

HOW CAN THE IRON FROM AMUR RIVER SUPPORT THE PRIMARY PRODUCTIVITY IN NORTH PACIFIC OCEAN ?

-“INTERMEDIATE-WATER IRON HYPOTHESIS” AND ITS EVIDENCES FROM THE RESEARCH CRUISE IN 2006-

NAKATSUKA TAKESHI AND ALL MEMBERS OF RESEARCH GROUPS 1 AND 2

Institute of Low Temperature Science, Hokkaido University and Others

INTRODUCTION

Before 20 years ago, most of oceanographers thought that marine ecosystem in open oceans are not influenced by short-term variability in land surface conditions, especially not affected by environment changes at inland areas. About 10 years ago, many oceanographers began to believe that ecosystem in open ocean is connected with environment of inland areas, because they have found that growth of phytoplankton at open ocean is often regulated by limitation of dissolved iron and long-distance transport of aerosols from arid continental regions to open ocean may supply significant amounts of iron into open ocean surface. After the proposal of this "Airborne Iron Hypothesis", many studies have been carried out to clarify the direct relationship between atmospheric iron inputs and primary productions in the open ocean. However, the connection between them is still unclear because we do not have sufficient information on the solubility of aerosol iron and we have seldom observed the sequential evidences of aerosol supply and phytoplankton bloom in the open ocean.

Another important background of "Airborne Iron Hypothesis" is the fact that iron can be hardly dissolved in the seawater. This intrinsic nature of iron inevitably suggests that riverine iron cannot reach the open ocean, because it must precipitate on bottom sediments near the river mouth. Therefore, most of oceanographers have been assuming that atmospheric transport is the only one way supplying iron into the surface water of open ocean. Here, we propose a new hypothesis, which connect the land surface conditions of inland areas and the primary production in open oceans by the iron transport through river and ocean flows. That is "Intermediate-Water Iron Hypothesis". Briefly to say, most of the riverine iron actually precipitates on the continental shelf and slope sediments, but parts of them are resuspended and transported to open ocean through intermediate layers and eventually supplied into the surface layer as dissolved forms of iron by upwelling and/or diffusion processes.

In this paper, first, we explain the details of this "Intermediate-Water Iron Hypothesis" based on previous our geochemical and oceanographic knowledge around the Sea of Okhotsk. Second, we show the direct evidences for this hypothesis obtained at Research Expedition of the Sea of Okhotsk during August-September 2006. Third, we discuss the implication of this hypothesis to the relationship between the human impacts on the land surface condition in Amur River basin and the biological productivity of the North Pacific Ocean.

"INTERMEDIATE-WATER IRON HYPOTHESIS" -(1) IT'S FINDING

Oyashio current is the subarctic western boundary current of Pacific Ocean, flowing southwestward just outside of the southeastern rim, Kuril archipelago, of the Sea of Okhotsk. Because of its nutrient-rich nature, Oyashio is the mother water mass for fishes growing in Pacific Ocean near Japan and brings huge benefits to Japanese fishery and Japanese people. This water mass is characterized by occurrence of large spring phytoplankton bloom (Saito et al., 2002), which is about ten times larger, on the basis of maximum amount of phytoplankton pigment (Chl-a), than that observed in eastern subarctic Pacific (Alaska bay) (Harrison et al., 1999). Because both of Oyashio region and Alaska bay are the High Nutrient and Low Chlorophyll (HNLC) regions where large amounts of nitrogenous and phosphorous nutrients remain unutilized in mid-summer surface water, the size of spring phytoplankton bloom at both regions are regulated by the amount of iron supplies into the surface layers just before spring. Therefore, this east-west contrast of the size of spring phytoplankton bloom in the subarctic Pacific inevitably suggest that there is much larger iron source in western region (Oyashio) than in eastern region (Alaska bay).

In fact, the "Airborne Iron Hypothesis" may explain the large iron supply to Oyashio region because the Oyashio current is located near Northeast Asia where large amounts of aerosol are originating and transported eastward by strong westerly wind. However, there are some mismatches between the Asian aerosols and the phytoplankton blooms. Although the strength of Asian dust event varies large interannually, the phytoplankton bloom occurs regularly every spring in Oyashio region. While the Asian dust event occurs mostly in spring, the dissolved iron in Oyashio surface water reaches its highest concentration in winter (Nishioka, unpublished data).

