

Surface and middle layer enrichment of dissolved copper in the western subarctic North Pacific

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Abstract: Vertical distributions of dissolved copper were investigated at two stations in the western subarctic and tropical North Pacific to elucidate the factors controlling its concentration. There was a significant correlation (p -value < 0.05) at the subarctic and tropical stations between dissolved copper and silicic acid between 400–3000 m and 300–2000 m depths, respectively, which implies the importance of diatoms in transporting copper. The dissolved copper concentration at depths shallower than 1000 m was 1.3–2.7 times higher at the subarctic station than that at the tropical station, and at depths shallower than 1500 m, it was 0.97–2.60 nM higher at the subarctic station than the average of other reported values of the North Pacific. This can be attributed to several processes. In the surface layer, horizontal advection of the coastal water by the East Kamchatka Current was considered to be a source of copper because a high concentration was observed within low-salinity surface waters. Supply of copper below the surface layer to 1500 m was probably owing to downward transport by the biological pump and horizontal advection. These results suggest that horizontal transport of copper from coastal or shelf area is important for biological production and Cu distribution in this region.

Keywords : *dissolved copper, North Pacific, subarctic, tropical*

1. Introduction

Copper (Cu) is a trace metal that is both a nutrient and toxin to phytoplankton. Copper is

required by phytoplankton, and works at the active center of a variety of Cu-containing proteins, such as plastocyanin, cytochrome oxidase, ascorbate oxidase, superoxide dismutase, and multicopper ferroxidase (TWINING and BAINES, 2013). It has often been pointed out that its concentration is low enough to limit phytoplankton growth (e.g., MOFFETT and DUPONT, 2007). On the contrary, a surplus of Cu is toxic to phytoplankton (COALE, 1991). Cu toxicity may control the composition and growth of the natural phytoplankton community (MOFFETT *et al.*, 1997; MANN *et al.*, 2002; PAYTAN *et al.*, 2009). These effects of Cu on phytoplankton are controlled by the spatiotemporal variability of its concentration

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in the nanomolar range. Therefore, it is important to elucidate the spatial variability of Cu concentration to understand whether Cu supports or limits phytoplankton growth in the environment.

To understand the spatial variability of Cu, knowledge of its sources and sinks are important. Known sources of Cu are aerosol deposition (PAYTAN *et al.*, 2009), riverine input (MARTIN and WHITFIELD, 1983), sediments in the coastal and shelf region (WESTERLUND and ÖHMAN, 1991), and hydrothermal vents (SANDER and KOSCHINSKY, 2011). Known sinks of Cu are consumption by organisms (KINUGASA *et al.*, 2005) and scavenging with sinking particles (BOYLE *et al.*, 1977; BRULAND, 1980). However, knowledge about spatial variation in Cu concentration in the open ocean has been limited to the subtropical Pacific and Atlantic Oceans (BOYLE *et al.*, 1981; SAAGER *et al.*, 1997).

To elucidate local sources and sinks of Cu, it is necessary to investigate its vertical profile. The typical vertical profile of dissolved Cu (D-Cu), which has been known since the late 1970's, is a hybrid-type of nutrient-type and scavenged-type. Since D-Cu has nutrient-type characteristics, its concentration is as low as 0.24 nmol l^{-1} in the surface water (BRULAND, 1980; MILLER and BRULAND, 1994; EZOE *et al.*, 2004), owing to consumption by microorganisms, and increases in the middle to deep layer (BOYLE *et al.*, 1977), owing to recycling associated with organic matter decomposition. Moreover, supply from bottom sediments and scavenging by particles throughout the column also affect the Cu profile (BOYLE *et al.*, 1977). In addition, Cu supply by aerosol deposition (PAYTAN *et al.*, 2009) in the surface or by horizontal advection in the surface and middle layer (YEATS and CAMPBELL, 1983) has also been reported.

The western North Pacific is a region with high Fe supply and its sources are aerosol deposition

from the East Asia (MOORE and BRAUCHER, 2008) and horizontal transport from the Sea of Okhotsk into the intermediate water of the Western Subarctic Gyre (NISHIOKA *et al.*, 2007). Although these processes can simultaneously supply Cu and Fe, the spatial variability of Cu concentration in this region is limited (FUJISHIMA *et al.*, 2001; EZOE *et al.*, 2004; TAKANO *et al.*, 2014). The fact that Cu can be used as an alternative to Fe under Fe deficient conditions in some diatoms (PEERS and PRICE, 2006) implies that Cu is an important element for the phytoplankton in this Fe-limited high-nitrate low-chlorophyll (HNLC) region.

In this study, we report differences in the D-Cu concentration between the subarctic and tropical regions in the western North Pacific, and discuss the possible sources and sinks of D-Cu.

2. Materials and Methods

Sampling

Sampling was conducted during the KH-08-2 cruise of the R/V Hakuho-maru at subarctic Stn. 5 ($47^{\circ}00' \text{ N}$, $160^{\circ}07' \text{ E}$, 5248 m depth, August 2008) and tropical Stn. 22 ($11^{\circ}30' \text{ N}$, $155^{\circ}00' \text{ E}$, 5795 m depth, September 2008) in the western North Pacific (Fig. 1). Seawater was collected using acid-washed Teflon-coated Niskin-X bottles at depths from 5000 m to 5 m. Seawater for D-Cu samples was filtered through an acid-washed $0.22 \text{ }\mu\text{m}$ pore-sized Millipak 100 filter (Merck-Millipore) attached to a Teflon spigot of a Niskin-X bottle. Acid-cleaned 125 ml low-density polyethylene (LDPE) bottles (Nalgene) were used for D-Cu sampling. Before sampling, the bottles were cleaned as described in KONDO *et al.* (2012). After sampling, the D-Cu samples were acidified to a pH of 1.7 by adding hydrochloric acid (Tama-pure-AA 100, Tama Chemicals).

Hydrography, chlorophyll *a* and nutrients

Vertical profiles of temperature, salinity, dissolved oxygen (DO), and fluorescence were

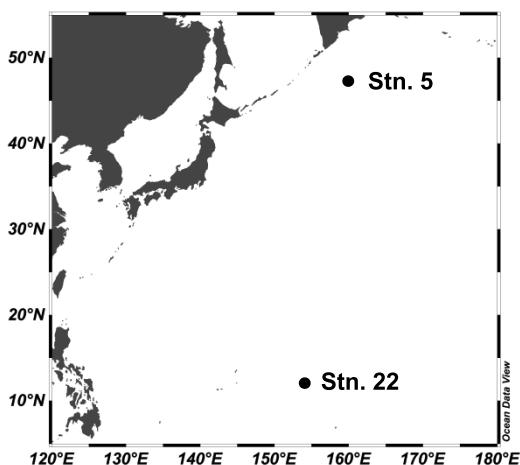


Fig. 1 Sampling was conducted at Stns. 5 ($47^{\circ} 00' N$, $160^{\circ} 07' E$) and 22 ($11^{\circ} 30' N$, $155^{\circ} 00' E$) during the KH-08-2 cruise of R/V Hakuho-maru (August-September 2008). The map was drawn using Ocean Data View (SCHLITZER, 2012).

monitored by sensors (Sea-bird Electronics) attached to a rosette. The mixed layer depth was defined to be where there was a 0.125 increase in sigma-t compared to that at the 10 m depth (SUGA *et al.*, 2004). The Brunt-Väisälä frequency was calculated from vertical profiles of temperature and salinity as described by MILLARD *et al.* (1990). Apparent oxygen utilization was calculated by subtraction of the ambient DO concentration from the DO saturated concentration (WEISS, 1970). 113–300 ml of seawater for chlorophyll *a* (Chl. *a*) analysis was filtered through 25-mm glass microfiber filters (GF/F, Whatman), and the Chl. *a* concentrations were measured fluorometrically using a 10-AU fluorometer (Turner Designs) after extraction with 5 ml of *N,N*-dimethylformamide on board. Seawater for nutrient analysis was frozen at $-20^{\circ} C$. Concentrations of nutrients were measured by an autoanalyzer (AACS III, Bran + Luebbe) on land. The salinity of the surface water pumped up from the bottom of the ship (5 m) was also monitored

(ACT-20, Alec Electronics) during the cruise. The surface sensor was calibrated against discretely determined salinity of seawater collected from the sea surface by bucket sampling during the leg 1 of this cruise (stations not shown).

