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## **Comparing the vertical distribution of iron in the eastern and western North Pacific Ocean**

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Running title: Iron distributions in the North Pacific

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Labile dissolved Fe ( $<0.22 \mu\text{M}$ ) in the western ( $165^\circ\text{E}$ ) and eastern ( $165^\circ\text{W}$ ) North Pacific Ocean had nutrient- and apparent oxygen utilization (AOU)-like profiles characterized by surface depletion and deep enrichment (5–3000 m depth). Dissolved Fe concentrations in the deep-water column at the mid-latitudes were approximately one-half lower in the eastern region (0.5–0.8 nM) than in the western region (0.8–1.3 nM) although the dissolved Fe concentrations in the surface mixed layer in both regions were extremely depleted to 0.1–0.2 nM. Surprisingly, the labile particulate Fe concentrations ( $\leq \sim 0.1$  nM, total dissolvable Fe minus labile dissolved Fe) throughout the water column at low latitudes in the eastern region were extremely lower than those ( $\sim 0.5$ –1 nM) in the western region. It is suggested that the low Fe levels in the eastern mid-latitude oceanic region are primarily due to the lower atmospheric Fe supply in the eastern region.

## 1. Introduction

Although iron is one of the most important biogeochemical trace elements in the ocean, its chemical speciation and distribution are not yet fully understood. Iron differs from other scavenged metals, such as Al and Pb, because of a strong biological requirement leading to iron uptake by living cells [e.g., *Kuma et al.*, 2000]. Therefore, it has a nutrient-like vertical distribution with low concentrations in surface water due to biological uptake and higher concentrations in deep water due to remineralization of biogenic matter. The remineralization of biogenic particles release iron, and this process is responsible for the vertical distribution of iron. However, several recent studies of iron distributions revealed that dissolved iron concentrations are about two times higher (0.8–1.5 nM) in deep waters in the western North Pacific [*Nakabayashi et al.*, 2001; *Nishioka et al.*, 2003] than (0.5–0.7 nM) around Stn P ( $50^\circ\text{N}$ ,  $145^\circ\text{W}$ ; Ocean Station Papa) in the Gulf of Alaska [*Martin et al.*, 1989; *Nishioka et al.*, 2003] and (0.4–0.5 nM) at the VERTEX-IV site in the center of the North Pacific subtropical gyre [*Bruland et al.*, 1994]. This probably reflects the regional patterns of the eolian source, physical transport, and the water column cycling of iron, such as biological uptake, remineralization of biogenic matter, scavenging onto particles, and iron complexation with organic ligands [*Johnson et al.*, 1997; *Parekh et al.*, 2004, 2005]. All of these factors point towards different residence times for iron in the surface and deep waters of these regions. Therefore, dissolved Fe profiles are generated by a complicated balance

between surface input, biological uptake, vertical flux, in-situ regeneration, particle scavenging, and physical mixing.

In the present study, we compare in detail the vertical distributions of labile dissolved ( $<0.22\ \mu\text{m}$ ) and total dissolvable (unfiltered) iron concentrations at the depth of 5–3000 m in the western and eastern (along  $165^\circ\text{E}$  and  $165^\circ\text{W}$  longitude lines) subarctic and subtropical North Pacific Ocean. The comparative vertical distributions of iron in the western and eastern regions are both interesting and valuable to chemical oceanographers and oceanic modelers due to the lack of iron data at depths greater than 1000 m.

## 2. Methods

Seawater samples were collected from the depths of 5–3000 m at six oceanic stations ( $47^\circ\text{N}$ ,  $44^\circ\text{N}$  and  $41^\circ\text{N}$  along  $165^\circ\text{E}$  and  $50^\circ\text{N}$ ,  $45^\circ30'\text{N}$  and  $41^\circ\text{N}$  along  $165^\circ\text{W}$ ) in the North Pacific Ocean (Fig. 1) in July 2004 using acid-cleaned, Teflon-coated, 10-liter Niskin X sampling bottles (General Oceanics) attached to a CTD-RMS. Sample filtration for analysis of labile dissolved Fe ( $<0.22\ \mu\text{m}$ ) concentration was carried out on deck by connecting an acid-cleaned  $0.22\text{-}\mu\text{m}$  pore size Durapore membrane filter (Cartridge type-Millipak 100, Millipore) to a sampling bottle spigot and then filtering the sample by gravity filtration. Unfiltered samples were used to measure total dissolvable Fe and dissolved oxygen. The filtered and unfiltered seawater (100 ml in precleaned 125-ml low density polyethylene bottles) used for labile dissolved and total dissolvable (unfiltered) Fe concentration analysis were buffered at pH 3.2 with formic acid-ammonium formate buffer solution in a class 100 clean room on board as soon as the samples were collected [Takata *et al.*, 2004 and 2005]. The buffered samples (pH 3.2) were kept in a refrigerator ( $5^\circ\text{C}$ ) for 3–4 months until Fe analysis in the laboratory. There were no differences in the labile dissolved and total dissolvable Fe concentrations of buffered oceanic water samples that had been kept for 1 month and 6 months in the present study and a previous study [Takata *et al.*, 2004]. Total dissolvable Fe has been defined as the total Fe that is solubilized at  $\text{pH}<2$  [Bruland and Rue, 2001]. Therefore, the weak acidification (pH 3.2) of filtered and unfiltered seawater samples may lead to an underestimate of the colloidal, very strongly complexed and particulate Fe fractions.

