— GROUP 2 REPORT —

IRON TRANSPORT PROCESSES AND THEIR IMPACTS ON PRIMARY PRODUCTIVITY IN THE SEA OF OKHOTSK

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1. INTRODUCTION

Iron is one of the most indispensable elements for primary productivity by marine phytoplankton. However, the source and transport process of the iron have been controversial during last two decades because iron can be hardly dissolved in seawater and it seemed very difficult to transport iron from coastal to open ocean area via ocean interior. After Duce and Tindale [1991] declared that huge amounts of iron are transported into open ocean area as atmospheric aerosol, many scientists have been tackling subjects to find the direct evidences which link the atmospheric iron transport and the phytoplankton bloom in the ocean. However, very few studies have succeeded to get their direct connection. On the other hand, many oceanographers have begun to notice the possibility that iron is transported from coastal region to open ocean through the intermediate water layer [Johnson et al., 1997; 1999; 2005; Wells et al., 1999; Bruland et al., 2005; Lam et al., 2006; Braucher and Moore, 2008] because the intermediate layer always contains much higher amounts of dissolved and particulate iron than surface layer. The huge amounts of intermediate water iron had been found in the Okhotsk Sea Intermediate Water (OSIW), too [Nishioka et al., 2007], and it could be explained by the combination of physical [Gladyshev et al., 2000; Itoh et al., 2003] and chemical [Nakatsuka et al., 2002; 2004a] oceanographic processes peculiar to the Sea of Okhotsk.

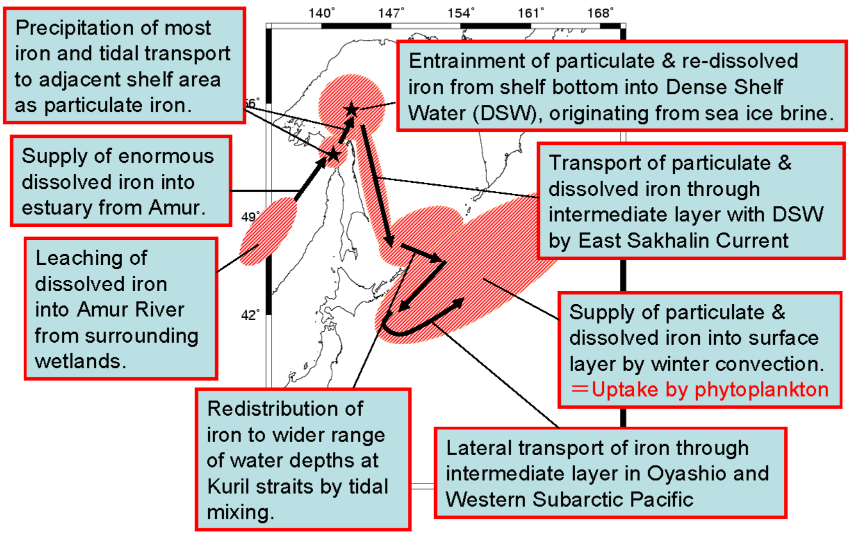

Figure 1. Framework of "Intermediate Water Iron" Hypothesis. Amur River watershed sustains primary productivity in Western Subarctic Pacific.

The "intermediate water iron hypothesis", which was the main target of marine biogeochemical studies (Group 2) in the Amur-Okhotsk Project, consists of many iron transport processes connecting the wetland area in Amur River middle reach to the primary productivity in the Sea of Okhotsk and the Oyashio region (Fig.1). From the vast wetland area, huge amounts of dissolved iron are discharged into Amur River main stream and flow into the Amur River mouth every year. Most of the dissolved iron must precipitate by flocculation in the estuary and only small fraction of original dissolved iron in river water is expected to spread over the surface water layer in the Sea of Okhotsk. However, certain parts of the precipitated iron can be resuspended together with sedimentary particles and entrained into the benthic water layer on the continental shelf of the northwestern Sea of Okhotsk due to the strong tidal current there. The benthic water layer consists of Dense Shelf Water (DSW) produced by seasonal sea ice formation in winter and it eventually flows out into the intermediate layer of deep basin due to its high density. Because the less biological activity in the intermediate water layer lets certain amounts of the resuspended fine iron particles escape from biological uptake or absorption onto the large biological particles, significant amounts of iron particles can reach to the southern Sea of Okhotsk by the strong southward flow of the East Sakhalin current. Although the intermediate water iron itself cannot be utilized by phytoplankton living in surface layer, the strong tidal mixing brings the iron into the near surface layer when the intermediate water mass crosses the Bussol strait, the deepest passage in the Kuril archipelago connecting the Sea of Okhotsk and Pacific Ocean. Iron at the subsurface can be easily entrained into the surface layer by winter convective mixing and finally utilized by phytoplankton at the Oyashio region along Kuril and Hokkaido islands.