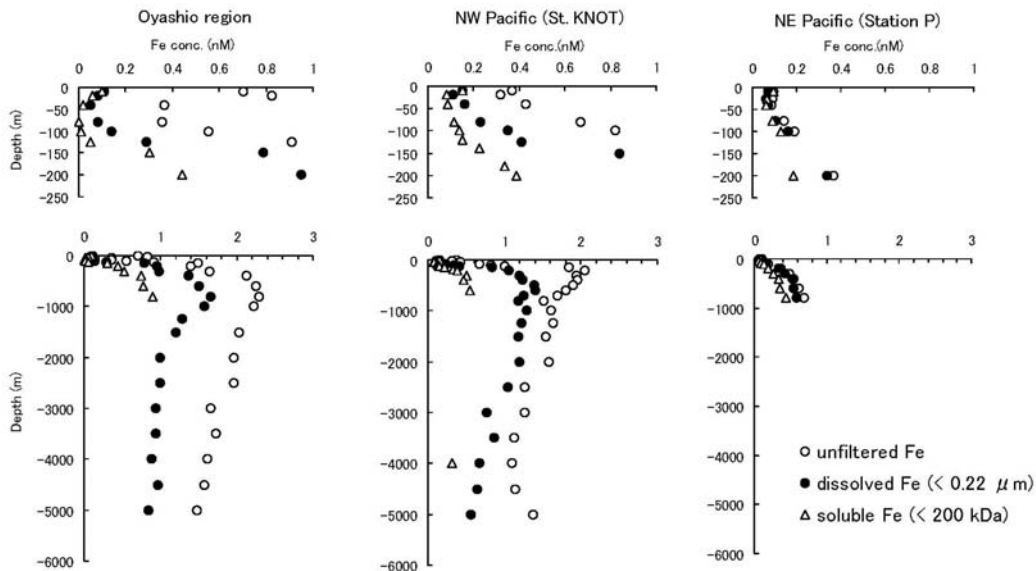


Figure 1. Comparison of vertical profiles of iron between western and eastern subarctic Pacific

Nishioka et al. (2003) found another big source of iron at the intermediate water layer in Oyashio region. Figure 1 shows the vertical distributions of "dissolved" and "unfiltered (total acid-dissolvable)" iron at Oyashio region together with those at western and eastern

subarctic Pacific Ocean. Obviously, the water columns in Oyashio region and western subarctic Pacific have predominant peaks of dissolved and particulate iron at intermediate depths just below surface water, although there is not such a feature in eastern subarctic Pacific. This iron-rich subsurface water mass can be entrained into surface layer during winter convective mixing and may support the primary productivity there. Nishioka et al. (2007) actually calculated that the upward flux of dissolved iron from the intermediate layer can support the spring phytoplankton bloom in Oyashio region.

What is source of the iron in the intermediate water of Oyashio and western subarctic Pacific ? Nishioka et al.(2007) suggested that the iron in the intermediate layer comes from the Sea of Okhotsk based on the comparison of iron concentrations along the isopycnal surfaces between the Sea of Okhotsk and Pacific Ocean (Figure 2). At all of three regions (Southern basin of the Sea of Okhotsk, Oyashio and western subarctic Pacific), there are large increases in iron concentration at common density layers corresponding to the intermediate depths. In the case of total acid-dissolvable iron (Figure 2-a), the concentration at intermediate layer is much higher in the Sea of Okhotsk than in Pacific side. Because the southern basin of Sea of Okhotsk and Pacific Ocean is connected by deep straits among Kuril archipelago, this characteristic feature in the iron distribution clearly indicates that the iron in the intermediate layer comes from the Sea of Okhotsk to the Pacific Ocean. In contrast to the "total acid-dissolvable iron", the "dissolved iron" shows almost equivalent increases at the intermediate layers among the three regions (Figure 2-b). This difference of horizontal gradients between total and dissolved iron concentrations suggests that the main form of iron in the intermediate water of Sea of Okhotsk is particle, but it may be continuously dissolved through the dissolution equilibrium which makes the dissolved iron concentration constant during the course of transport of intermediate water mass from the Sea of Okhotsk to the Pacific Ocean.

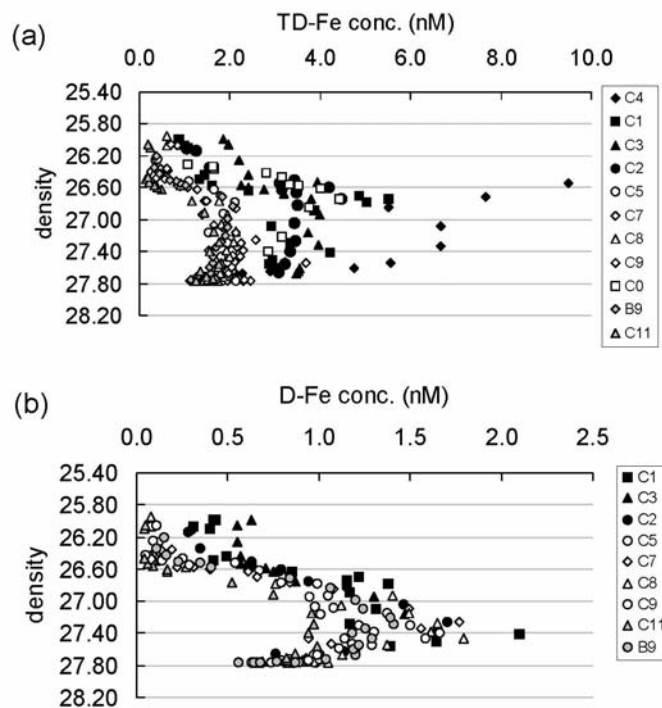


Figure 2. Iron distributions along isopycnal surfaces (Solid:Okhotsk; Open:Oyashio; Gray Western subarctic)