Reagents for dissolved copper

Salicylaldoxime (SA) (Sigma) was dissolved in 0.1 mol l^{-1} hydrochloric acid (Tamapure-AA 100, Tama Chemicals) at a concentration of 10 mmol l^{-1} , to be used as a stock solution, and left at $4\text{--}6^{\circ} C$ for a few days to achieve complete dissolution. For the second measurements without UV irradiation described later, SA was dissolved in Milli-Q water at 100 mmol l^{-1} and was used as a stock solution. It was heated in a microwave oven for complete dissolution before use. Then, it was diluted with Milli-Q water to a final concentration of 10 mmol l^{-1} and used as the working solution. Boric acid (suprapure, Merck-Millipore) was dissolved in 0.35 mol l^{-1} ammonia water (Tamapure-AA 100, Tama Chemicals) at a final concentration of 1 mol l^{-1} to obtain the pH buffer. For additional measurements, the borate buffer was purified twice by the MnO_2 method (GRASSHOFF *et al.*, 1999). 3-[4-(2-Hydroxyethyl)-1-piperazinyl]-propanesulfonic acid (EPPS) (Sigma-Aldrich) was dissolved in 1 mol l^{-1} ammonia water (Tamapure-AA 100, Tama Chemicals) at a final concentration of 1.2 mol l^{-1} to be used as another pH buffer. A standard Cu solution was prepared by serial dilution from copper standard solution (Cu: $1,000 \text{ mg l}^{-1}$, JCSS, $Cu(NO_3)_2$ in 0.1 mol l^{-1} HNO_3 , Wako Pure Chemical Industries) with $0.05\text{--}0.1 \text{ mol l}^{-1}$ hydrochloric acid (Tamapure-AA 100, Tama Pure Chemical Industries).

Measurement of dissolved copper

D-Cu concentration was measured by cathodic stripping voltammetry (CSV) using SA (CAMPOS and VAN DEN BERG, 1994). Measurement of D-Cu

concentration was conducted after 16 months of preservation. Twelve milliliters of samples were pipetted in a quartz tube and UV-irradiated for 4 hours (CAMPOS and VAN DEN BERG, 1994) at 80–90 °C by a 705 UV digester with a 150 W lamp (Metrohm) to decompose dissolved organics that could interfere with the CSV measurement by preventing Cu from forming a complexation with SA or saturate at the surface of the mercury drop of the working electrode. After irradiation, 10 ml of the sample was neutralized to a pH of 8.3–8.4 with 100 μl of borate buffer and ammonia water (Tmapure-AA 100, Tama Chemicals). SA was added at a final concentration of 25 $\mu\text{mol l}^{-1}$. Then the Teflon[®] perfluoroalkoxy (PFA) measuring vessel (Metrohm) was set at 757 or 797 VA Computrace (Metrohm). The voltammetric setting was slightly modified from that of CAMPOS and VAN DEN BERG (1994). Deposition potential was set at -1.06 V. The scan range was from -0.11 to -0.56 V. The concentration of D-Cu was determined using the standard addition method. The detection limit was 0.05 nmol l^{-1} , which is three times the standard deviation of the peak height obtained by the replicate measurement of Cu in Milli-Q water. The measured concentration of standard seawater (NASS-5), using the EPPS buffer (final concentration of 6.0 mmol l^{-1} and final pH of 8.3=8.4) without UV irradiation, was $5.16 \pm 0.19 \text{ nmol l}^{-1}$ ($n = 3$), which is within the range of the certified values of $4.67 \pm 0.72 \text{ nmol l}^{-1}$. Although we used the EPPS buffer in the beginning, it was later replaced by the borate buffer to eliminate the effect of the EPPS complexing with copper (SOARES and BARROS, 2001). Moreover, since the conditional stability constant of Cu-EPPS is much weaker than that of Cu-SA, the effect of EPPS on the measurements was negligible. Therefore, data measured using each buffer was treated equally in this study.

In the first measurement, we conducted UV

irradiation on the sample seawater. However, we left out this process in the second measurement, because measurements of SAFe reference samples S and D2 without UV irradiation ($n = 3$; 0.50 ± 0.03 and $2.35 \pm 0.15 \text{ nmol l}^{-1}$ for S and D2, respectively) agreed with consensus values of 0.52 ± 0.05 and $2.28 \pm 0.15 \text{ nmol kg}^{-1}$ for S and D2, respectively, reported in May 2013 (www.geotraces.org). The voltammetric setting was the same as described by CAMPOS and VAN DEN BERG (1994). Values determined without UV irradiation were at 3500 and 4500 m at Stn. 5 and at 5 and 50 m at Stn. 22, which are realistic values compared with values just above and below the depth measured with UV irradiation. Some values were the average of results by both methods with and without UV irradiation at 5, 50, 150, and 1500 m at Stn. 5 and at 10 m at Stn. 22 because no clear difference was observed between the results with and without UV irradiation (data not shown).

Blanks were corrected assuming that the Cu concentration in Milli-Q water was zero. Since the pH buffer varied between measurements, we measured blanks separately for these different measurements (the final pH was the same in both measurements). Thus, the reported values in this study are comparable to each other despite the different pH buffers used.

Phytoplankton Pigment Composition

To analyze phytoplankton pigment composition, 0.7–5.2 l of seawater collected from 5, 10, 20, 30, and 50 m at Stn. 5 and from 5, 10, 30, 50, 100, 140, 150, and 200 m at Stn. 22 was filtered through glass microfiber filters (GF/F, Whatman). The filters were flash-frozen in liquid nitrogen or frozen at -80 °C in a freezer, and were preserved at -80 °C until analysis on land. Pigments on the filters were extracted in 3.6 ml of 95% methanol (for liquid chromatography, Wako Pure Chemical Industries) with sonification (Sonifier 150,

Branson) to destroy phytoplankton cells. After > 1 h extraction at 5 °C, glass microfiber filters in the extracts were eliminated by filtration using a 0.2- μm polytetrafluoroethylene (PTFE) syringe driven filter unit (Millex[®]-FG, Merck-Millipore). Finally, 1.6 ml of the extract was mixed with 0.4 ml of Milli-Q water just prior to injection into a high-performance liquid chromatography (HPLC) system.

Pigments in the extracts were quantified by HPLC according to a method of ZAPATA *et al.* (2000) slightly modified as MIKI *et al.* (2008). The measured pigments were identified by comparing retention time and absorbance spectra with those of standard pigments. Data of absorbance and spectra used in this study were from FURUYA *et al.* (2003) and MIKI *et al.* (2008). The measured pigments were monovinyl (MV) Chl. *a*, MV Chl. *b*, divinyl (DV) Chl. *a*, zeaxanthin (Zea), alloxanthin (Allo), diadinoxanthin (Diad), 19'-hexanoyloxyfucoxanthin (Hex), prasinoxanthin (Pras), fucoxanthin (Fuco), 19'-butanoyloxyfucoxanthin (But), peridinin (Peri), Chl. *c*₃, Neoxanthin (Neo), and Chlorophyllide *a* (Chld. *a*).

3. Results

Hydrography, chlorophyll *a*, phytoplankton pigments and nutrients

Salinity monotonically increased with depth at Stn. 5 from 32.6 at the surface to 34.7 at 5000 m depth (Fig. 2a). Potential temperature at Stn. 5 was highest (13.2 °C) at the surface, sharply decreased with depth, and was minimum (1.14 °C) at 93 m. Then, temperature increased to about 3.67 °C at 256 m, and decreased again with depth to 1.08 °C at 5009 m (Fig. 2a). At Stn. 22, salinity was stable at 34.6 at the surface (at 43 m), and increased with depth to its maximum (35.1) at 158 m (Fig. 2b). The salinity maximum is typical of North Pacific Tropical Water (SUGA *et al.*, 2000). Salinity, then decreased and reached a

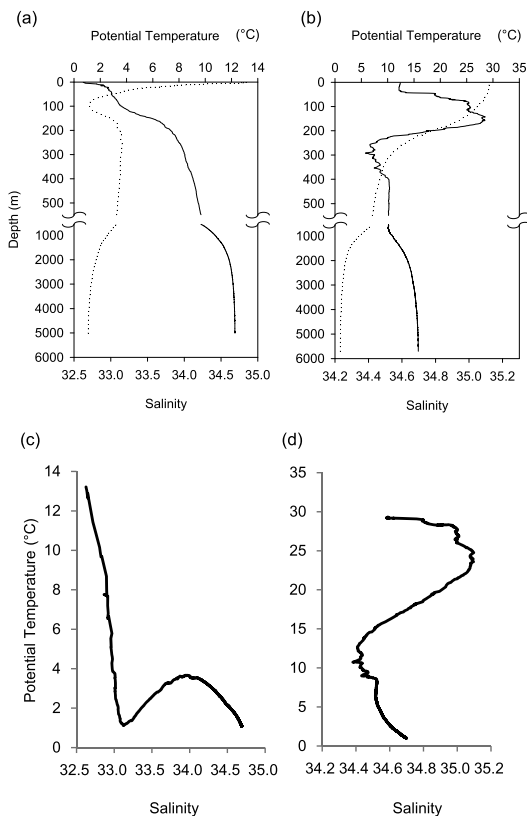


Fig. 2 Salinity (solid line) and Potential temperature (dotted line) profiles at Stns. 5 (a) and 22 (b). T-S diagrams were also depicted from these data at Stns. 5 (c) and 22 (d).

minimum (34.4) at 292 m, and increased again with depth to 34.7 at 5702 m. Potential temperature at Stn. 22 was the highest (29.3 °C) at the surface and monotonically decreased to 1.01 °C at 5702 m (Fig. 2b).