In order to clarify this "Intermediate Water Iron Hypothesis", we have conducted two long research cruises, in the Sea of Okhotsk during summer of 2006 and 2007 (Fig.2), which were the Joint Japanese-Russian Research Expeditions using R/V Professor Khromov belonging to Far Earstern Regional Hydrometeorological Research Institute, Vladivostok, Russia. During these cruises, the iron distribution in the water column and sediment could be investigated first at the western Sea of Okhotsk and Bussol straits (Fig.2). There were several big subjects and questions which should be solved in these cruises as follows.

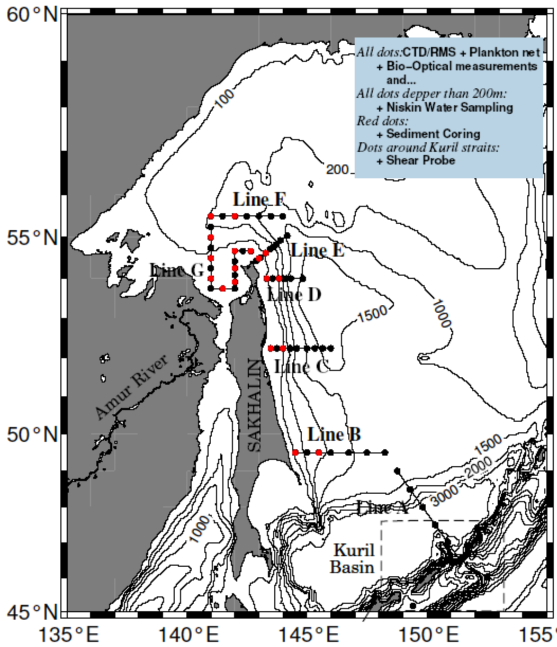

Figure 2. Research Areas in Aug-Sep 2006 & 2007

(1) To clarify the distribution of iron in the Sea of Okhotsk

*Does the "intermediate water iron" actually come from the northwestern continental shelf (Amur River)?

(2) To estimate the budget of iron on the continental shelf
*How much % of Amur River iron flows out into the open ocean?
*How long does the iron stay on the shelves?

(3) To understand factors controlling primary production in the Sea of Okhotsk
*Is the iron sufficient for phytoplankton productivity in the Sea of Okhotsk?

(4) To investigate processes relating iron transport and productivity
*Where does the riverine "surface iron" go?
*How much "aerosol iron" is coming onto the Sea of Okhotsk?
*How much % of the "intermediate water iron" is upwelling at the Bussol strait?
*How are the biological and chemical environments in the intermediate water in the Sea of Okhotsk (zooplankton~dissoloved organic matter)?

(5) To reconstruct past environments in the Sea of Okhotsk
*How long has the Amur River influenced the productivity in the Sea of Okhotsk?

In this paper, we review the research results focusing on the first and third subjects mainly. Of course, for example, the second subject is very important for the whole framework of the "Intermediate Water Iron Hypothesis", because the "residence time of iron on the continental shelf" revealed by the second subject directly determines the degree of linkage between the inland wetland and the open ocean primary production. If the residence time is in the order of thousand years, human-caused land use change in the Amur River middle reach cannot influence the primary productivity in the Oyashio region at once. However, after the research cruise in 2006, the residence time of iron on the continental shelf around Amur River mouth was found to be as short as months. Actually, the accumulation rate of sedimentary iron on the continental shelf near Amur River mouth is almost zero and/or much smaller than that on the continental slope, demonstrating that most of the precipitated iron cannot stay on the continental shelf but flows out into the deep basin immediately with DSW due to the very strong tidal currents on the shelf (Minami H. and Kato Y.; Personal communications).