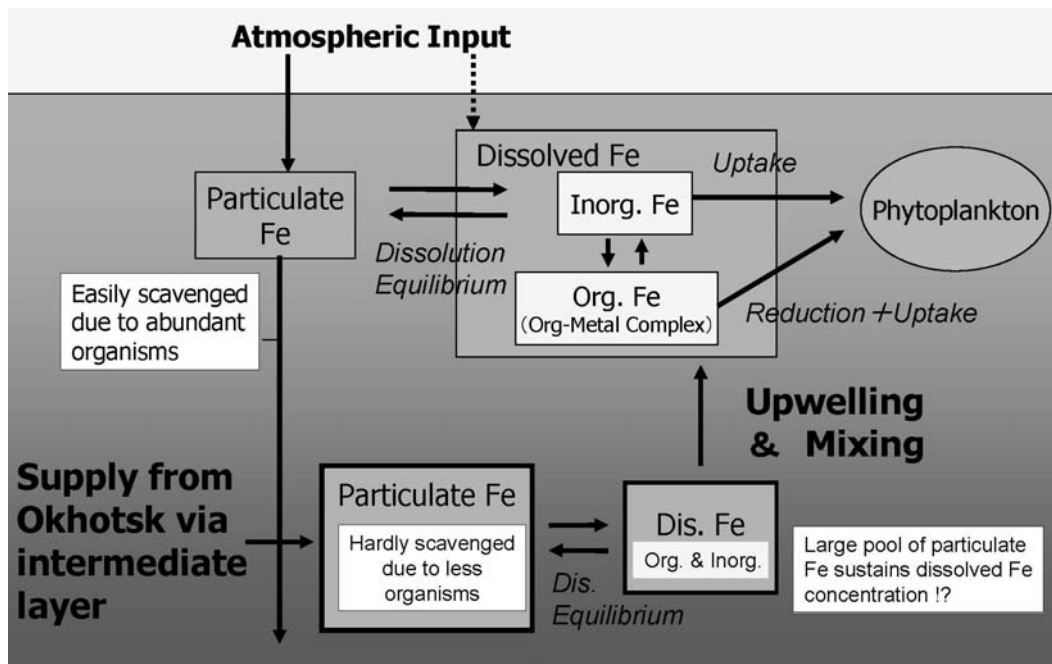


Figure 3. Possible iron sources in Oyashio & western subarctic Pacific regions

Figure 3 shows the possible schema of iron dynamics in the Oyashio region. In fact, large amount of iron must be supplied onto surface water from atmosphere as aerosol particles intermittently. However, it may be scavenged downward very rapidly because a lot of planktonic organisms in the surface water uptake and/or adsorb the aerosol particles and settle down as large sinking particles. In contrast, the particles containing iron in the intermediate layer of the Sea of Okhotsk must be very fine and cannot be scavenged easily because there are scarce numbers of organisms in the intermediate water. During the course of intermediate water transport, the particulate iron is dissolved partly according to the dissolution equilibrium and finally entrained into surface water by winter convective mixing and/or upwelling of water. Of course, iron can be hardly dissolved in the seawater. In order to make the concentration of dissolved iron in the intermediate layer as high as seen in Figure 2-b, there must be some organic ligands, which increase the solubility of iron in this water mass. Previous study on the iron solubility in the Sea of Okhotsk reported that there are plenty of autochthonous organic ligands of iron (Tani et al., 2003).

"INTERMEDIATE-WATER IRON HYPOTHESIS" -(2) IT'S MECHANISMS

If the intermediate water of the Sea of Okhotsk contains large amounts of fine iron particles that can be dissolved easily, what is the source of this particulate iron? Our previous studies can suggest the potential mechanisms to bring huge amounts of fine iron particles to the intermediate layer of the Sea of Okhotsk.

Nakatsuka et al. (2002) found extremely turbid (particle-rich) intermediate water masses in the depth ranges of 200-500m around northeast slope of Sakhalin Island. These water masses also had another predominant feature that is very cold. The Sea of Okhotsk is characterized as the lowest latitudinal area of seasonal sea-ice cover in the world, and main

part of sea ice is created along the continental shelf on the northwest of Sakhalin Island. Because sea ice consists of pure water crystals, extremely saline water, so-called brine water, is rejected during the formation process of sea ice. The brine water has higher density than surrounding waters. Therefore it settles down onto the bottom of continental shelf and eventually flows out into the intermediate layer of offshore basin. That is the cause of very cold temperature of the intermediate water masses there.