The hydrography at Stn. 5 was categorized into two water masses, Subarctic Upper Water (0–2000 m) and Pacific Deep Water (2000–5000 m) (Fig. 2c), based on temperature and salinity (TOMCZAK and GODFREY, 2005). At Stn. 22, the Western North Pacific Central Water, North Pacific Intermediate Water, and Pacific Deep Water (TOMCZAK and GODFREY, 2005) were observed at depths of approximately 175–250 m,

250–2000 m and 2000–5702 m, respectively (Fig. 2d). Water masses with low salinity at depths shallower than 175 m were not denominated as far as we know, but probably resulted from the formation of high-salinity North Pacific Tropical Water (SUGA *et al.*, 2000) observed around 175 m. That is, high-salinity water mass was formed around the sea surface by evaporation and was subsided owing to its high density while being transported laterally, which resulted in more saline subsurface water than the surface one. The mixed layer depth (MLD) was 12 m and 45 m at Stns. 5 and 22, respectively. At Stn. 5, the Brunt-Väisälä frequency sharply increased around the bottom of the mixed layer from 0.0509 at 11 m to 0.204 at 12 m, and then decreased with depth to 0.0552 at 200 m (Fig. 3a). The surface water at depths shallower than 12 m at Stn. 5 was characterized by low salinity (32.6–32.9) and was distinguishable in the T-S diagram (Fig. 2c). The low-salinity water in the sea surface (5 m) was widely observed in the northern area during the cruise (Fig. 4). At Stn. 22, the Brunt-Väisälä frequency was relatively stable (0.01–0.03) from 10 m to 43 m. Then, it sharply increased to 0.0553 at 46 m, coinciding with the mixed layer depth.

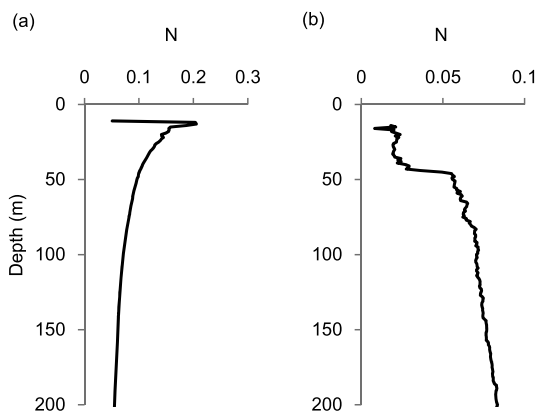


Fig. 3 Vertical distributions of Brunt-Väisälä frequency (N) were calculated from temperature and salinity at Stns. 5 (a) and 22 (b).

Below 46 m, it gradually increased with depth to 0.0834 at 200 m (Fig. 3b).

Chl. *a* concentration was highest at the surface ($0.67 \mu\text{g l}^{-1}$), and sharply decreased from the 50 to 100 m depth at Stn. 5 (Fig. 5a). Although a low Chl. *a* value ($0.23 \mu\text{g l}^{-1}$) was observed at 40 m, it is uncertain whether it was actually low or was caused by a mishandling of samples in the measurement because there was no drastic

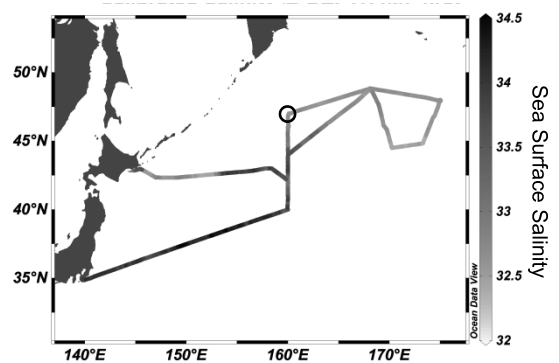


Fig. 4 Salinity on the surface during the first leg of the cruise (from 29 Jul to 9 Aug 2008) was plotted on the map using Ocean Data View. Location of Stn. 5 was shown by a circle on the map.

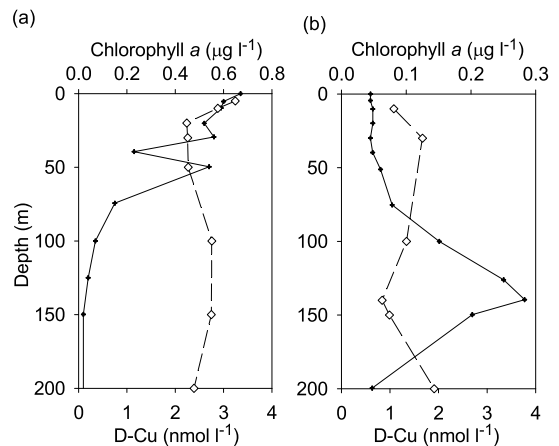


Fig. 5 Chlorophyll *a* (cross, solid line) and dissolved copper (white diamond, dashed line) at Stns. 5 (a) and 22 (b).

change of *in vivo* fluorescence, temperature, or salinity around this depth. At Stn. 22, Chl. *a* was low ($0.04\text{--}0.08\ \mu\text{g l}^{-1}$) throughout the top 75 m and the subsurface Chl. *a* maximum was observed (SCM, $0.28\ \mu\text{g l}^{-1}$) at 140 m depth (Fig. 5b).

At Stn. 5, among the algal pigments determined in the present study, MV Chl. *a*, But, Hex, Fuco, Chl. *b*, Chl. *c*₃ and Diad were dominant (Table 1), implying that diatoms, prymnesiophytes and dinoflagellates were the dominant phytoplankton groups. At Stn. 22, the concentrations of MV and DV Chl. *a*, and Zea were high in the top 100 m. From SCM (140 m) to 150 m, Chl. *b* in addition to the above pigments was also abundant (Table 1). These results imply that the dominant phytoplankton groups were cyanobacteria and prochlorophytes. Although Fuco was also detected at Stn. 22, its concentration was low, which suggests a low abundance of diatoms.

The oxygen minimum was observed at 700 m ($7.18\ \text{ml l}^{-1}$) and 1160 m ($5.86\ \text{ml l}^{-1}$) at Stns. 5 and 22, respectively (Fig. 6a-d). The layers of the oxygen minima corresponded to the Subarctic Upper Water and the North Pacific Intermediate Water at Stns. 5 and 22, respectively.

Nitrate, phosphate, and silicic acid concentrations were lowest in the surface ($7.52\ \mu\text{mol l}^{-1}$, $0.932\ \mu\text{mol l}^{-1}$ and $8.76\ \mu\text{mol l}^{-1}$, respectively), and highest around 300–600 m for nitrate and phosphate ($45.7\text{--}46.2\ \mu\text{mol l}^{-1}$ and $3.17\text{--}3.19\ \mu\text{mol l}^{-1}$, respectively), and at 1500 m for silicic acid ($163\ \mu\text{mol l}^{-1}$); all these values were observed to occur within the Subarctic Upper Water. At Stn. 22, nitrate, phosphate and silicic acid concentrations were lowest above the SCM, and had their maxima at 1000 m ($40.3\ \mu\text{mol l}^{-1}$), 1500 m ($2.90\ \mu\text{mol l}^{-1}$) and 3000 m ($155\ \mu\text{mol l}^{-1}$), respectively. The concentration maxima occurred within the Western North Pacific Central Water and the North Pacific Intermediate Water for nitrogen and phosphorus and occurred deeper in the

Pacific Deep Water for silicon.

Dissolved copper

Vertical profiles of D-Cu had nutrient-type characteristics at both subarctic and tropical stations (Fig. 6b and d), although the relative variation in the D-Cu concentration between surface and deep waters was smaller than that in the nitrate concentration. At the subarctic Stn. 5, a relatively high concentration was observed near the surface ($3.2\ \text{nmol l}^{-1}$ at 5 m), within low-salinity water ($32.6\text{--}32.9$). Below the MLD (12 m), D-Cu concentration had its minimum ($2.24\text{--}2.26\ \text{nmol l}^{-1}$) at 20–30 m, the region where Chl. *a* was still high (Fig. 5a). The range of D-Cu concentration was $2.2\text{--}3.2\ \text{nmol l}^{-1}$ at a depth of 5–1000 m. The D-Cu concentration increased between 1000–1500 m and 3000–4000 m, and reached $5.0\ \text{nmol l}^{-1}$ at a depth of 4000–5000 m (Fig. 6b). The D-Cu continued to increase below the layer of the AOU, nitrate, phosphate and silicic acid (Figs. 6a and b) maxima. The correlation between D-Cu concentration and silicic acid concentration (Fig. 7a) was significant between 400–3000 m ($p < 0.05$). On the other hand, no significant correlation was observed between D-Cu concentration and nitrate and phosphate concentration or AOU (not shown).