2. DISTRIBUTION OF IRON IN THE SEA OF OKHOTSK

In summer of 2006 and 2007, we carried out the direct observation of iron in the western Sea of Okhotsk, including north-western continental shelf area, and the Bussol strait (Fig. 2). During the cruises, vertical profiles of Fe concentration and hydrographic data were collected using a clean CTD-CMS system modified with trace metal clean technique. Before chemical analyses, the collected water samples were filtrated using the 0.22 μm pore size of filters (Millipac 100, Millipore Co. Ltd) to separate "total" and "dissolved" forms of iron. The total and dissolved iron concentrations were analyzed by FIA chemiluminescence detection system after dilute acid treatments, respectively [Obata et al., 1993]. All samples were treated in a laminar flow clean-air hood at a clean-air laboratory. Nutrients and chlorophyll *a* concentrations were also analyzed in the water samples collected from the same sampling stations.

2-1. Fe in the DSW and the OSIW

Nakatsuka et al. [2002] reported that the DSW consistently contains large amounts of re-suspended sedimentary particles, due to strong tidal mixing on the shelf, and it was also found that the outflow of DSW results in a large flux of particulates and dissolved materials from the shelf to the OSIW [Nakatsuka et al., 2004a]. In 2006 summer, we conducted direct observation in the north-western continental shelf area of the Sea of Okhotsk, and actually detected extremely high total Fe concentration (> 150 nM) with high turbidity in original seawater of the DSW (Fig. 3). Combining of the previous reports and our new iron data, we can conclude that the large amounts of dissolved and particulate Fe in the DSW were introduced by the re-suspension of the sediments from the north-western continental shelf region. Yoshikawa et al., [2006] reported that the OSIW has extremely low N* value (($[NO_3^-]-16*[PO_4^{3-}]+2.9)*0.87$) due to the denitrification (or exudation of phosphate) process occurring in the anoxic sediment on the north-western shelf

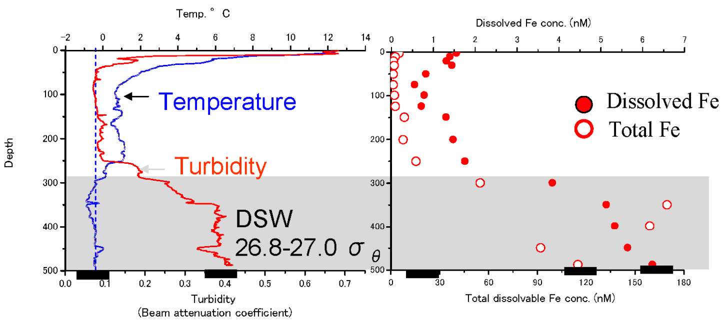

Figure 3. Vertical profiles of Temperature, Turbidity, Dissolved and Total Iron concentrations at the northwestern shelf region in the Sea of Okhotsk (Offshore station on Line E in Figure 2). Density range 26.8-27.4 is indicated in gray colour.

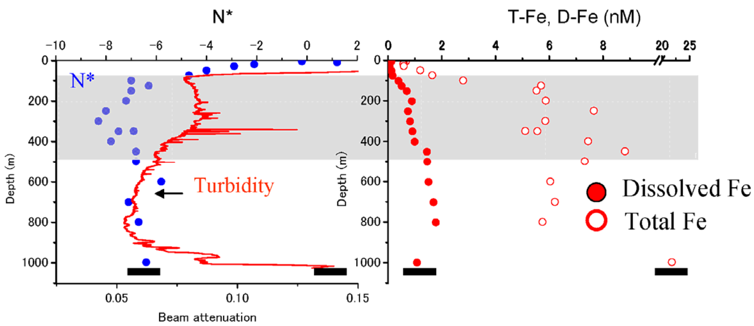

Figure 4. Vertical profiles of N*, Turbidity, Dissolved and Total Iron concentrations at the in the southern part of the Sea of Okhotsk (Offshore station on Line B in Figure 2). Density range 26.8-27.4 is indicated in gray colour.

