

IRON STUDY IN THE SEA OF OKHOTSK - COMPARISON TO THE SUBARCTIC PACIFIC -

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1. INTRODUCTION

After the development of trace metal clean techniques for the sampling and analysis for iron in seawater, vertical profiles of iron have been characterized in many regions of the open ocean. Recent large scale *in situ* iron enrichment experiments in equatorial Pacific and Southern Ocean, examining the relationship between iron supply and phytoplankton production in high-nutrient low-chlorophyll (HNLC) regions, clearly showed that iron is an important factor controlling phytoplankton growth in these waters (Martin et al., 1994; Coale et al., 1996; Boyd et al., 2000; Gervais et al., 2002; Coale et al., 2004). This hypothesis was also investigated in the western and the eastern subarctic Pacific (Tsuda et al., 2003; Boyd et al., 2004), and the results clearly demonstrated that iron fertilization stimulated the utilization of surplus nutrients and the uptake of carbon dioxide by phytoplankton growth.

The Sea of Okhotsk is a marginal sea in the northwestern edge of Pacific Ocean and known as a seasonal sea ice area at the lowest latitude in the world. (Kimura and Wakatsuchi, 2000). Several previous reports indicate that the primary productivity of the Sea of Okhotsk is very high, especially on the continental shelf (Sorokin and Sorokin, 1999; Saito et al., 1996). However, there is little information on iron concentration in the sea of Okhotsk and it is not known whether iron bioavailability limit phytoplankton growth or not, because there is little number of iron study in this region

This review focuses mainly on a comparison iron condition of the subarctic Pacific (west and east) and the Sea of Okhotsk for predicting the role of iron for biological production in the Sea of Okhotsk.

2. IRON AND BIOLOGICAL CONDITION IN THE WESTERN AND THE EASTERN SUBARCTIC PACIFIC

The entire subarctic is a high-nutrient low-chlorophyll (HNLC) region where nitrate is rarely depleted at the surface. Despite the general similarities on nutrient condition between western and eastern region in the subarctic Pacific, there are important difference in temporal variability of phytoplankton biomass. Chlorophyll *a* concentrations are consistently low at the eastern stations (0.3-0.4 mg/m³) (Boyd and Harrison, 1999) and are higher and more variable in the western region (0.2-1.6 mg/m³) (Imai et al., 2002), especially high in Oyashio region (0.3-8 mg/m³) (Kasai et al., 2001). The experimental results of the mesoscale iron enrichment experiments (Tsuda et al, 2003; Boyd et al., 2004) clearly showed that iron is one of the limiting factors for phytoplankton growth during the late spring to summer in the both region. Although

the source of naturally supplied iron are not clear quantitatively, several investigators have indicated the gradient in flux of iron dust from west to east and absence of iron in the east explain the lack of spring bloom in the Alaskan Gyre. Moreover, horizontal transport of iron rich coastal water and vertical transport could be important source at certain times of the year in addition to dust input (Harrison et al., 2004). Several previous studies (Suzuki et al., 2002; Nishioka et al., 2003) have reported evidence for higher iron concentrations in the western subarctic Pacific than in the eastern part. Nishioka et al. (2003) observed the high labile particulate (detectable at pH 3.2, see below) iron concentrations in the ambient surface mixed layer in the western region (0.22-0.46 nM in west, 0.035 in east, Table 1) and the result would indicate that significant supply of iron to the surface mixed layer occurs in western region. Additionally, estimated iron flux from below the surface is several times higher at the western region than the eastern region (Nishioka unpublished data). Therefore, the difference in input of bioavailable iron to the ocean could cause significant difference in temporal variation of phytoplankton abundance between the western and eastern region, with light and physical conditions. However, in western region, even if dissolved iron concentrations in surface seawater increase after natural iron supply, such as atmospheric deposition and vertical iron flux, the increased dissolved iron would be rapidly transformed to the less-bioavailable particulate fraction (Nishioka et al., 2003), and this might be a reason why phytoplankton growth is limited by iron availability in western region in spite of the relatively high iron input (Fig. 1). I summarize the iron and biological condition in western and eastern region in Table 2.

Table 1 Comparison of iron concentration in labile particle and dissolved fractions in surface mixed layer between subarctic Pacific and the Sea of Okhotsk

| | subarctic Pacific | | | The Sea of Okhotsk |
|------------------------------|-------------------|---------------------------|----------------|--------------------|
| | Eastern region | Western region Oyashio | Western region | |
| labile particle iron (nM) | 0.035 ± 0.03* | 0.46 ± 0.17* | 0.22 ± 0.09* | 0.85 ± 0.45 |
| dissolved iron (nM) | 0.08 ± 0.04* | 0.11 ± 0.04* | 0.09 ± 0.03* | 0.46 ± 0.12 |