The Fe concentration in each buffered sample was measured with an

automated Fe analyzer (Kimoto Electric) using a combination of chelating resin concentration and luminol-hydrogen peroxide chemiluminescence detection [Obata *et al.*, 1993]. Hydrographic data (temperature, salinity and depth) were obtained using a CTD.

### 3. Results and Discussion

Labile dissolved and total dissolvable Fe in the western and eastern North Pacific Ocean had nutrient- and apparent oxygen utilization (AOU)-like profiles characterized by surface depletion and deep enrichment (Fig. 2, 3). However, there are major differences between the AOU and Fe profiles which may reflect the different time scales that the remineralization processes effecting each is operating on. In the surface waters in both regions, the iron levels were depleted to 0.1–0.2 nM for labile dissolved Fe and 0.1–0.6 nM for total dissolvable Fe (unfiltered) in the surface mixed layer (upper 50-m depth except for a few data at 5–10 m depths) and increased with depth (Fig. 2). The higher dissolved Fe ( $> 0.3$  nM) concentrations were found at 5 m depth (44°N, 165°E) and 5–10 m depths (50°N, 165°W), probably due to atmospheric iron input and lateral iron-rich subarctic water, respectively. Relatively low labile particulate Fe ( $>0.22$   $\mu\text{m}$ ; total dissolvable Fe minus labile dissolved Fe) concentrations in the surface mixed layer probably resulted from the effective biological uptake of atmospheric or lateral iron in the surface waters. The iron levels below the surface mixed layer ( $>50$  m depth) appeared to increase rapidly with depth at high latitudes (subarctic stations) and gradually with depth at the lower latitudes (subtropical stations). The northward increasing trend in the iron levels in mid-depth waters is due to the effect of upwelling and strong biological productivity at higher latitude [Nakabayashi *et al.*, 2001; Takata *et al.*, 2004]. At low latitudes (45°30'N and 41°N) along 165°W line, the labile dissolved Fe concentrations in the surface water were nearly the same as the total dissolvable Fe concentrations (Fig. 2B-1, 2B-2), resulting in the low labile particulate Fe in the surface water in the eastern mid-latitude oceanic region.

The vertically integrated total dissolvable Fe inventories in the upper 200 m (5–200 m) ranged from 41–53  $\mu\text{mol Fe m}^{-2}$  in the eastern mid-latitude oceanic region farther from the Asian continent, to 77–172  $\mu\text{mol Fe m}^{-2}$  in the western region and 120  $\mu\text{mol Fe m}^{-2}$  at high latitude (50°N) in the eastern region close to the Aleutian Islands (Fig. 2A-2, 2B-2). Labile dissolved Fe inventories were  $48\pm 10\%$  of the total dissolvable

Fe present. We estimated residence times for total dissolvable Fe at each station by dividing the total dissolvable Fe inventories in the upper 200 m by the Fe flux estimates (approximately 5 and 0.5  $\mu\text{mol Fe m}^{-2} \text{d}^{-1}$  along 165°E and 165°W, respectively) in our study region in the previous studies [Duce and Tindale, 1991; Tegen and Fung, 1995; Croot *et al.*, 2004]. The residence times for total dissolvable Fe were short ranging from 15–34 days in the western region to 81–106 days in the eastern mid-latitude oceanic region. These values in the western region are similar to estimates for the Sargasso Sea of ~18 days [Jickells, 1999] and the eastern-western Atlantic Ocean (60°W to 10°W at 10–11°N) of 6–62 days [Croot *et al.*, 2004], probably indicating the higher dust flux in the western region than the eastern region in the present study.