The continental shelf on the northwest of Sakhalin has another physical oceanographic characteristic. That is the existence of very large tidal current (Kowalik and Polyakov, 1998). After precipitation of the brine water on the bottom of northwestern continental shelf of the Sea of Okhotsk, the dense shelf water (DSW) is created by continuous tidal mixing of brine water and surrounding bottom waters. During the DSW formation, bottom sediment particles are resuspended and entrained into the DSW and finally involved in the formation of extremely turbid intermediate water masses. Nakatsuka et al. (2002) called the mechanisms which create extremely turbid intermediate water as "Tidal and Brine Pump". In this area, the collaboration between tidal current and sea ice formation on the continental shelf brings large amounts of sedimentary particles into the intermediate layer in offshore region.

Amur River mouth is located at the very adjacent place to the source area of this extremely turbid and cold intermediate water mass. Huge amounts of dissolved iron, about 1.5×10^{11} gFe/yr ($0.5 \text{ mgFe/L} \times 300 \text{ km}^3/\text{yr}$), are transported into the Amur River mouth. Almost all of them must precipitate around the river mouth by flocculation due to the contact with sea water. However, the particulate iron may not stay there, because strong tidal current prevents any fine particles from settling down there. Most of newly produced fine iron particles must be discharged onto the continental shelf on the north of Amur River mouth and join the formation of the DSW. This is the potential cause of the existence of abundant fine iron particles that may be easily dissolved again in the intermediate layer of the Sea of Okhotsk.

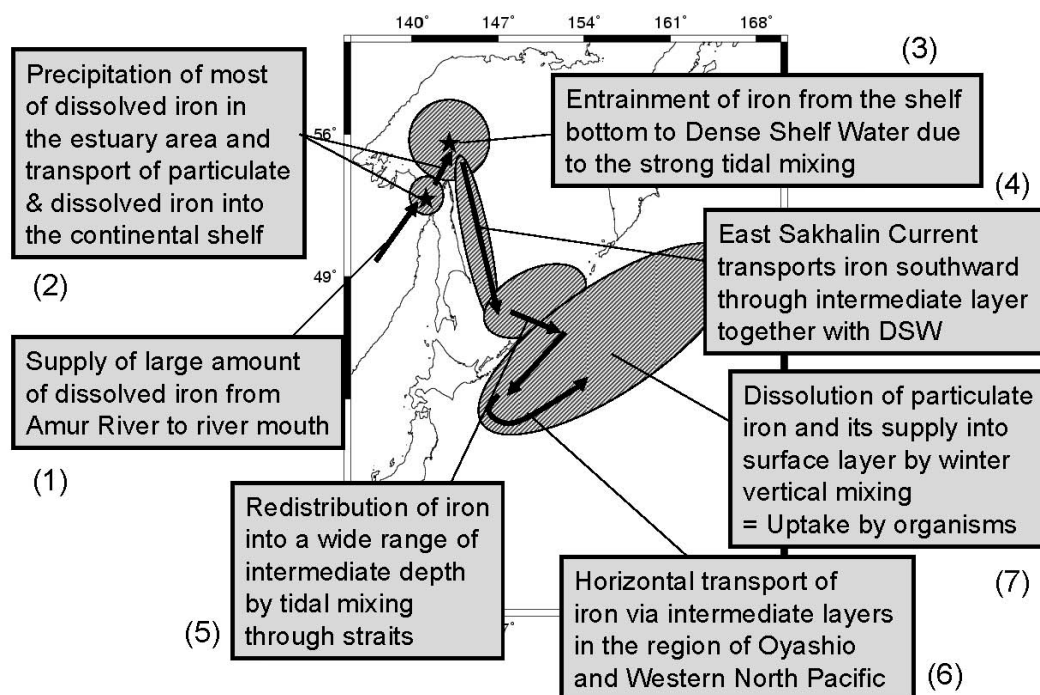


Figure 4. Iron transport from Amur River to Western Subarctic Pacific (Intermediate-Water Iron Hypothesis)

Figure 4 shows a schematic illustration of the potential processes which bring iron from the Amur River to Oyashio surface water. It contains some additional physical oceanographic features in the Sea of Okhotsk. (1) Amur River brings huge amount of dissolved iron to its river mouth, (2) Most of the dissolved iron precipitate around river mouth, but the iron particles are eventually discharged into continental shelf region due to strong tidal current there, (3) Dense shelf water entrains fine iron particles and penetrates into the intermediate layer of offshore basin, (4) East Sakhalin Current, the southward-flowing western boundary current, transports the iron-rich intermediate water mass rapidly to the southern Sea of Okhotsk, (5) The iron-rich particles are redistributed into the wider depth range due to strong tidal vertical mixing during passage through a narrow deep strait in Kuril archipelago, (6) The water currents distribute the iron-rich intermediate water masses into the wider horizontal area around western subarctic Pacific, (7) The particulate and re-dissolved iron are finally entrained into the surface water of Oyashio and western subarctic Pacific areas, and support the primary productivity there.