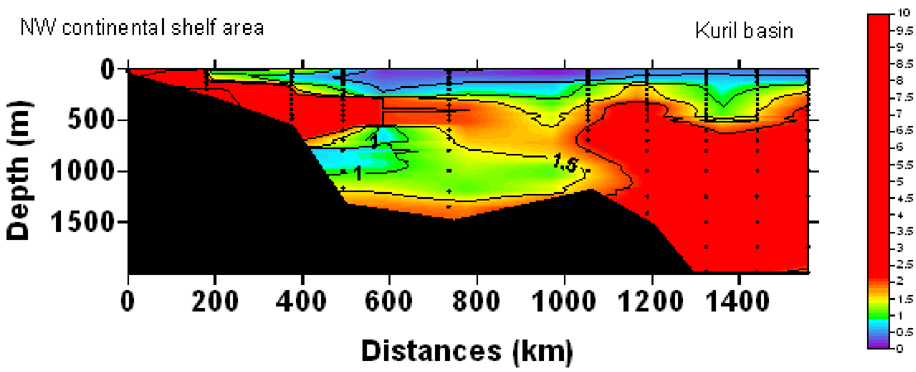

Figure 5. Vertical Section of Dissolved Iron Concentrations along East Sakhalin Current in the Sea of Okhotsk (from north-western continental shelf to the Kuril basin). Nishioka unpublished data.

area, and the N* can be utilized as a conservative tracer of the DSW. The iron-rich intermediate water masses clearly have low N* values in the southern part of the Sea of Okhotsk (Fig. 4), and that the low N* and high Fe intermediate waters were also found in the water column of the Oyashio region [Nishioka et al., 2007]. The Vertical section of dissolved Fe concentrations in the Sea of Okhotsk (Fig. 5) clearly reveals that substantial amounts of iron are transported by the southward East Sakhalin Current through OSIW from north-western continental shelf to southern part of the Sea of Okhotsk.

2-2. Tidal mixing at the Kuril strait

The total and dissolved iron concentrations were also determined around the Bussol strait, the main passage connecting Pacific Ocean and the Sea of Okhotsk. Vertical profiles of the iron, temperature, salinity and nitrate are shown in Fig. 6. The relatively homogeneous vertical profiles of temperature and salinity demonstrated that water columns at Bussol straits were well mixed from surface to the intermediate layer (~ 600 m). Dissolved iron concentrations in the surface layer at the Bussiol strait are obviously higher than that found in the surface water in the Western Subarctic Pacific (WSP) and the Oyashio region (~ 0.6 nM) [Nishioka et al., 2007]. The strong vertical mixing occurring around the Kuril straits, including Bussol strait, is caused by tidal flows through the straits and influences the temperature and salinity properties of the OSIW everywhere along the Kuril archipelago [Tally et al., 1991; Wong et al., 1998; Yamamoto et al., 2002]. Therefore, the vertical profiles of iron at Bussol strait clearly indicates that iron in the OSIW can influence the primary productivity at the surface layer around the Kuril straits directly. The mixing process at Kruil straits raises the concentrations of surface and sub-surface iron concentrations together with those of macro-nutrients, which must result in the high primary productivity in the Oyashio region adjacent to the Kuril archipelago.

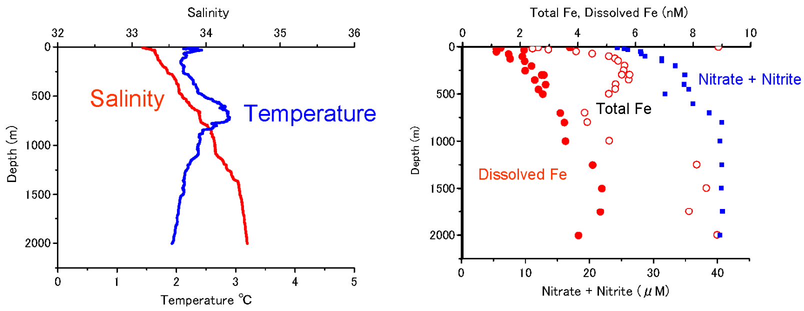

Figure 6. Vertical profiles of Temperature, Salinity, Nitrate+Nitrite, Dissolved and Total Iron concentrations at the Bussol Strait.