* The data are from Nishioka et al., 2003

Table 2 Comparison forecast of iron and biological condition between the Sea of Okhotsk and the subarctic Pacific

| | subarctic Pacific | | Okhotsk (??) |
|-------------------|-------------------|--------------------------------------|--|
| | Eastern | Western | |
| Chl.a variability | Low | Variable | Higher variable |
| Fe concentration | Low | High in Par-Fe* (in early summer) | High in Par-Fe* High in Diss-Fe* (in early summer) |
| Fe supply | Low | Higher than Eastern region | Higher than subarctic Pacific (??) |
| Fe limitation | Yes | Yes | No (??) |

*Par-Fe: Particulate

*Diss-Fe: Dissolved

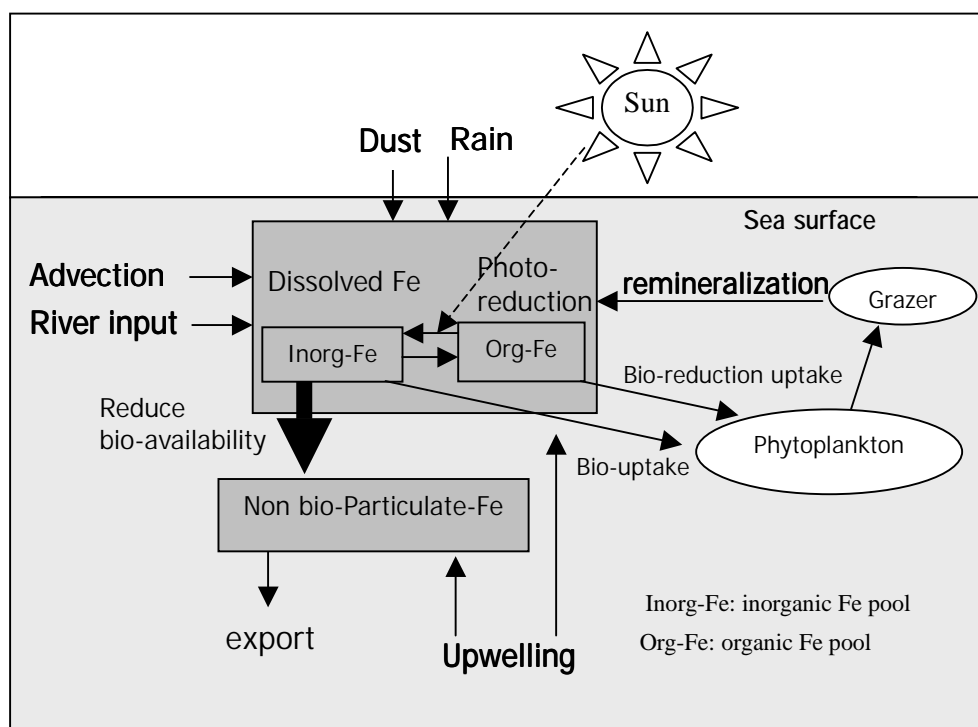


Fig. 1 Schematic draw of iron source, form, transformation and biological uptake processes in seawater. Thick arrow indicate that transformation of dissolved iron to the less-bioavailable particulate, and this might be a reason why phytoplankton growth is limited by iron availability in western subarctic Pacific.

3. IRON CONCENTRATION IN THE SEA OF OKHOTSK

To characterize vertical profiles of total labile iron (detectable at pH 3.2 without filtration) and dissolved iron (detectable at pH 3.2 in 0.22 μm filtrate) concentration in the Sea of Okhotsk, seawater samples were collected using trace metal clean technique in 2000 May - June. Concentration of Fe (III) in the filtrate samples were determined using an automatic Fe (III) analyzer (Kimoto Electric Co. Ltd.) using chelating resin concentration and chemiluminescence detection (Obata et al., 1993). Total labile iron concentration that may contain the chemically labile fraction of particulate iron at pH 3.2 was also measured by the unfiltered samples (labile particulate).

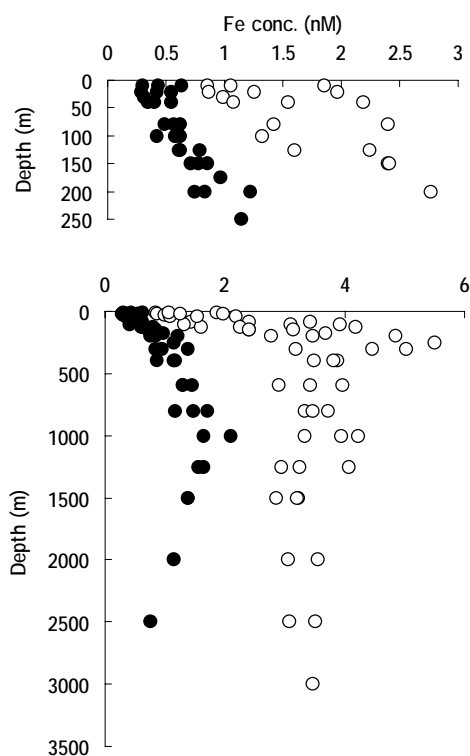


Fig. 2 Total labile (unfiltered) and dissolved ($< 0.2 \mu\text{m}$) iron concentration in the Sea of Okhotsk. Samples were collected at three stations which located at west side of the Kuril islands (48.30°N , 150.30°E ; 47.40°N , 151.10°E ; 49.00°N , 153.10°E) and every data are plotted on this graph. Open and solid symbols indicate total labile iron concentration and dissolved iron concentration, respectively.

