remaining in the particle phase was not available for phytoplankton growth.

(2) *Enhancement of phytoplankton growth in the surface water by the addition of atmospheric deposition samples*

Atmospheric deposition samples collected at Kushiro in spring, rain water, and atmospheric aerosols collected at the sea, were added to the surface water obtained from the high-nitrate, low-chlorophyll region of the subarctic western North Pacific, and the water samples with an ambient phytoplankton assemblage were incubated on board for 6 days. The addition of atmospheric deposition samples stimulated the phytoplankton growth mainly in large diatom species (Fig. 10). There was a significant relationship between the magnitude of phytoplankton growth response and the amount of added iron in the dissolved fraction. The atmospheric deposition samples affected by anthropogenic sources tended to have a higher amount of biologically-available iron compared to those without such influences.

Since atmospheric aerosols of an anthropogenic origin sometime contain high concentrations of trace elements having a toxicity to marine microbes, such as cop-

per and cadmium, the inhibition of phytoplankton production by atmospheric deposition has been discussed (Paytan *et al.* 2009). However, inhibition of algal growth was not observed in our incubation experiments using atmospheric deposition samples affected by anthropogenic activities, suggesting that contamination of atmospheric aerosols by toxic heavy metals over the western North Pacific is not so high at present. It is possible that excess organic ligands in the surface water are playing a role in reducing the toxicity of deposited heavy metals by forming less reactive organic complexes. Another experiment conducted in the East China Sea showed that the plankton assemblage released copper-complexing organic ligands in response to the addition of inorganic copper sulfate. Therefore, it is necessary to consider the biological responses to the atmospheric deposition, which may alter the chemical speciation of released metal ions and their biological availability in the surface water.

In the oligotrophic surface waters of the subtropical western North Pacific and the southeastern East China Sea, growth stimulation of phytoplankton (e.g.

Synechococcus) by the addition of Asian dust, and rain water samples, was observed mainly due to an increase in inorganic nitrogen concentration together with the supply of micronutrients such as iron (Fig. 11). The results also indicated that physiological activity of unicellular nano-size cyanobacteria, which might be diazotrophic, was enhanced by the supply of ammonium ions and dissolved iron. Other incubation experiments conducted in the Indian Ocean revealed that small-size phytoplankton could respond to the addition of rain water within 1 day, while it took about 3 days for large-size phytoplankton to respond.

(3) Possible influences on phytoplankton productivity by volcanic ash deposited in the subarctic North Pacific during summer

During the subarctic North Pacific cruise in August, 2008, we encountered an atmospheric deposition event of volcanic ash which had been transported from Mt. Okmok in the Aleutian Islands. Four days after the volcanic ash deposition, we observed a growth response of the resident phytoplankton assemblage in the deposited waters (Fig. 12), and chlorophyll *a* concentrations in the surface waters increased to approximately 3 times compared with its value just before the volcanic ash deposition event. Improvement of photosynthetic activity of the resident phytoplankton was also confirmed in these waters, where pennate diatoms and prymnesiophytes dominated in the phytoplankton communities.

There were unusually many volcanic eruptions at the Aleutian Islands, and the Kamchatka Peninsula, during the summer of 2008, when we observed a growth stimulation of the phytoplankton assemblage in the subarctic western North Pacific. In the same year, similar increases in sea-surface chlorophyll *a* concentrations were observed over wide areas of the eastern subarctic North Pacific, and its relation to the volcanic ash deposition was

considered (Hamme *et al.* 2010). It has been reported that 35–107 nmol iron could be released from 1 g of volcanic ash within 1 hour, when the ash is suspended in seawater in a ratio of 1:400 (Olgun *et al.* 2011). Reactions of ash particles with acidic fog during the atmospheric transportation process may enhance the solubility of iron, and other trace elements, in the volcanic ash, and thus volcanic ash could be one of the important sources of trace elements in the subarctic North Pacific.

Conclusions

In the surface waters of the western North Pacific Ocean, we investigated biogeochemical processes of trace metals, which were supplied through the deposition of atmospheric aerosols, such as Asian dust, and its bioavailability for phytoplankton growth. Atmospheric aerosols influenced by anthropogenic sources, during transport from the Asian continent to the North Pacific, showed a relatively high trace-metal solubility. Our results showed that 1–20% of iron in the atmospheric aerosols deposited in the western North Pacific became a dissolved form which was available for phytoplankton in the surface water. However, the solubility of Asian dust varied significantly due to influences of the mixing with anthropogenic aerosols, as well as the low pH owing to reactions with nitric acid and sulphuric acid in the urban atmosphere, and it is difficult to apply a single average value as the solubility of Asian dust in seawater. Deposited dust particles may continuously supply dissolved iron to phytoplankton, if these particles remain suspended in the euphotic zone. A detailed study is needed to understand the behaviour of deposited aerosol particles in the water column. Regarding the trace metals other than iron, we observed a high solubility (20–80%) for manganese, zinc and copper, in which the contribution of an-

thropogenic sources were significant. However, atmospheric deposition fluxes of these elements were not so large compared with ambient concentrations in the surface water, suggesting that atmospheric aerosols played a minor role in the biogeochemical cycles of these element in the surface ocean.

Volcanic ash depositions were found to initiate phytoplankton blooms in the high-nitrate, low-chlorophyll waters of the subarctic North Pacific, where the ambient phytoplankton assemblage was under a strong iron-limitation stress. Asian dust has been considered as an important iron source for the subarctic phytoplankton communities, but the peak of the Asian dust deposition event usually occurs in spring, when deep mixing of the surface water prevents phytoplankton growth by light limitation. On the other hand, volcanic eruption could happen throughout the year, and, thus, iron supply from volcanic ash may have a strong impact on phytoplankton productivity during the stratified summer. Although the future desertification of the Asian continent may result in a lengthening of the high-dust season, our findings support the conclusion that volcanic ash is playing an important role as a source of limiting trace elements in controlling phytoplankton productivity in the subarctic North Pacific which is surrounded by a lot of active volcanoes.

Along with the ongoing economic development of East Asia, the atmospheric deposition of anthropogenic materials will continuously increase in the western North Pacific (Duce *et al.* 2008). Therefore, the relative importance of atmospheric nutrient supply in the biogeochemical processes within the surface ocean will increase in the future. Our findings relating to phytoplankton responses to the atmospheric supply of trace elements could be introduced into global physical-ecosystem models that describe the interaction between the atmosphere and ocean. Through such scientific efforts, this study would contribute to a better prediction of future climate changes and the global impact of human activities on marine ecosystems.

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