In the western North Pacific (along 165°E), the labile dissolved Fe concentrations were generally low at the surface (0.1–0.3 nM upper 100 m depth), high from 750 m to 2500 m (0.9–1.4 nM), and decreased to 0.8–1.0 nM at 2750–3000 m depths (Fig. 3A-1, 3A-2, 3A-3). The vertical distributions of labile dissolved Fe in the western region in the present study were very similar to those at the same and nearby stations in previous studies [Nakabayashi *et al.*, 2001; Nishioka *et al.*, 2003]. The vertical distributions of total dissolvable Fe in the western region were also characterized by surface depletion (0.1–0.6 nM), a rapid increase with depth at intermediate depths and deep enrichment (approximately 1.5–2.0 nM). The labile particulate Fe (> 0.22  $\mu\text{m}$ ) concentrations in the intermediate and deep waters were high (0.3–0.9 nM). High concentrations of labile particulate Fe throughout the water column have previously been reported in the western North Pacific Ocean [Nishioka *et al.*, 2003; Takata *et al.*, 2005; unpublished data] and in semi-closed oceans such as the Sea of Japan and the Bering Sea [Takata *et al.*, 2005].

In the eastern North Pacific (along 165°W), the Fe levels at high latitude (50°N) were very similar to those in the western region, with the labile dissolved Fe concentrations one-third lower than the total dissolvable Fe concentrations (Fig. 3B-1), while at lower latitudes (45°30'N and 41°N) the vertical distributions of labile dissolved Fe and total dissolvable Fe were very similar with almost same value at each depth (Fig. 3B-2, 3B-3). The labile dissolved Fe concentrations at low latitudes in the eastern region (Fig. 3B-2, 3B-3) were low at 0–100 m depths (0.06–0.12 nM), higher at 750–1000 m depths (0.81–0.88 nM at 45°30'N and 0.57–0.62 nM at 41°N), and decreased slightly at 2500–3000 m depths (0.6–0.7 nM at 45°30'N and 0.4–0.5 nM at

41°N) although AOU depth profiles were similar in both oceanic regions. The labile dissolved Fe levels at low latitudes in the eastern region were approximately one-third to one-half lower than those at high latitude in the eastern region and at all stations in the western region and were remarkably similar to that (0.6–0.7 nM in intermediate and deep waters) at Stn P (50°N, 145°W) in the Gulf of Alaska [Martin *et al.*, 1989]. In addition, the labile particulate Fe concentrations (0.02–0.2 nM) throughout the water column at low latitudes in the eastern region were much lower than those at 50°N in the eastern region and at all stations in the western region. Remarkably low labile particulate Fe concentrations have also been observed in the center of the North Pacific subtropical gyre [28°N, 155°W; Bruland *et al.*, 1994] and the Gulf of Alaska [50°N, 145°W; Johnson *et al.*, 1997; Nishioka *et al.*, 2003].

It has been reported that dissolved and particulate Fe levels throughout the deep water column in the Gulf of Alaska are high near the Alaskan margin with a tendency towards higher values closer to the Alaskan continental margin [Martin *et al.*, 1989; de Baar and de Jong, 2001; Fig. 1] due to the input of Fe along the continental margin. High Fe levels have also been reported in nearshore shelf areas off the California continental margin [Martin and Gordon, 1988; Johnson *et al.*, 1997]. Therefore, the high Fe levels in deep waters observed at 50°N in the eastern region (Fig. 2B-1) may be due to the input of Fe from the Alaskan continental margin to the Alaskan Stream [Martin *et al.*, 1989]. Profiles of salinity, AOU and labile dissolved Fe concentrations against  $\sigma_\theta$  have strong gradients in a narrow  $\sigma_\theta$  range of 26.6–27.2, while profile of AOU at 50°N in the eastern region has in a wide range of 25.6–27.0 because the surface water mass differed from that at 45°30'N and 41°N in the eastern region (Fig. 4A, 4B and 4C).

The AOU and labile dissolved Fe concentrations had the maximum values at a  $\sigma_\theta$  range of 27.2–27.6, and then rapidly decreased with depth at  $\sigma_\theta$  values higher than 27.6, although the labile dissolved Fe data where  $\sigma_\theta$  was greater than 27.0 were somewhat scattered with a southward decrease (Fig. 4C). There are large differences in the dissolved Fe (Fig. 4C) but the AOU at each station has hardly changed (Fig. 4B). This suggests that Fe is responding on a faster timescale than AOU. The AOU and Fe depth profiles appear to be more decoupled in the deeper waters suggesting there is not a link between AOU and Fe. Additionally the majority of eolian Fe may sink through the photic zone and may be released via abiotic processes and not microbial action.