At the tropical Stn. 22, D-Cu concentration had its minimum ($0.84\ \text{nmol l}^{-1}$) at SCM (140 m), although it was relatively constant within the surficial 200 m (Fig. 5b). We eliminated the D-Cu data at 5 m because heavy contamination was suspected ($10.1\ \text{nmol l}^{-1}$). Increase of the D-Cu concentration was observed below 400 m depth in the North Pacific Intermediate Water, reaching $4.0\text{--}4.5\ \text{nmol l}^{-1}$ at depths of 3000–5000 m (Fig. 6d) in the Pacific Deep Water. Below this depth, the D-Cu further increased to $5.15\ \text{nmol l}^{-1}$ at 5587 m, which was approximately 200 m above the sea floor. As observed at Stn. 5, the D-Cu continued increasing much below the AOU, nitrate, phos-

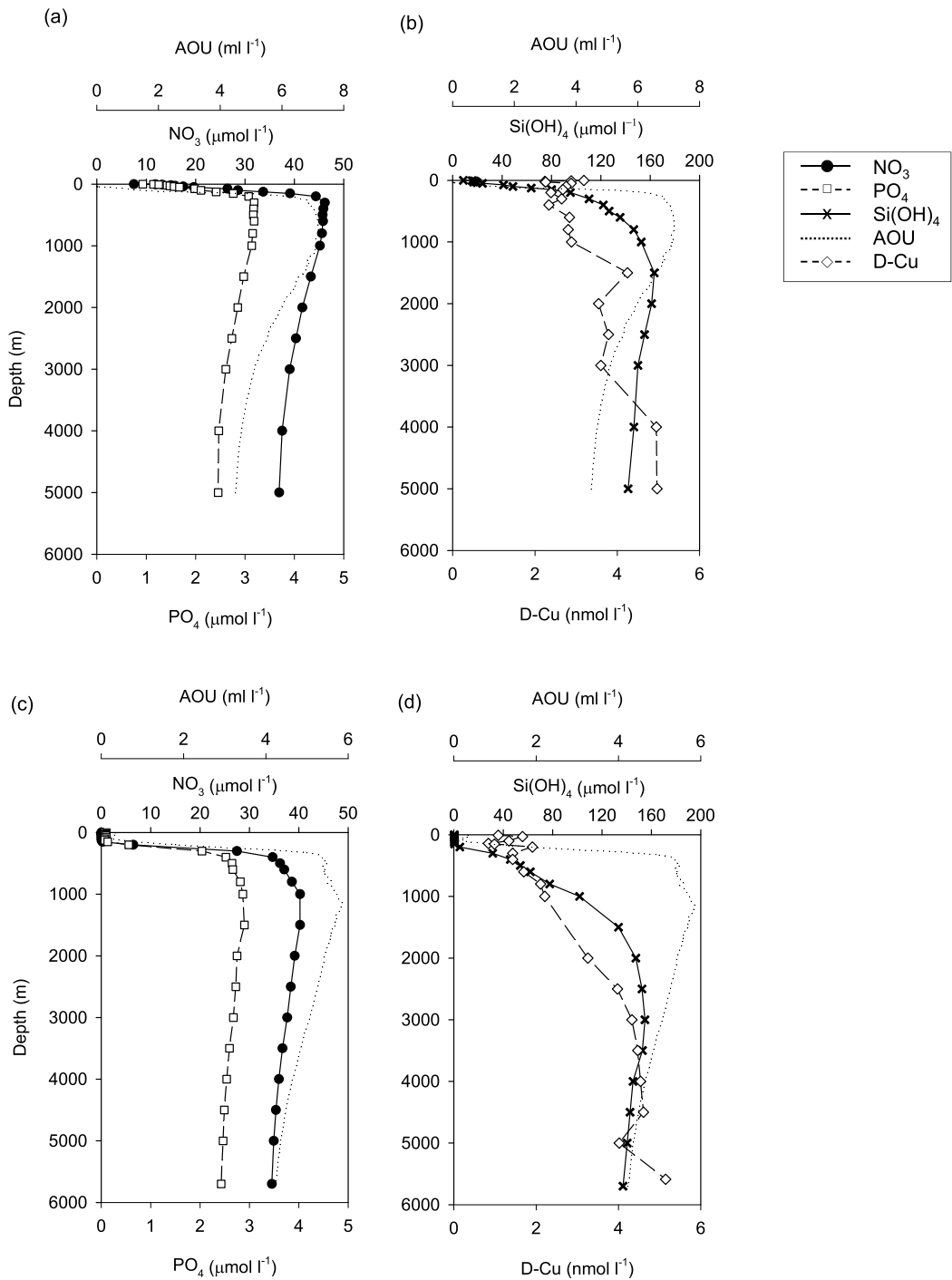


Fig. 6 Nitrate (a, c), phosphate (a, c), Silicate (b, d), dissolved copper (b, d) and AOU (a, b, c, d) profiles at Stns. 5 (a, b) and 22 (c, d).

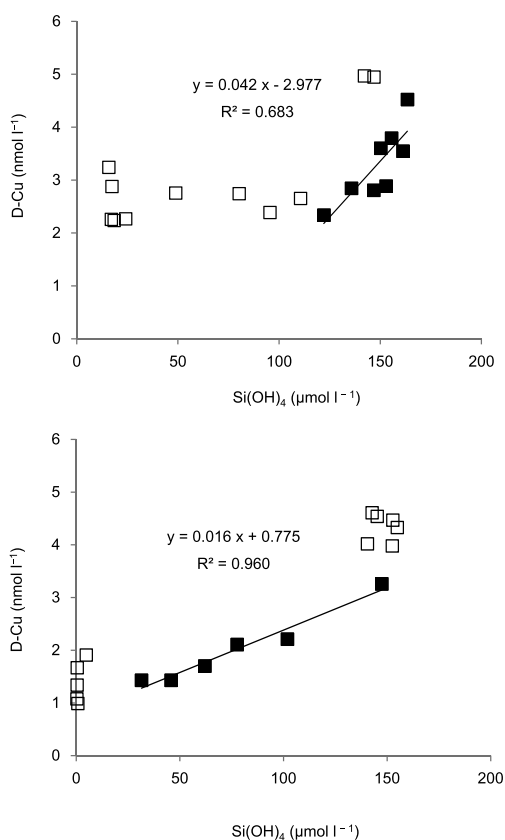


Fig. 7 Relationship between concentrations of dissolved copper and silicic acid at Stns. 5 (a) and 22 (b) throughout the water column (open and filled squares). Significant correlation was observed between 300–2000 m and 400–3000 m depth at Stns. 5 and 22, respectively (shown by filled squares, $p < 0.05$).

phate, and silicic acid maxima at this station. Within a limited depth from 300–2000 m, the D-Cu concentration showed a significant correlation with the silicic acid concentration ($p < 0.05$) (Fig. 7b). Below 2000 m, the silicic acid concentration was relatively constant, while the D-Cu continued to increase with depth, resulting in no significant correlation ($p > 0.05$) within this depth range. The distribution of nitrate, phosphate, and AOU had no relationship with that of D-Cu ($p > 0.05$).

With respect to Stns. 5 and 22, D-Cu was higher at Stn. 5 than at Stn. 22 at depths shallower than 1500 m, which corresponds to the Subarctic Upper Water at Stn. 5 and the Western North Pacific Central Water and the North Pacific Intermediate Water at Stn. 22. In contrast, the D-Cu was at the same level below 2000 m, which corresponds to the Pacific Deep Water at both stations.

4. Discussion

Characteristics of D-Cu profile

Nutrient-type characteristics of D-Cu profiles are commonly observed in the Atlantic (MOORE, 1978; YEATS and CAMPBELL, 1983; DANIELSSON *et al.*, 1985), the Pacific (BOYLE *et al.*, 1977; BRULAND, 1980), and the Indian Oceans (DANIELSSON, 1980; SAAGER *et al.*, 1992). The D-Cu concentration minimum coincided with the Chl. *a* concentration maximum at both subarctic and tropical stations, suggesting D-Cu consumption by phytoplankton. D-Cu concentration increased with depth below the middle depths (1000 and 600 m at Stns. 5 and 22, respectively), which is likely due to integrated effect of remineralization accompanied by organic matter decomposition and lateral transport of aged water mass by deep sea circulation (FEELY *et al.*, 2004).