RESEARCH EXPEDITION IN THE SEA OF OKHOTSK DURING AUGUST-SEPTEMBER 2006

In order to prove this "Intermediate-Water Iron Hypothesis" and clarify the relating geochemical, biological and physical processes in the Sea of Okhotsk, we have conducted a research cruise in the Sea of Okhotsk in collaboration with a Russian institute (Far Eastern Regional Hydrometeorological Research Institute, Vladivostok, Russia). The research cruise was carried out from 13 August to 14 September using R/V Professor Khromov along the cruise track shown in Figure 5.

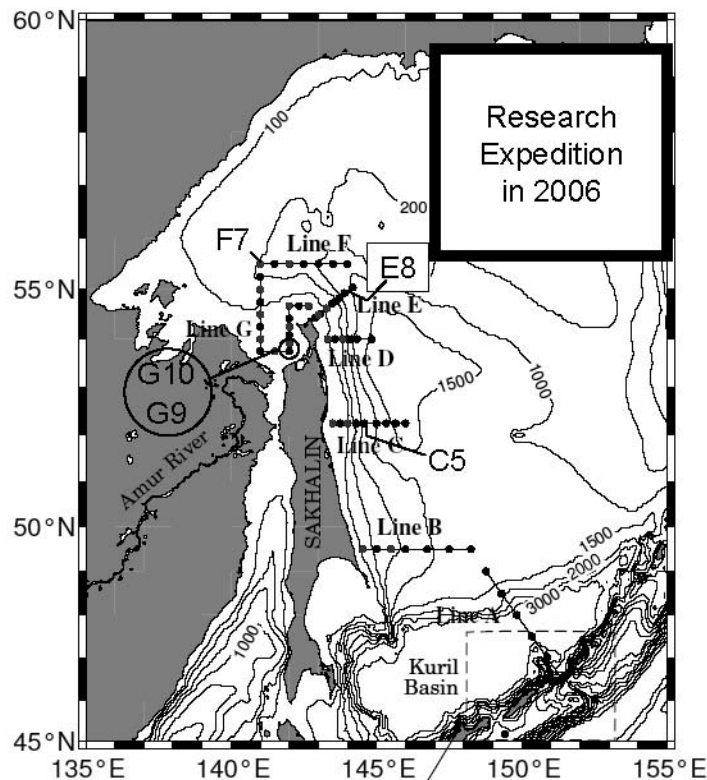


Figure 5. Cruise track of the Research Expedition in the Sea of Okhotsk in August-September 2006

Main purpose of this research expedition was to clarify following subjects.

- (1) Three-dimensional iron distribution in the Sea of Okhotsk and Pacific Ocean, including Amur River mouth area and intermediate layers off east coast of Sakhalin.
- (2) Budget of iron on the continental shelf around Amur River mouth, especially how much % of Amur River iron is discharged into offshore intermediate layers
- (3) Limitation factors of primary productivity in the Sea of Okhotsk, whether it is limited by iron or not.
- (4) Other important processes relating the iron transportation and its consequences such as “Riverine iron remaining in the surface water of the Sea of Okhotsk”, “Iron flux from atmosphere”, “Vertical dispersion of iron due to tidal mixing at Kuril strait”, “Ecological situations of Okhotsk Sea Intermediate Water” etc.

At all of the stations shown in Figure 5, CTD observations (vertical measurements of conductivity (salinity), temperature, depth, turbidity and dissolved oxygen using wired in-situ sensors) and water samplings were carried out. Water samples were distributed on board for many chemical and biological measurements, such as dissolved oxygen, salinity, nutrients, dissolved and total iron, carbonate systems, dissolved organic matter, chlorophyll-a, bacteria, primary productivity and so on, using ultra-clean water treatment techniques. At several sites on the continental shelf and slope, bottom sediment cores were collected using a kind of multiple corer for measurements of major metal concentrations and sedimentation rates as well as the chemical compositions of pore waters. Zooplankton samples were also collected from subsurface and intermediate water depths using plankton nets at many stations along the cruise track. Turbulence caused by tidal mixing was measured by free-falling “Shear Probe Sensor” at the area around Bussol strait and the northwestern continental shelf. On the cruise track, radiosonde observation of atmosphere, aerosol samplings and bio-optical measurements were continuously conducted every day.

Because only parts of the collected samples have been analyzed by the time of writing this paper (January 2007), we would like to show here the most important data, iron distributions in water on the continental shelf and slope where iron has never analyzed until now, as the evidences of “Intermediate-Water Hypothesis”. Those data were provided by Dr. Jun Nishioka and Professor Kenshi Kuma in Group 2 using “Iron Analyzer” equipped with iron concentration resin column for ultra-trace amount of iron measurements (Kimoto Electric Co., EN-701).