2-3. Quantitative evaluation of Fe transport system

Here, we try to evaluate the lateral Fe transport system in the Sea of Okhotsk more quantitatively (Fig. 7). For this purpose, we combined following three items. 1) Iron concentrations obtained at the 2006 and 2007 research cruises in the Sea of Okhotsk, 2) Reported water volume of the DSW [Ito et al., 2004], 3) Reported current velocity of East Sakhalin Current [Ohshima et al., 2002]. The details of the calculation are described in elsewhere [Nishioka et al. in preparation]. This estimation clearly indicates that the iron transport is much efficient through the intermediate water layer than that on the surface layer, and the iron transported by intermediate water can reach more remote area than that by the surface layer.

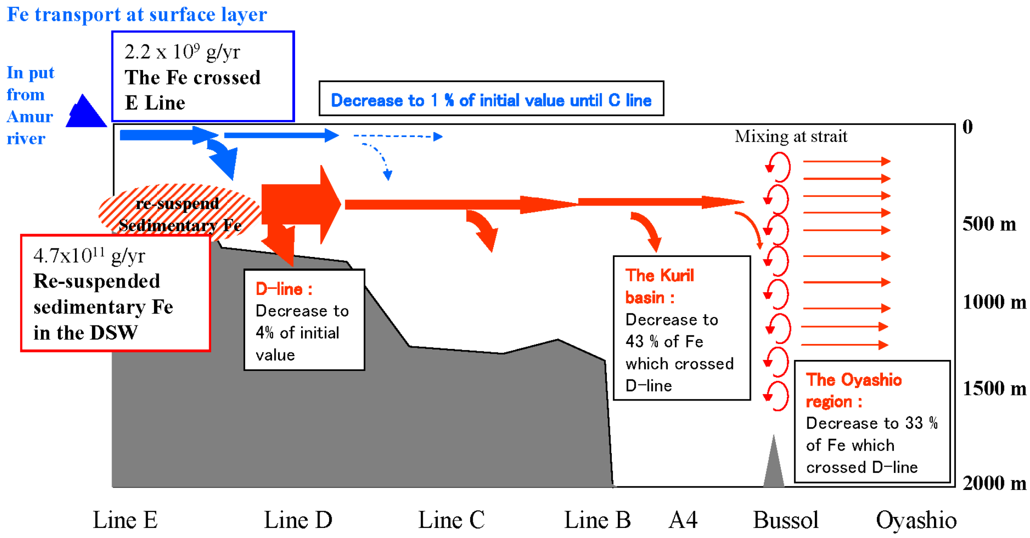

Figure 7. Quantitative Evaluation of Iron Transport System in the Sea of Okhotsk

3. PRIMARY PRODUCTIVITY IN THE SEA OF OKHOTSK

Sorokin and Sorokin [1999; 2002] reported that high abundance and productivity of phytoplankton are observed in the Sea of Okhotsk from spring to early summer. Although the shallowing of pycnocline in spring obviously provide the phytoplankton of suitable conditions for spring bloom, "supply and demand" of major and minor nutrients for in-situ phytoplankton have not been clarified yet in the Sea of Okhotsk. In fact, the Sea of Okhotsk is not the HNLC (High Nutrient Low Chlorophyll) region [Nakatsuka et al., 2004b], suggesting that supply of major nutrients such as nitrate are limiting the phytoplankton growth in summer, while the WSP is a typical HNLC region and abundant in nitrate at surface layer. In contrast to major nutrients, large amounts of minor nutrients, such as iron, must be supplied to the Sea of Okhotsk from Amur River. Although the only small part of Amur River iron spreads on the surface water to reach northeast coast of Sakhalin Island at the most, major part of Amur River iron can be transported through intermediate water layer and entrained into the surface layer again around Kuril straits.