In the present study, the correlation between D-Cu and silicic acid was observed at both Stns. 5 and 22, though in different depth ranges (Fig. 7). A correlation between D-Cu and silicic acid caused by Cu consumption by diatoms and the following downward transport through the biological pump has previously been reported (WESTERLUND and ÖHMAN, 1991; NOLTING *et al.*, 1991; LÖSCHER 1999; BOYE *et al.*, 2012). The slope of this correlation at Stn. 22 was 0.016 in this study, which is within the range of reported values in the subtropical and subarctic eastern North Pacific (0.006–0.029) (NOLTING *et al.*, 1991). In the

subtropical region, despite a generally low abundance of diatoms, a correlation between Cu and Si has previously been frequently observed (NOLTING *et al.*, 1991; BOYE *et al.*, 2012). In addition, at Stn. 22, which is located in the tropical region, the abundance of diatoms was low as shown by the low Fuco/Chl. *a* ratio (0.02–0.07) that is an order of magnitude lower than that at Stn. 5 (0.22–0.32). Moreover, the opal contribution to total sinking particle flux has also been reported to be lower in the western subtropical North Pacific than in the subarctic region (KAWAHATA, 2002). These observations imply that dissolved copper between 300 and 2000 m at Stn. 22 was mainly supplied by lateral transport from diatom-dominated high productive areas. In contrast, at Stn. 5, the correlation between Cu and silicic acid was not observed around the silicocline between 5–300 m. However, then, D-Cu increased below 400 m, where increase of silicic acid was small. This resulted in the larger slope (0.042) of the correlation at Stn. 5 (Fig. 7a) than that at Stn. 22 (0.016, Fig. 7b). To explain the fact that D-Cu kept increasing below the silicic acid maximum at both stations, it is necessary to consider downward transport of Cu by sinking particles other than diatoms, such as mineral particles, or supply of Cu from the bottom sediments (BOYLE *et al.*, 1977; BRULAND, 1980) even if Cu supply by lateral transport is taken into account. Since D-Cu gradient was observed from the bottom to 2000 m at Stn. 22 despite the low value at 5000 m, D-Cu increase between 2000–5587 m seems to have been attributed to the bottom source. On the other hand, discontinuity of D-Cu gradient was observed between 3000 m and 4000 m at Stn. 5. Therefore, supply from the bottom source at this station seems to have been limited between 4000 and 5000 m if lateral transport of water mass was not considered. Between 2000 and 3000 m, D-Cu may have been supplied by sinking mineral

particles. Although mineral particles can also supply silicic acid together with Cu, its relative influence on silicic acid concentration seems to be low because the concentration of autochthonous silicic acid is high. On the contrary, D-Cu concentration can be relatively strongly influenced by supply from mineral particles because D-Cu concentration is initially low. In addition to the supply from mineral particles, supply by northern horizontal transport of Cu-rich water by deep-sea circulation is another possible reason to explain the discontinuity of D-Cu gradient. Therefore, it is necessary in the future study to elucidate vertical distributions of Cu from the high-resolution latitudinal survey.

High concentration of D-Cu near sea surface

In this study, high D-Cu concentrations were observed at 5 and 10 m at Stn. 5 and at 5 m at Stn. 22. High concentrations of D-Cu near the sea surface have been reported, which are attributed to D-Cu supply by aerosol deposition or contamination from ships (BOYLE *et al.*, 1977; COALE and BRULAND, 1990; EZOE *et al.*, 2004). At the very least, the sample collected from 5 m at Stn. 22 is suspected to be contaminated because the concentration here (10.1 nmol l^{-1} , eliminated from figures) is an order of magnitude higher than previously reported values in the open ocean and because aerosol was sparse at this station (data not shown). Although the sampling side of the ship was toward the wind during sampling to avoid contamination from exhaust gas, completely avoiding contamination, at least for Cu, in samples taken near surface waters by a rosette sampler is difficult (BRULAND, 1980). On the contrary, the high D-Cu near the surface at Stn. 5 was at a level that has been explained by aerosol deposition or horizontal transport in previous reports (BOYLE *et al.*, 1977, 1981). In addition, from the surface to 12 m depth at Stn. 5, the salinity was lower (32.6–32.9) than that of the

Subarctic Upper Water (32.9–33.1) (Fig. 2c). Since low-salinity surface water was observed in large areas between 160° E and 180° in the north of 44.5° N during the cruise (Fig. 4), it is more likely to have been caused by a water mass, influenced by coastal supply, that was probably horizontally transported by the East Kamchatka Current (FAVORITE *et al.*, 1976), and not by precipitation. However, it is also possible that Cu was loaded by aerosol deposition onto the low-salinity surface water during its horizontal transport. D-Cu supply by the horizontal transport of the low-salinity surface water seems plausible because a high D-Cu concentration was observed in the low-salinity water (<12 m).

Comparison of D-Cu profile in the North Pacific

D-Cu vertical profiles in the eastern and western North Pacific, including both subarctic and subtropical areas, were compiled from the present and previous studies (BRULAND, 1980; BUCK *et al.*, 2012; COALE and BRULAND, 1990; EZOE *et al.*, 2004; FUJISHIMA *et al.*, 2001; HIROSE *et al.*, 1982; MIDORIKAWA *et al.*, 1990; MILLER and BRULAND, 1994; MOFFETT and DUPONT, 2007; SEMENIUK *et al.*, 2009; TAKANO *et al.*, 2014) (Fig. 8). Here, values of MOFFETT and DUPONT (2007) were read from figures. The D-Cu concentration at depths shallower than 1500 m at Stn. 5 vs. that of the compiled data without the data of Stn. 5 in this study and of MOFFETT and DUPONT (2007) was 2.23–4.52 nM vs. 0.46–2.94 nM (0.94–2.56 nM higher than average of the values at other stations), and remained at almost the same level below 2000 m (Fig. 8). MOFFETT and DUPONT (2007) also reported similarly high concentration of D-Cu between 500–1500 m in the subarctic North Pacific. However, these high values (2.35–4.52 nM) are not unrealistic, since the complexing capacity of organic ligand in the subarctic Pacific (generally ~3–4 nM, COALE and BRULAND, 1990; MILLER and BRULAND, 1994; MOFFETT and DUPONT,

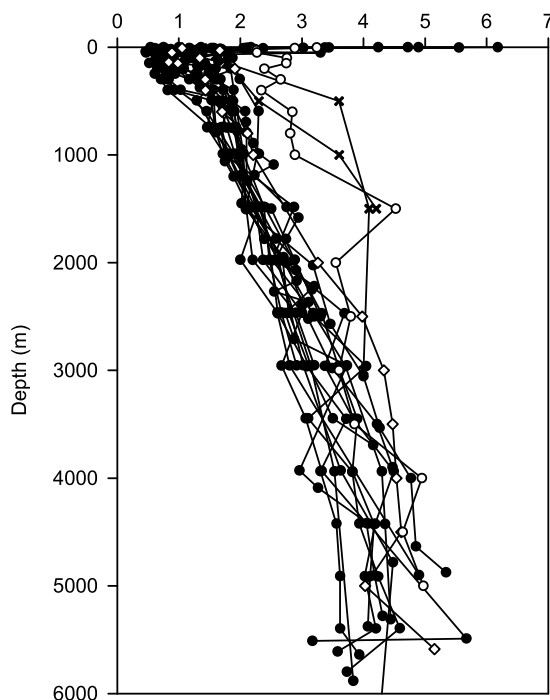


Fig. 8 Compiled data of vertical profile of D-Cu in previous studies in the Pacific Ocean (filled circle, BRULAND, 1980; BUCK *et al.*, 2012; COALE and BRULAND, 1990; EZOE *et al.*, 2004; FUJISHIMA *et al.*, 2001; HIROSE *et al.*, 1982; MIDORIKAWA *et al.*, 1990; MILLER and BRULAND, 1994; SEMENIUK *et al.*, 2009; TAKANO *et al.*, 2014: cross, MOFFETT and DUPONT, 2007) and in this study (Stn. 5: open circle, Stn. 22: open diamond). Unit of nmol kg^{-1} in TAKANO *et al.* (2014) was converted into nmol l^{-1} using 1.02 kg l^{-1} as seawater density.

2007) is even higher than or at the same level as these values. To account for the high D-Cu concentration, it is necessary to consider supply and removal processes.

Sources and sinks of D-Cu in the euphotic layer

Within the euphotic layer, which is reported to be around 45–60 m in the western subarctic gyre (MOCHIZUKI *et al.*, 2002; TSUDA *et al.*, 2005), aerosol deposition is an important source of Cu (PAYTAN *et al.*, 2009). PAYTAN *et al.* (2009) estimated

atmospheric deposition of Cu to be high in the western North Pacific, especially around 35–45° N, which is similar to the pattern of dust deposition estimates by other studies (UEMATSU *et al.*, 2003; MEASURES *et al.*, 2005). Although station BO01 (39° 59′ N, 160° 00′ E; June 23–24, 2000) of EZOE *et al.* (2004) is located closer to the center of the high Cu deposition region described above than Stn. 5 in the present study, the surface D-Cu concentration there was lower than that at Stn. 5. Moreover, the monthly averaged aerosol optical thickness at 550 nm as monitored by MODIS-Terra (Jul 2000) and MODIS-Aqua (Aug 2008) and produced with the Giovanni online data system at a website of the Goddard Earth Sciences Data and Information Services Center (GES DISC), showed higher aerosol density at station BO01 (0.157, Jul 2000) than at Stn. 5 (0.143, Aug 2008) at each sampling time. Additionally, in the Atlantic Ocean, the surface D-Cu distribution (BOYLE *et al.*, 1981) was clearly different from that of D-Fe, which was covaried with dust deposition on a latitudinal transect (MOORE *et al.*, 2009). Therefore, it is unlikely that dust deposition was the main cause of the high D-Cu concentration at Stn. 5, and it is necessary to consider other supply processes.