Vertical iron profiles at stations in the Sea of Okhotsk are shown in Figure 2. At the sampling station in the Sea of Okhotsk, west side of the Kuril islands, dissolved and total labile iron concentration did not have familiar nutrient like distribution. Dissolved Fe concentration was not depleted in surface layer. Dissolved Fe ($< 0.22 \mu\text{m}$) concentrations in surface mixed layer were $0.46 \pm 0.12 \text{ nM}$ during the late spring season, with maximum concentration of $1.5 \sim 2.0 \text{ nM}$ observed at $800 \sim 1000 \text{ m}$ depth. On the other hand, labile particulate iron (Total labile minus dissolved fraction) concentration in surface mixed layer were $0.85 \pm 0.45 \text{ nM}$, with maximum concentration of $4.0 \sim 5.5 \text{ nM}$ observed at $250 \sim 1250 \text{ m}$ depth. These values in surface water and deep water were higher than reported iron concentration in the western subarctic Pacific. Comparison of iron concentration in labile particle and dissolved fractions in surface mixed layer between the subarctic Pacific and the Sea of Okhotsk was shown in Table 1. The higher labile particulate and dissolved iron concentration we observed in surface mixed

layer in the Sea of Ohotsk would indicate that significant supply of iron to the surface mixed layer occurs in this region.

4. PREDICTION OF IRON CONDITION AND BIOLOGICAL RESPONSE IN THE SEA OF OKHOTSK

The Sea of Okhotsk may differ from other HNLC region in that this marginal sea may have iron supplies from several possible sources, such as atmospheric deposition, iron from Amur-river input and re-suspended sediment from the continental shelf with iron remineralization. The primary productivity of the Sea of Okhotsk is very high, especially on the continental shelf (Sorokin and Sorokin, 1999; Saito et al., 1996), and major nutrients, nitrate, was depleted after the spring phytoplankton bloom (Nakatsuka et al., 2004). Therefore, we are able to assume that iron supply is higher in the Sea of Okhotsk than the western subarctic Pacific and, probably, phytoplankton growth is not limited by iron availability in the Sea of Okhotsk. If these points are true, this gives us the following interest concerning iron input and behavior in the Sea of Okhotsk. I summarize the comparison forecast of iron and biological condition between the Sea of Okhotsk and the subarctic Pacific in Table 2.

5. FUTURE IRON STUDY IN THE SEA OF OKHOTSK

I indicate several major areas for future research to study iron dynamics and phytoplankton growth in the Sea of Okhotsk as follows.

- 1) What are the sources of iron?
- 2) Which chemical form of iron are supplied to the Sea of Okhotsk?
- 3) Iron behavior and transformation after natural iron supply in the Sea of Okhotsk.
- 4) How to keep high dissolved iron concentration and its bio-availability in the photic zone?
- 5) How phytoplankton access to naturally supplied iron (inorganic-iron, organic-iron)?
- 6) The role of the Sea of Okhotsk for iron supply to the western subarctic Pacific region.

There are several possible iron sources in the Sea of Okhotsk, such as sporadic or seasonal event of atmospheric deposition, continuous iron flux from Amur-river input, re-suspended sediment from the continental shelf with iron remineralization, and iron flux from vertical mixing caused by physical oceanographic processes. Each iron source should be evaluated quantitatively and clarify how contribute to biological production in the Sea of Okhotsk. Iron retention and loss rate may be controlled by physical and chemical conditions. We especially need to know more about chemical conditions, such as role of organic ligands and colloidal iron (organic and inorganic colloid), on iron concentrations and loss rates. We still need more information about iron behavior in different chemical form after natural iron supply into the Sea of Okhotsk. Moreover, we do not have enough knowledge regarding the bioavailable iron species in natural seawater. There may be complex interactions between the organic fraction and soluble, colloid and particle iron. We need to investigate these interactions for a better

understanding of how phytoplankton acquire iron species in seawater. At last, the Sea of Okhotsk may have very important role for iron supply to the western subarctic Pacific. There are several reports indicate water export from the Sea of Okhotsk into the western subarctic Pacific through Kuril islands (Yasuda, 1997; Wong et al., 1998). Therefore, it can be considered that seawater, which contains iron in high concentration, export into the subarctic Pacific from the Sea of Okhotsk, and have influence on biological response in the western subarctic Pacific, especially in Oyashio region.

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