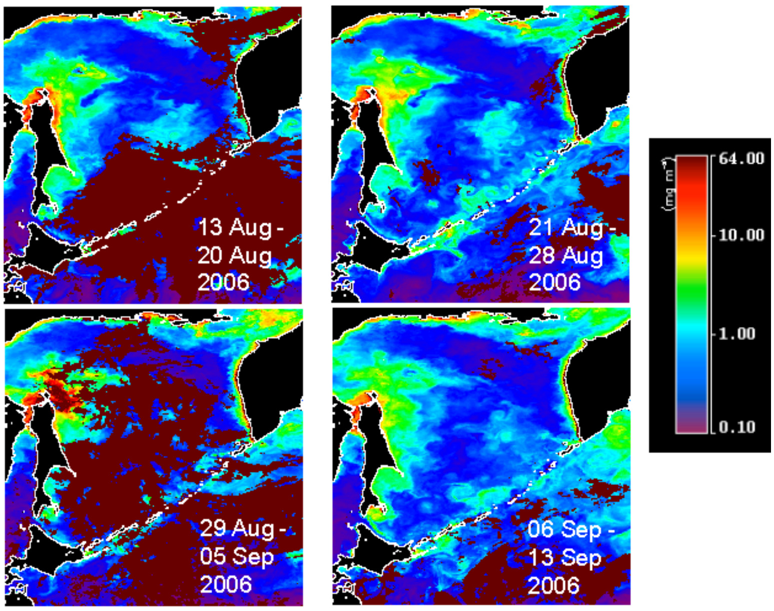

Figure 8. Eight-Day Composites of Surface Chlorophyll a (mg/m^3) by MODIS/Aqua from 13 Aug. to 13 Sep. in 2006

Therefore, there were two questions to be solved on the primary productivity of the

Sea of Okhotsk during the research cruises in 2006 and 2007. 1) Is the high productivity around the northern Sakhalin Island directly supported by Amur River iron? 2) Is the intermediate water iron re-entrained into the surface water around Kuril straits sufficient for the phytoplankton growth there?

As for the first question, the abundance of phytoplankton seems very high around the northern Sakhalin Island during the research cruise as illustrated by satellite remote sensing images (Fig. 8). The ^{13}C incubation experiment of surface waters during the cruise also demonstrated that the primary production around the northern Sakhalin Island was very high even in late summer, which was comparable to Sorokin and Sorokin [2002] observed in early summer (Fig.9). The zone of high primary productivity is obviously overlapped to the area directly affected by the discharge from the Amur River water.

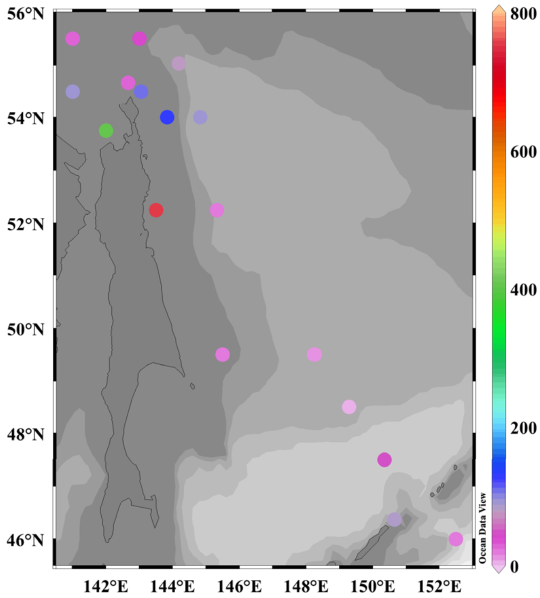

Figure 9. Surface Primary Productivity ($mgC/m^3/d$) meaured by ^{13}C incubation.