Another possible source of D-Cu into the euphotic layer is the transport of coastal water by horizontal advection (YEATS and CAMPBELL, 1983). There are two lines of evidence that show D-Cu supply by horizontal advection at Stn. 5. First, low-salinity water was observed at the surface around Stn. 5 as described above, which suggests horizontal advection of coastal water. Second, a satellite image of monthly-averaged surface Chl. *a* during August 2008, monitored by SeaWiFS (9 km) and produced with the Giovanni online data system, showed that high Chl. *a* water extends from the coast to large oceanic areas, around Stn. 5 (Fig. 9). Therefore, horizontal transport of

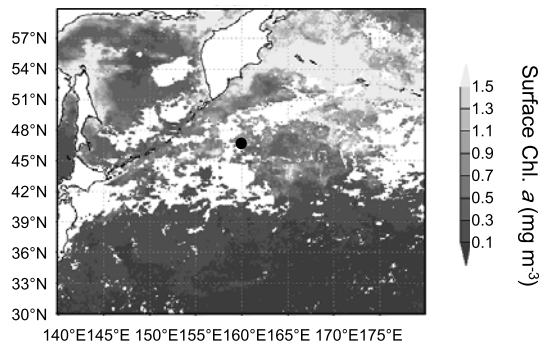


Fig. 9 Satellite images of surface Chl. *a* concentration during August 2008. Monthly averaged SeaWiFS 9 km data were depicted with Giovanni online data system (<http://disc.sci.gsfc.nasa.gov/giovanni>). Locations of Stn. 5 of this study were shown as dots on the map.

coastal water, rather than aerosol deposition, is considered to have been the main cause of the high D-Cu concentration at Stn. 5, although aerosol deposition could have also contributed to the Cu supply to some extent. Cu supply into the surface layer at Stn. 5 was also implied from Cu-Si relationship. Comparing D-Cu concentrations at same silicic acid concentration between 15–80 $\mu\text{mol l}^{-1}$, they were approximately 0.6–1.8 nmol l^{-1} higher at Stn. 5 than that at Stn. 22 (Figs. 7a and b). Therefore, Cu supply from atmosphere or coastal water was considered to raise D-Cu concentration near the sea surface.

The removal of D-Cu in the euphotic zone is mainly driven by biological consumption as shown by its nutrient-type profile. Primary production in the western subarctic North Pacific has been reported to be higher than in the tropical region (NORIKI *et al.*, 1995; YAMADA *et al.*, 2012). Moreover, surface Chl. *a* at Stn. 5 was relatively high in the western subarctic North Pacific. Although Fe could have been supplied with the transport of the coastal water, the high nitrate concentration in the surface water at Stn.

Table 1. Phytoplankton pigment composition at each depth was shown in $\mu\text{g l}^{-1}$.

Station	Depth	Chl c_3	Chld α	Peri	But	Fuco	Neo	Pras	Hex	Diad	Allo	Zea	Chl b	DV Chl α	MV Chl α
5	5	0.063	0.025	0.021	0.046	0.123	0.008	0.007	0.171	0.052	0.017	0.018	0.049	0	0.556
	10	0.061	0.017	0.016	0.045	0.114	0.008	0.008	0.172	0.044	0.011	0.013	0.053	0	0.472
	20	0.082	0.014	0.013	0.063	0.117	0.01	0.005	0.191	0.035	0.007	0.006	0.034	0	0.425
	30	0.091	0.01	0.01	0.074	0.151	0.012	0.017	0.147	0.024	0.008	0.009	0.054	0	0.48
	50	0.061	0	0	0.04	0.14	0.016	0.032	0.038	0.011	0.014	0.006	0.119	0	0.474
22	5	0	0	0.001	0.002	0.002	0	0	0.006	0.003	0	0.032	0.004	0.017	0.027
	10	0.001	0	0.002	0.002	0.003	0	0	0.009	0.004	0	0.032	0.005	0.017	0.051
	30	0.001	0	0.002	0.002	0.004	0	0	0.009	0.003	0	0.031	0.006	0.016	0.036
	50	0.003	0	0.003	0.003	0.005	0	0	0.012	0.004	0	0.044	0.007	0.028	0.044
	100	0.006	0	0.004	0.008	0.003	0.001	0	0.026	0.004	0	0.05	0.024	0.075	0.073
	140	0.024	0	0.002	0.037	0.004	0.002	0.001	0.005	0.003	0.001	0.034	0.15	0.136	0.106
	150	0.022	0	0.001	0.033	0.003	0.002	0.001	0.043	0.003	0.001	0.021	0.12	0.095	0.097
200	0.008	0	0	0.01	0.001	0	0	0.014	0.001	0	0.002	0.029	0.013	0.03	

Chl c_3 : chlorophyll c_3 , Chld α : chlorophyllide α , Peri: peridinin, But: 19'-butanoyloxyfucoxanthin, Fuco: fucoxanthin, Neo: neoxanthin, Pras: prasinoxanthin, Hex: 19'-hexanoyloxyfucoxanthin, Diad: diadinoxanthin, Allo: alloxanthin, Zea: zeaxanthin, Chl. b : chlorophyll b , DV Chl α : divinyl chlorophyll α , MV Chl α : monovinyl chlorophyll α

5 (Fig. 6) implies that the station is located in a high-nitrate low-chlorophyll region, where primary production is limited by iron deficiency. Under such environments, some oceanic diatoms could replace Fe-containing enzymes with Cu-containing enzymes (PEERS and PRICE, 2006) and utilize multicopper oxidase for uptake of organically complexed Fe (ANNETT *et al.*, 2008; MALDONADO *et al.*, 2006), which could enhance the biological utilization of Cu by phytoplankton. Therefore, removal of D-Cu in the surface layer is considered to have been larger in the subarctic region than in the tropical region. Thus, supply process is probably responsible for the high concentration of D-Cu observed at Stn. 5.

Sources and sinks of D-Cu below the euphotic layer

Below the euphotic layer, one of the sources of D-Cu is regeneration accompanied by decomposition of sinking particles transported from the euphotic layer by the biological pump. As discussed above, the biological uptake of Cu at Stn. 5 is expected to have been relatively high. Thus, the supply of Cu by regeneration in the deeper layer is estimated to have been higher in this region than that in the other regions. However, below 2000 m, there was no discernible difference in D-Cu concentrations between Stn. 5 and the other stations (Fig. 8). This is probably because the organic matter was almost fully decomposed around this depth.

Supply of D-Cu by deep sea circulation is also possible to be a cause of high D-Cu above 1500 m at Stn. 5. The subarctic North Pacific is an end region of deep sea circulation, where the deeper water is upwelling with high D-Cu. As described above, MOFFETT and DUPONT (2007) also reported high D-Cu concentration between 500–1500 m in the subarctic North Pacific. Therefore, such a supply process of D-Cu is possible. However, values reported by TAKANO *et al.* (2014) in the

western subarctic north Pacific were not as high as those observed at Stn. 5 in this study. Thus, concentration of D-Cu may be spatially or temporally variable in this region.

Another supply process of Cu in deeper layers is transport by horizontal advection. To evaluate Cu sources other than the biological pump of diatoms, vertical profiles of the D-Cu:silicic acid (Cu:Si) ratio at Stns. 5 and 22 were plotted (Fig. 10). The ratio at Stn. 5 was highest (2.1) at the surface, had its minimum (0.019) at a 1000 m depth, and then slightly increased toward the bottom (0.035). The high Cu:Si ratio near the surface was caused by biological Si consumption and relatively high Cu at the surface. On the contrary, the high Cu:Si ratio near the bottom can be explained by Cu supply from bottom sources and a decrease in silicic acid below the Si maximum. Profiles of the Cu:Si ratio at both stations ranged within the same level (approximately 0.02–0.03) between 400 and 2000 m, suggesting that Cu and Si were mainly controlled by the biological pump by diatoms in this depth range along the advection pathway of water masses in this layer. However, a slightly high ratio was observed at 1500 m at Stn. 5, which corresponded to a high concentration of D-Cu

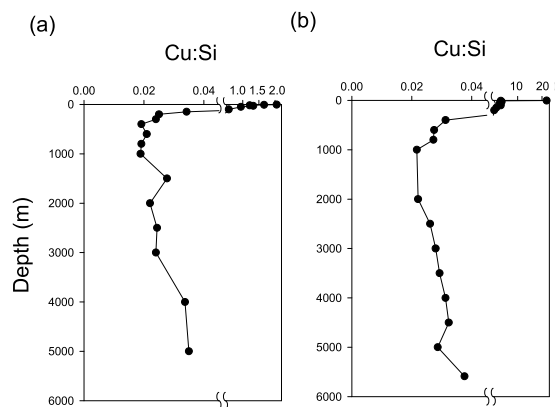


Fig. 10 Vertical profiles of Cu:Si ratio at Stns. 5 (a) and 22 (b).