‘INTERMEDIATE-WATER IRON HYPOTHESIS’ - (3) IT’S EVIDENCES

Figure 6 shows vertical distributions of total (acid-dissolvable) and dissolved iron together with salinity and temperature at G-9 and G-10 in Sakhalin Bay (Figure 5). You can find enormous amounts of total iron in the bottom water, which is equivalent to several hundreds times higher concentration than in Oyashio intermediate water. Because these sites are very close to Amur River mouth, the surface layers were covered by fresh water from Amur River, which originally contains very large amount of dissolved iron (~10000nM-Fe). However, higher concentrations of total iron are not detected in the surface layer but observed

in the bottom layer. Concentrations of dissolved iron in surface layer were actually higher than those in bottom layer or offshore surface layer (Figure 7). But, they were much less than the particulate (acid-dissolvable) iron at G-9 and G-10. These facts inevitably suggest that most of riverine dissolved iron had precipitated by flocculation due to contact with sea water and settled down into the bottom layer of Sakhalin Bay, illustrating the proposed iron transport mechanisms (1) and (2) shown in Figure 4.

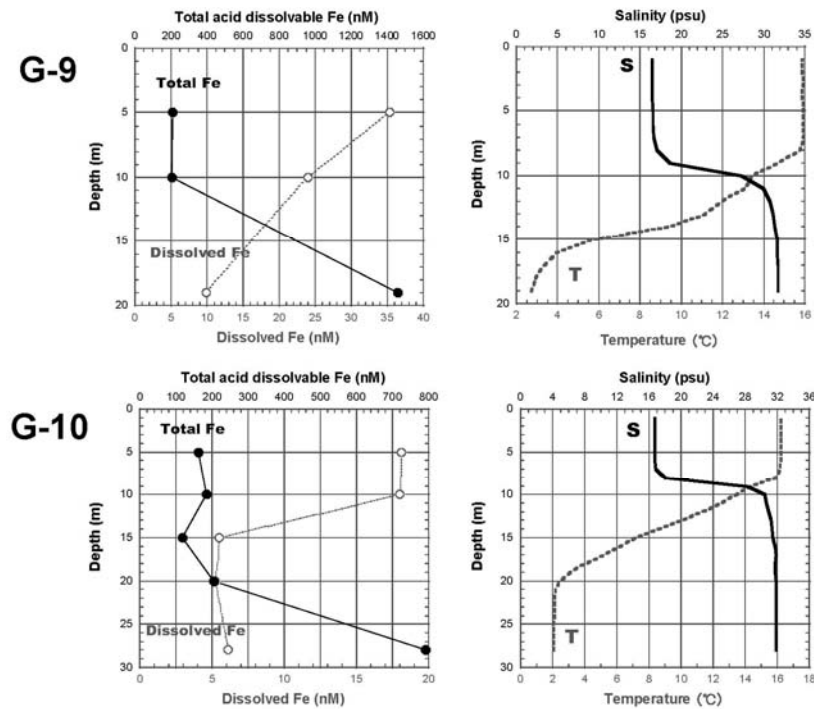


Figure 6. Vertical profiles of total and dissolved iron, salinity and temperature at G-9 & G-10 (Sakhalin Bay)

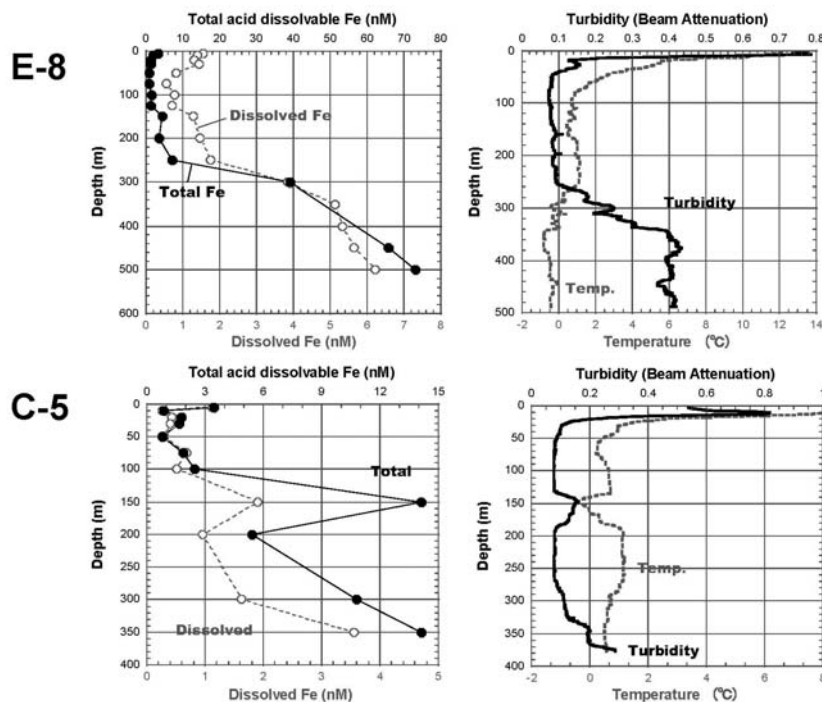


Figure 7. Vertical profiles of total and dissolved iron, turbidity and temperature at E-8 & C-5 (Continental Slope off northeast Sakhalin)

Figure 7 illustrates vertical profiles of total (acid-dissolvable) and dissolved iron concentrations together with those of water temperature and turbidity (beam-attenuation) at E-8 and C-5 on the continental slope near northeast Sakhalin (Figure 5). You can find very cold and turbid water masses in the intermediate water depths at both sites, indicating the outflows of Dense Shelf Water from the northwestern continental shelf region. Interestingly, both of total and dissolved iron show remarkable high concentrations at the corresponding layer, indicating that iron is actually transported into the offshore intermediate layer together with the DSW outflows. Total iron concentrations in these layers are equivalent to dozens times higher than those at Oyashio intermediate water and prove the proposed iron transport mechanisms (3) and (4) in Figure 4.