Thus in high dust input regions there can be a stronger decoupling between AOU and Fe. Aeolian Fe is the major source of Fe to remote oceanic surface waters. The Fe released from microbial decomposition of sinking organic matter is the primary source for dissolved Fe in deep waters, and particle scavenging is the major Fe removal pathway [Duce and Tindale, 1991; Bruland *et al.*, 1994; Wu and Boyle, 2002]. The dissolved Fe concentrations in deep ocean waters are controlled primarily by Fe(III) complexation with natural organic ligands, which are possibly released through the bacterial production of siderophores and the chemical transformations of organic matter in deep ocean water [Powell and Donat, 2001; Kuma *et al.*, 2003]. Parekh *et al.* [2004] argued that a weaker ligand and greater total ligand concentration are more appropriate to lead to uniform concentration of dissolved Fe in the deep ocean. Therefore, the dissolved Fe depth profiles are controlled by the sinking particulate organic matter (POM), the production of dissolved Fe from POM during carbon remineralization, the scavenging of dissolved Fe, the Fe(III) solubility, and physical water transport [Johnson *et al.*, 1997; Kuma *et al.*, 2003; Parekh *et al.*, 2004, 2005].

It is simply assumed that there is a competition between Fe input from the microbial decomposition of sinking biogenic organic matter and Fe removal in deep sea by particle scavenging [Wu and Boyle, 2002]. Therefore, the imbalance of these two main processes along deep-water flow paths would lead to a variation of dissolved Fe depth profile with distance along the deep-water flow path from the western region (165°E) to the eastern region (165°W) in the subarctic North Pacific Ocean in the present study. The dissolved Fe depth profile is maintained by a mechanism that reduces the scavenging rate of dissolved iron at concentrations less than the Fe(III) solubility [Kuma *et al.*, 2003]. The dissolved and particulate Fe depth profiles in remote oceanic regions with less atmospheric iron supply would be regulated primarily by the Fe(III) solubility, resulting in the depth profiles of lower labile dissolved Fe and particulate Fe concentrations observed in the eastern mid-latitude oceanic region. Recent model studies by Parekh *et al.* [2004, 2005] suggest that iron in the deep ocean is critically controlled by the ratio of conditional stability constant ( $K_{FeL}$ ) to the scavenging rate ( $k_{SC}$ ),  $K_{FeL}/k_{SC}$ . Increasing this ratio enhances the protection of dissolved iron from scavenging by binding iron more strongly to the organic ligand. Future work is to confirm that the geographically different dissolved Fe depth profiles are controlled by the sinking POM, the production of dissolved Fe from POM, the scavenging of

dissolved Fe, the Fe(III) solubility and the physical transport of deep waters.

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Figure caption

**Figure 1.** Locations of sampling stations at 47°N (A-1), 44°N (A-2), and 41°N (A-3) along 165°E in the western North Pacific and at 50°N (B-1), 45°30'N (B-2), and 41°N (B-3) along 165°W in the eastern North Pacific Ocean during July 2004.

**Figure 2.** Surface vertical distributions of labile dissolved Fe (<0.22 μm: open circles, squares and triangles) and total dissolvable Fe (unfiltered: solid circles, squares and triangles) concentrations at the depths of 5–300 m at 47°N, 44°N and 41°N in the western North Pacific Ocean (A) and at 50°N, 45°30'N, and 41°N in the eastern North Pacific Ocean (B).

**Figure 3.** Vertical distributions of labile dissolved Fe (<0.22 μm: open circles), total dissolvable Fe (unfiltered: solid circles) concentrations, and apparent oxygen utilization (AOU: cross) from the depths of 5–3000 m at 47°N (A-1), 44°N (A-2), and 41°N (A-3) in the western North Pacific Ocean and at 50°N (B-1), 45°30'N (B-2), and 41°N (B-3) in the eastern North Pacific Ocean (Fig. 1). A little higher total dissolvable Fe concentrations in parenthesis (B-2, B-3) may be contaminated.

**Figure 4.** (A) Salinity, (B) AOU, (C) labile dissolved Fe concentration versus potential density ( $\sigma_\theta$ ) at 47°N (solid circles), 44°N (solid squares), and 41°N (solid triangles) in the western North Pacific and at 50°N (open circles), 45°30'N (open squares), and 41°N (open triangles) in the eastern North Pacific Ocean.