(4.52 nM). To this region, Fe is supplied by horizontal advection of water mass from the Sea of Okhotsk, which contains high dissolved-Fe. This water mass is characterized by σ_θ of 26.6–27.5 (NISHIOKA *et al.*, 2007), which corresponds to 116–1110 m at Stn. 5. Therefore, the horizontal advection of this water mass cannot explain the D-Cu concentration anomaly at 1500 m. However, it is possible that this process supplied D-Cu between 116–1110 m at Stn. 5 although no apparent signal of the supply was observed in the D-Cu profile and the Cu:Si plot at this station.

Considering the high sinking particle flux in the western subarctic North Pacific (NORIKI *et al.*, 1995; KAWAHATA, 2002), removal by scavenging is likely to have also been high. Thus, the supply of D-Cu is considered to have been high enough to sustain the high D-Cu concentration, compensating for its high removal in the euphotic zone (biological uptake) and below (scavenging).

Comparison with Ni

Among the trace metal elements, the distribution pattern of dissolved nickel (Ni) was similar to that of D-Cu in the point of view that it was higher in the subarctic North Pacific than in the subtropical above the maximum at around 1500 m, and almost no regional variation was observed below the maximum (EZOE *et al.*, 2004). Nickel showed a nutrient-type profile that frequently correlated with phosphate and silicic acid (BRULAND 1980; BOYLE *et al.*, 1981), which implies the importance of control by the biological pump, related to diatoms, on both Cu and Ni distributions.

Future directions

In the present study, vertical profiles of D-Cu were examined at the western North subarctic and tropical stations, together with other hydrographic and biological parameters. This study presents high D-Cu concentrations in the western subarctic North Pacific. Our results suggest that

Cu was supplied to the surface layer of the western subarctic North Pacific primarily by horizontal advection and, to a lesser extent, by aerosol deposition. The Cu was then transported downward through the biological pump to a depth of 1500 m. Moreover, a direct supply of Cu to the same depth by horizontal advection is also implied, although the source of the water mass and mechanism of the advection are unclear. More detailed observation is necessary to elucidate them in the future. The present study also suggests that the biological pump is the main source of Cu in the middle layer in the western subarctic North Pacific. Therefore, it is important to determine the amount of Cu utilized by microbes and the amount of Cu supporting primary production in the Fe-depleted region as this will enable us to further understand the Cu transport process. Furthermore, it is important to understand the effect of changes in aerosol deposition accompanied by future climate change on Cu concentration in the natural environment, because change of Fe supply from dust affects Fe deficiency of ocean surface and thus Cu requirement of phytoplankton and accordingly downward flux of Cu by biological pump.

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References

ANNETT, A.L., S. LAPI, T.J. RUTH, and M.T. MALDONADO

- (2008): The effects of Cu and Fe availability on the growth and Cu:C ratios of marine diatoms. *Limnol. Oceanogr.* **53**, 2451-2461.
- BOYE, M., B.D. WAKE, P. LOPEZ GARCIA, J. BOWN, A. R. BAKER, and E.P. ACHTERBERG (2012): Distributions of dissolved trace metals (Cd, Cu, Mn, Pb, Ag) in the southeastern Atlantic and the Southern Ocean. *Biogeosciences* **9**, 3231-3246.
- BOYLE, E. A., F. R. SCLATER, and J. M. EDMOND (1977): The distribution of dissolved copper in the Pacific. *Earth Planet. Sci. Lett.* **37**, 38-54.
- BOYLE, E. A., S. S. HUESTED, and S. P. JONES (1981): On the distribution of copper, nickel, and cadmium in the surface waters of the North Atlantic and North Pacific Ocean. *J. Geophys. Res.* **86**, 8048-8066.
- BRULAND, K.W. (1980): Oceanographic distributions of cadmium, zinc, nickel, and copper in the North Pacific. *Earth Planet. Sci. Lett.* **47**, 176-198.
- BUCK, K.N., J. MOFFETT, K.A. BARBEAU, R.M. BUNDY, Y. KONDO, and J. WU (2012): The organic complexation of iron and copper: an intercomparison of competitive ligand exchange-adsorptive cathodic stripping voltammetry (CLE-ACSV) techniques. *Limnol. Oceanogr.* **10**, 496-515.
- CAMPOS, M.L.A.M., and C.M.G. VAN DEN BERG (1994): Determination of copper complexation in sea water by cathodic stripping voltammetry and ligand competition with salicylaldoxime. *Anal. Chim. Acta* **284**, 481-496.
- COALE, K. H. (1991): Effects of iron, manganese, copper, and zinc enrichments on productivity and biomass in the subarctic Pacific. *Limnol. Oceanogr.* **36**, 1851-1864.
- COALE, K.H., and K.W. BRULAND (1990): Spatial and temporal variability in copper complexation in the North Pacific. *Deep-Sea Res.* **37**, 317-336.
- DANIELSSON, L. G. (1980): Cadmium, cobalt, copper, iron, lead, nickel and zinc in Indian Ocean water. *Mar. Chem.* **8**, 199-215.
- DANIELSSON, L.G., B. MAGNUSSON, and S. WESTERLUND (1985): Cadmium, copper, iron, nickel and zinc in the north-east Atlantic Ocean. *Mar. Chem.* **17**, 23-41.
- EZOE, M., T. ISHITA, M. KINUGASA, X. LAI, K. NORISUYE, and Y. SOHRIN (2004): Distributions of dissolved and acid-dissolvable bioactive trace metals in the North Pacific Ocean. *Geochem. J.* **38**, 535-550.
- FAVORITE, F., A. J. DODIMEAD, and K. NASU (1976): Oceanography of the subarctic Pacific region, 1960-71. *Bulletin of the International North Pacific Fishery Commission.* **33**, 1-187.
- FEELY, R.A., C.L. SABINE, R. SCHLITZER, J.L. BULLISTER, S. MECKING, and D. GREELEY (2004): Oxygen utilization and organic carbon remineralization in the upper water column of the Pacific Ocean. *J. Oceanogr.* **60**, 45-52.
- FUJISHIMA, Y., K. UEDA, M. MARUO, E. NAKAYAMA, C. TOKUTOME, H. HASEGAWA, M. MA and Y. SOHRIN (2001): Distribution of trace bioelements in the subarctic North Pacific Ocean and the Bering Sea (the R/V Hakuho Maru Cruise KH-97-2). *J. Oceanogr.* **57**, 261-273.
- FURUYA, K., M. HAYASHI, Y. YABUSHITA, and A. ISHIKAWA (2003): Phytoplankton dynamics in the East China Sea in spring and summer as revealed by HPLC-derived pigment signatures. *Deep-Sea Res. Pt. II* **50**, 367-387.
- GRASSHOFF, K., K. KREMING, and M. EHRHARDT (1999): *Methods of Seawater Analysis*, Wiley-VCH, 3rd edition, 632pp.
- HIROSE, K., Y. DOKIYA, and Y. SUGIMURA (1982): Determination of conditional stability constants of organic copper and zinc complexes dissolved in seawater using ligand exchange method with EDTA. *Mar. Chem.* **11**, 343-354.
- KAWAHATA, H. (2002): Suspended and settling particles in the Pacific. *Deep-Sea Res. Pt. II* **49**, 5647-5664.
- KINUGASA, M., T. ISHITA, Y. SOHRIN, K. OKAMURA, S. TAKEDA, J. NISHIOKA, and A. TSUDA (2005): Dynamics of trace metals during the subarctic Pacific iron experiment for ecosystem dynamics study (SEEDS2001). *Prog. Oceanogr.* **64**, 129-147.
- KONDO, Y., S. TAKEDA, and K. FURUYA (2012): Distinct trends in dissolved Fe speciation between shallow and deep waters in the Pacific Ocean. *Mar. Chem.* **134-135**, 18-28.
- LÖSCHER, B.M. (1999): Relationships among Ni, Cu, Zn, and major nutrients in the Southern Ocean. *Mar.*