Both of Figure 6 and 7 are no more than snapshots of the iron transport mechanism from Amur River to Oyashio region, illustrated in Figure 4. In order to understand the role of Amur River for variations of ocean productivity in Oyashio region, it is necessary to clarify each step of the iron transport mechanisms more quantitatively. Especially, it is very important to estimate how much percentage of Amur River iron is transported into the offshore intermediate layer and how long it stays on the continental shelf. Those estimations critically affect the time lags between changes in land surface conditions and ocean productivity. If all the iron discharged from Amur River quickly penetrates into the offshore intermediate layer without significant residence time on the shelf, changes in Amur River can potentially affect the ocean productivity immediately. However, if the residence time of iron on the shelf is very long such as 1000 years, we cannot anticipate any influences in the near future on ocean productivity from human alterations of Amur River basin.

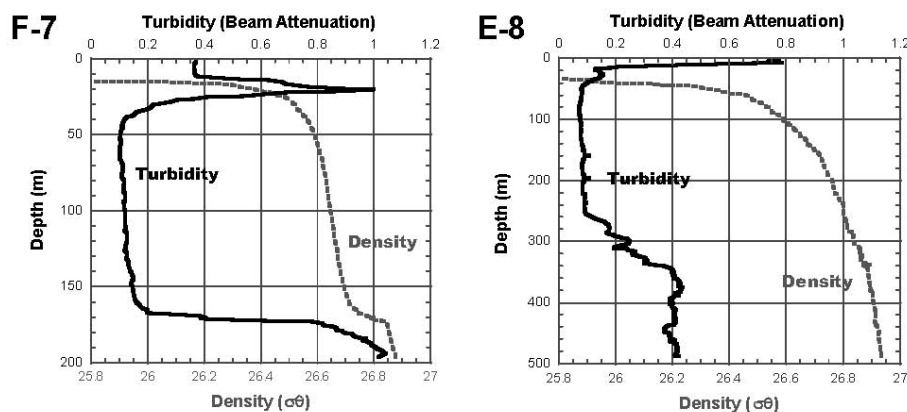


Figure 8. Vertical profiles of turbidity and water density at F-7 & E-8

Because we know approximate input of dissolved iron from Amur River (1.5×10^{11} gFe/yr), it is necessary to estimate outcomes of iron for the establishment of iron budget on the continental shelf near Amur River mouth. There are two potential outcomes from the shelf. One is sedimentation on the shelf bottom. The other is outflow with DSW. Unfortunately, at present, we have not finished the measurements of sedimentation rates. Therefore, we try to calculate the outflow of iron with DSW. In fact, there are not cold and dense water masses (DSW) at G-9 and G-10 sites (Figure 6), because their water depths are too shallow. On the other hand, at E-8, DSW had been already diluted by mixing with offshore intermediate water

(Figure 7). We can find the purely cold and dense, $\sigma\theta > 26.8$, water (DSW) at the bottom of F-7 on the continental shelf (Figure 8), where the iron concentration has not been analyzed yet. In order to calculate the outflow of iron into the offshore intermediate layer tentatively, we assume that turbidity and total iron concentrations are proportional between the DSW at F-7 and diluted DSW at E-8. Because the values of turbidity (beam attenuation) in the corresponding layers are 1.0 and 0.4 at F-7 and E-8, respectively (Figure 8), and the total iron concentration at the corresponding layer of E-8 is about 70 nM (Figure 7), we can estimate the total iron concentration of bottom water (DSW) at F-7 as 175 nM.

Multiplying this value, 175 nM, by the previously reported flow rate of DSW into offshore intermediate layer, $0.5 \times 10^6 \text{ m}^3/\text{s}$ (Gladyshev et al., 2000), we can calculate the approximate flow rate of total (acid-dissolvable) iron into the intermediate layer as $1.5 \times 10^{11} \text{ gFe}/\text{yr}$. Surprisingly, this estimate is very equal to the discharge rate of dissolved iron from Amur River. Of course, this is a very tentative rough estimate, but this coincidence suggests that almost all of the Amur River iron can enter into the offshore intermediate layer together with DSW outflow and the residence time of iron on the shelf is very short, possibly less than 1 year. The reason why Amur River iron does not deposit on the shelf must be attributable to the very strong tidal current there (Kowalik and Polyakov, 1998). These tentative explanations should be checked in details by further measurements of the iron sedimentation rates on the shelf and the spatial distributions of iron in the water columns, using the collected samples in 2006, within several months.