This matching between the high productivity zone and Amur River discharge can be explained by a biochemical index of phytoplankton, "Ferredoxin (Fdx) index". For the iron-deficient algal cells, the iron-containing photosynthetic protein "ferredoxin (Fdx)" is replaced by the non-iron-containing "flavodoxin (Flv)" at the acceptor side of their photosystem I. Therefore, the ratio of Fdx to the sum of Fdx and Flv in the sample water, that is Fdx index, indicates the availability of iron for the phytoplankton living there. During the 2006 cruise, Diatom-specific Fdx and Flv abundances were estimated with SDS-PAGE and western blotting method [Suzuki et al., 2009] to calculate the Fdx index in Fig.10. Around the northern Skhalin Island, the sites of high primary productivity are corresponding to the sites of high Fdx index and high dissolved iron concentrations directly connected to the Amur River mouth (Fig.10). These

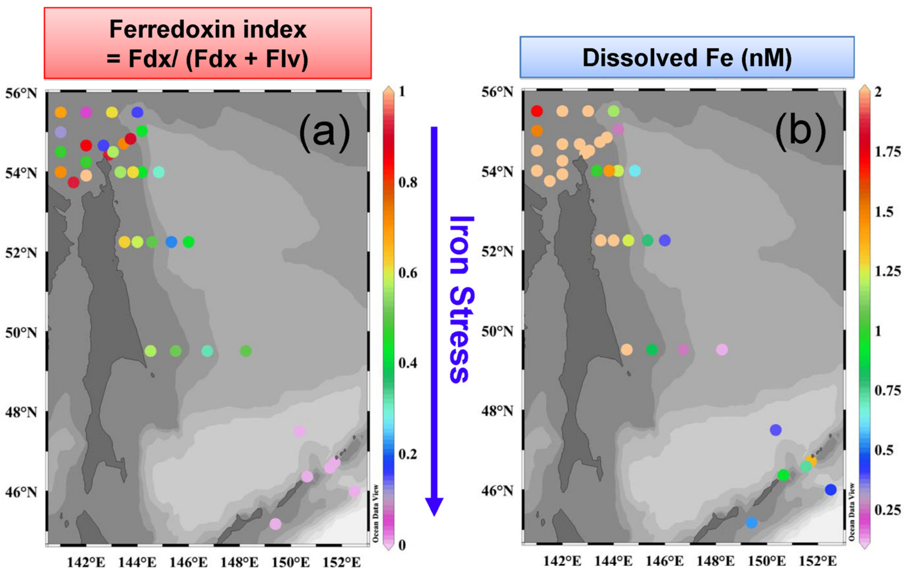

Figure 10. Ferredoxin(Fdx)/Flavodoxin(Flv) assays for micro-sized diatoms (20-200 µm in size) (a) and Dissolved Iron Concentrations (b) at surface waters

horizontal patterns clearly indicate that the high primary productivity around the northern Sakhalin Island is directly supported by material discharges from Amur River.

On the contrary, the Fdx indices are much lower around the Bussol strait than those at the western and central areas of Sea of Okhotsk during the cruise, although the dissolved iron concentrations were substantially higher at the surface layers around Bussol strait than those in the central Sea of Okhotsk (Fig.10). This suggests that phytoplankton around the Bussol straits required much more iron for their growth probably due to the light limited condition for phytoplankton growth there. In fact, the heavy cloud covers during the cruise period and the strong tidal mixing at the strait [Nakamura and Awaji, 2004] must reduce the light availability there, requiring the construction of much more photosynthetic pigment-protein complexes, resulting in the iron-stress in the diatoms there. This finding clearly suggests that changes in iron flux through the OSIW directly influence the primary productivity around the Kuril archipelago, including the Bussol strait, and finally in the Oyashio region.

4. CONCLUSION

During the research cruises in 2006 and 2007, we could verify the framework of “Intermediate Water Iron Hypothesis”. The extraordinarily high iron concentration in the intermediate water previously found in the Oyashio region [Nishioka et al., 2007] was proven to be connected to Amur River mouth by the sea-ice driven transports of particulate and dissolved iron through OSIW and DSW in the Sea of Okhotsk. The intermediate water iron is not only utilized by phytoplankton around the Kuril straits via tidal mixing but also distributed much further into the wide area of Western Subarctic Pacific (WSP), including the Oyashio region, supporting the primary productivity there [Nishioka et al., submitted]. Therefore, in addition to the traditional view of dust input, the iron transported by intermediate water circulation should be considered as an important source of iron for phytoplankton blooms in the Oyashio region and the Oyashio-Kuroshio transition zone. The lateral transport of iron from the marginal sea, such as the Sea of Okhotsk, is the key process to understand the biogeochemical responses in the WSP.

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