- Chem. **67**, 67–102.
- MALDONADO, M.T., A.E. ALLEN, J.S. CHONG, K. LIN, D. LEUS, N. KARPENKO, and S.L. HARRIS (2006): Copper-dependent iron transport in coastal and oceanic diatoms. *Limnol. Oceanogr.* **51**, 1729–1743.
- MANN, E.L., N. AHLGREN, J.W. MOFFETT, and S.W. CHISHOLM (2002): Copper toxicity and cyanobacteria ecology in the Sargasso Sea. *Limnol. Oceanogr.* **47**, 976–988.
- Martin, J. M., and M. Whitfield (1983): The significance of the river input of chemical elements to the ocean. *In* Trace Metals in Sea Water. WONG, C. S., E. BOYLE, K. W. BRULAND, J. D. BURTON and E. D. GOLDBERG (eds.), Plenum Press, New York and London, p. 265–296
- MEASURES, C.I., M.T. BROWN, and S. VINK (2005): Dust deposition to the surface waters of the western and central North Pacific inferred from surface water dissolved aluminum concentrations. *Geochemistry, Geophys. Geosystems* **6**.
- MIDORIKAWA, T., E. TANOUÉ, and Y. SUGIMURA (1990): Determination of complexing ability of natural ligands in seawater for various metal ions using ion selective electrodes. *Anal. Chem.* **62**, 1737–1746.
- MIKI, M., N. RAMAIAH, S. TAKEDA, and K. FURUYA (2008): Phytoplankton dynamics associated with the monsoon in the Sulu Sea as revealed by pigment signature. *J. Oceanogr.* **64**, 663–673.
- MILLARD, R., W. OWENS, and N. FOFONOFF (1990): On the calculation of the Brunt-Väisälä frequency. *Deep-Sea Res.* **37**, 167–181.
- MILLER, L.A., and K.W. BRULAND (1994): Determination of copper speciation in marine waters by competitive ligand equilibration/liquid-liquid extraction: an evaluation of the technique. *Anal. Chim. Acta* **284**, 573–586.
- MOCHIZUKI, M., N. SHIGA, M. SAITO, K. IMAI, and Y. NOJIRI (2002): Seasonal changes in nutrients, chlorophyll *a* and the phytoplankton assemblage of the western subarctic gyre in the Pacific Ocean. *Deep-Sea Res. Pt. II* **49**, 5421–5439
- MOFFETT, J.W., L.E. BRAND, P.L. CROOT, and K.A. BARBEAU (1997): Cu speciation and cyanobacterial distribution in harbors subject to anthropogenic Cu inputs. *Limnol. Oceanogr.* **42**, 789–799.
- MOFFETT, J.W., and C. DUPONT (2007): Cu complexation by organic ligands in the sub-arctic NW Pacific and Bering Sea. *Deep-Sea Res. Pt. I* **54**, 586–595.
- MOORE, R.M. (1978): The distribution of dissolved copper in the eastern Atlantic Ocean. *Earth Planet. Sci. Lett.* **41**, 461–468.
- MOORE, J.K., and O. BRAUCHER (2008): Sedimentary and mineral dust sources of dissolved iron to the world ocean. *Biogeosciences* **5**, 631–656.
- MOORE, C.M., M.M. MILLS, E.P. ACHTERBERG, R.J. GEIDER, J. LAROCHE, M.I. LUCAS, E.L. McDONAGH, X. PAN, A.J. POULTON, M. J. A. RIJKENBERG, D. J. SUGGETT, S. J. USSHER, and E.M.S. WOODWARD (2009): Large-scale distribution of Atlantic nitrogen fixation controlled by iron availability. *Nat. Geosci.* **2**, 867–871.
- 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, and A. TSUDA (2007): Iron supply to the western subarctic Pacific: Importance of iron export from the Sea of Okhotsk. *J. Geophys. Res.* **112**, C10012
- NOLTING, R.F., H.J.W. DE BAAR, A.J. VAN BENNEKOM, and A. MASSON (1991): Cadmium, copper and iron in the Scotia Sea, Weddell Sea and Weddell/Scotia Confluence (Antarctica). *Mar. Chem.* **35**, 219–243.
- NORIKI, S., T. IWAI, A. SHIMAMOTO, S. TSUNOGAI, and K. HARADA (1995): Spatial variation of Al flux in the North Pacific observed with sediment trap. *In* Biogeochemical Processes and Ocean Flux in the Western Pacific. SAKAI H. and Y. NOZAKI (eds.), Terra Scientific Publishing Company, Tokyo, p. 345–354.
- PAYTAN, A., K.R.M. MACKEY, Y. CHEN, I.D. LIMA, S.C. DONEY, N. MAHOWALD, R. LABIOSA, and A.F. POST (2009): Toxicity of atmospheric aerosols on marine phytoplankton. *Proc. Natl. Acad. Sci. U. S. A.* **106**, 4601–4605.
- PEERS, G., and N.M. PRICE (2006): Copper-containing plastocyanin used for electron transport by an oceanic diatom. *Nature* **441**, 341–344.
- SAAGER, P. M., H. J. W. DE BAAR, and R. J. HOWLAND. (1992): Cd, Zn, Ni and Cu in the Indian Ocean.

- Deep-Sea Res. **39**, 9–35.
- SAAGER, P.M., H.J.W. DE BAAR, J.T.M. DE JONG, R.F. NOLTING, and J. SCHIJF (1997): Hydrography and local sources of dissolved trace metals Mn, Ni, Cu, and Cd in the northeast Atlantic Ocean. *Mar. Chem.* **57**, 195–216.
- SANDER, S.G., and A. KOSCHINSKY (2011): Metal flux from hydrothermal vents increased by organic complexation. *Nat. Geosci.* **4**, 145–150.
- SCHLITZER, R., Ocean Data View, <http://odv.awi.de>, 2012.
- SEMENIUK, D.M., J.T. CULLEN, W.K. JOHNSON, K. GAGNON, T.J. RUTH, and M.T. MALDONADO (2009): Plankton copper requirements and uptake in the subarctic Northeast Pacific Ocean. *Deep Sea Res. Pt. I* **56**, 1130–1142.
- SOARES, H.M.V.M., and M.G. R. T. BARROS (2001): Electrochemical Processes of cadmium, copper, lead, and zinc in the presence of *N*-(2-hydroxyethyl) piperazine-*N*-3-propanesulfonic acid (HEPPS): Possible implications in speciation studies. *Electroanalysis* **13**, 325–331.
- SUGA, T., A. KATO, and K. HANAWA (2000): North Pacific Tropical Water: its climatology and temporal changes associated with the climate regime shift in the 1970s. *Prog. Oceanogr.* **47**, 223–256.
- SUGA, T., K. MOTOKI, Y. AOKI, and A. M. MACDONALD (2004): The North Pacific climatology of winter mixed layer and mode waters. *J. Phys. Oceanogr.* **34**, 3–22.
- TAKANO, S., M. TANIMIZU, T. HIRATA, and Y. SOHRIN (2014): Isotopic constraints on biogeochemical cycling of copper in the ocean. *Nat. Commun.* **5**, 5663.
- TOMCZAK, M., and J. S. GODFREY (2005): *Regional Oceanography: an Introduction*, pdf version 1.1, Butler and Tanner Ltd, London, 391pp.
- TSUDA, A., H. KIYOSAWA, A. KUWATA, M. MOCHIZUKI, N. SHIGA, H. SAITO, S. CHIBA, K. IMAI, J. NISHIOKA, and T. ONO (2005): Responses of diatoms to iron-enrichment (SEEDS) in the western subarctic Pacific, temporal and spatial comparisons. *Prog. Oceanogr.* **64**, 189–205.
- TWINING, B., and S. BAINES (2013): The trace metal composition of marine phytoplankton. *Ann. Rev. Mar. Sci.* **5**, 191–215.
- UEMATSU, M., Z.F. WANG, and I. UNO (2003): Atmospheric input of mineral dust to the western North Pacific region based on direct measurements and a regional chemical transport model. *Geophys. Res. Lett.* **30**, 1342.
- WEISS, R.F. (1970): The solubility of nitrogen, oxygen and argon in water and seawater. *Deep-Sea Res.* **17**, 721–735.
- WESTERLUND, S., and P. ÖHMAN (1991): Cadmium, copper, cobalt, nickel, lead, and zinc in the water column of the Weddell Sea, Antarctica. *Geochim. Cosmochim. Acta* **55**, 2127–2146.
- YAMADA, N., H. FUKUDA, H. OGAWA, H. SAITO, and M. SUZUMURA (2012): Heterotrophic bacterial production and extracellular enzymatic activity in sinking particulate matter in the western North Pacific Ocean. *Front. Microbiol.* **3**, 379.
- YEATS, P.A., and J.A. CAMPBELL (1983): Nickel, copper, cadmium and zinc in the northwest Atlantic Ocean. *Mar. Chem.* **12**, 43–58.
- ZAPATA, M., F. RODRÍGUEZ, and J. GARRIDO (2000): Separation of chlorophylls and carotenoids from marine phytoplankton: a new HPLC method using a reversed phase C8 column and pyridine-containing mobile phases. *Mar. Ecol. Prog. Ser.* **195**, 29–45.

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