PERSPECTIVES OF THE “INTERMEDIATE-WATER IRON HYPOTHESIS”

At first, we must integrate all data which can be provided by analyses of all samples collected in 2006 together with many physical parameters as soon as possible, and check the “Intermediate-Water Iron Hypothesis” in details. But, there remains some question which cannot be answered by the analyses of samples obtained in 2006. It is the fate of particulate iron discharged into the intermediate layer of the Sea of Okhotsk. Part of them must settle down on the deep basin and part of them may be dissolved again with the help of organic ligands. Therefore, we must examine the iron budget in the intermediate water layer at the next chance of observation by collecting sediment cores of deep basin, sinking particles by sediment traps and large volume waters for electrochemical analyses and so on.

While there remain some unrevealed mechanisms in this “Intermediate-Water Iron Hypothesis”, it has many important implications for Amur-Okhotsk Project. Based on the previous and current observations of material transport system, including iron, in the Sea of Okhotsk, we can conclude that Amur River iron can be actually transported into North Pacific, and potentially support the primary productivity especially in Oyashio and western subarctic Pacific region. Because of the highly effective outflow of Amur River iron from the shelf to the offshore intermediate layer, this system may transfer impacts of the land use changes in Amur River basin to the biological productivity in North Pacific very rapidly.

On the other hand, what can the “Intermediate-Water Iron Hypothesis” suggest for global scale? Of course, this iron transport system is supported by combination of many

intrinsic natures of the Sea of Okhotsk and surrounding areas, such as iron-rich Amur River water, sea-ice formation on the continental shelf, strong tidal current near Amur River mouth, existence of southward-flowing western boundary current (East Sakhalin Current), deep and narrow straits among Kuril archipelago, vast HNLC region in subarctic Pacific and so on. Therefore, it may be difficult to find the same situation of land-ocean linkage elsewhere in the world. However, the finding of intermediate-water iron transport system suggests the potential importance of riverine iron for open ocean primary productivity. The vertical profile of iron is similar to major nutrients, such as nitrogen and phosphorous, and higher concentrations of iron are always detected in the intermediate layer than in surface layer. Parts of riverine iron deposited on the shelf and slope sediment can be re-suspended and/or re-dissolved there and parts of them are transported into open ocean areas more or less in the global scale. Because oceanographers have not clarified the direct relationship between atmospheric iron input and marine phytoplankton activity yet, it is worth reconsidering the iron budget of surface water in the world open ocean in combination with upward iron supply from the intermediate water depth.

REFERENCES

- Gladyshev, S., Martin, S., Riser, S. & Figurkin, A (2000): Dense water production on the northern Okhotsk shelves: comparison of ship-based spring-summer observations for 1996 and 1997 with satellite observations. *J. Geophys. Res.* **105**, 26,281-26,299.
- Harrison P.J., P. W. Boyd, D. E. Varela & S. Takeda (1999): Comparison of factors controlling phytoplankton productivity in the NE and NW subarctic Pacific gyres. *Progress in Oceanogr.* **43**, 205-234.
- Kowalik, K. & Polyakov, I. (1998): Tides in the Sea of Okhotsk. *J. Phys. Oceanogr.* **28**, 1389-1409.
- Nakatsuka, T., C. Yoshikawa, M. Toda, K. Kawamura & M. Wakatsuchi (2002): An extremely turbid intermediate water in the Sea of Okhotsk : Implication for the transport of particulate organic carbon in a seasonally ice-bound sea. *Geophys. Res. Letter*, **29**, 10.1029/2001GL014029
- Nishioka, J., S. Takeda, I. Kudo, D. Tsumune, T. Yoshimura, K. Kuma & A. Tsuda, (2003): Size-fractionated iron distributions and iron-limitation processes in the subarctic NW Pacific, *Geophys. Res. Letters*, **30**, 14, 1730, doi:10.1029/2002GL016853.
- Nishioka, J., T. Ono, H. Saito, T. Nakatsuka, S. Takeda, T. Yoshimura, K. Suzuki, K. Kuma, S. Nakabayashi, D. Tsumune, H. Mitsudera, W. K. Johnson, & A. Tsuda (2007): Iron supply to the western subarctic Pacific: Importance of iron export from the Sea of Okhotsk, *J. Geophys. Res.* (Submitted)
- Saito H, A. Tsuda, & H. Kasai (2002) Nutrient and plankton dynamics in the Oyashio region of the western subarctic Pacific Ocean. *Deep-Ses Res. Part II*, **49**, 5463-5486.
- Tani H, J. Nishioka, K. Kuma, H. Takata, Y. Yamashita, E. Tanoue & T. Midorikawa (2003): Iron(III) hydroxide solubility and humic-type fluorescent organic matter in the deep

water column of the Okhotsk Sea and the northwestern North Pacific Ocean. *Deep-Sea Res. Part I*, **50**, 1063-1078.