

# Distribution and speciation of dissolved zinc in the western North Pacific and its adjacent seas



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## ABSTRACT

Total dissolved zinc (Zn) and its speciation was investigated by cathodic stripping voltammetry (CSV) in the western North Pacific and its marginal seas, the Sea of Okhotsk and the Sea of Japan (East Sea). In these high latitude areas, Zn complexing ligands in most samples were saturated with zinc because of the high dissolved Zn concentration. Relatively high total ligand concentrations ( $C_L$ ) and relatively low conditional stability constants ( $K'_{ZnL,Zn^{2+}}$ ) have been obtained in the surface waters of the Sea of Okhotsk ( $C_L = 2.6$  nM,  $\log K'_{ZnL,Zn^{2+}} = 9.5$ ) and the Sea of Japan (East Sea) ( $C_L = 1.3$  nM,  $\log K'_{ZnL,Zn^{2+}} = 9.1$ ) compared with those in the open ocean (sub-tropical and subarctic North Pacific,  $C_L = 0.2$ – $1.2$  nM,  $\log K'_{ZnL,Zn^{2+}} = 9.1$ – $10.8$ ). The fraction of  $Zn_{labile}$  in the deep waters of the Sea of Okhotsk was relatively small (34–38%, > 1479 m), which might indicate the presence of high concentrations of Zn complexing ligands in deep waters of the Sea of Okhotsk. In the western North Pacific, positive relationships were obtained between total ligand and chlorophyll *a* concentrations, suggesting that Zn complexing ligands in the surface water might be derived from bacteria and phytoplankton in the western North Pacific. However, relatively high concentrations of the ligands exist in low chlorophyll-*a* surface water in the Sea of Okhotsk and the Sea of Japan (East Sea), implying that Zn complexed ligands in those marginal seas have a different origin.

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## 1. Introduction

Zinc (Zn) is used in numerous enzyme systems involved with a range of metabolic processes (Vallee and Auld, 1990). In the ocean, total dissolved Zn has a nutrient-like vertical profile with strong correlations in particular with silicate (Bruland, 1980). However, previous study suggests that zinc is not involved in silicon uptake or in silicon transporter proteins (Thamatrakoln and Hildebrand, 2008). Ellwood and Hunter (2000) also showed that biogenic opal has low Zn content suggesting that zinc is not directly involved with silicon uptake and the amount of Zn incorporated into opal represents only 1–3% of the total amount of Zn taken up by diatoms. Low Zn concentrations could limit CO<sub>2</sub> uptake and ultimately the growth rate in some cells through reduced production of the enzyme carbonic anhydrase (CA) (Lane and Morel, 2000; Morel et al., 1994; Price and Morel, 1990). Low rates of phosphate uptake from dissolved organic phosphorus in oligotrophic waters have been linked to the limitation of available Zn in seawater via its central role in the enzyme alkaline phosphatase (Shaked et al., 2006). At high concentrations, Zn could be toxic to phytoplankton and bacteria (Chen et al., 2008; Sunda and Huntsman, 1996, 1998), but Zn concentrations in surface seawater could be biolimiting for

phytoplankton growth (Brand et al., 1983; Sunda and Huntsman, 1998, 2000), although Zn limitation has not been observed in field studies (Coale et al., 2003; Crawford et al., 2003; Jakuba et al., 2012; Lohan et al., 2005).

In most surface waters, natural organic ligands strongly bind Zn and dominate the speciation of the total Zn pool. Organic complexation reduces the fraction of free metal ion ( $Zn^{2+}$ ) to a level as low as 1 pM (Bruland et al., 1991; Ellwood and Van den Berg, 2000). Culture experiments have shown that a  $Zn^{2+}$  concentration of less than 1 pM limits the growth of some phytoplankton species (Brand et al., 1983; Sunda and Huntsman, 1992, 1995). Therefore, the study of Zn speciation is important for understanding biogeochemical cycling of Zn in the ocean. In the open oceans, studies of zinc complexation in surface water of the North Pacific and North Atlantic reveal that greater than 95% of zinc is complexed to organic ligands (Bruland, 1989; Donat and Bruland, 1990; Ellwood and Van den Berg, 2000; Jakuba et al., 2012), while Zn predominated as inorganic Zn in both surface and deep water of the Southern Ocean (Baars and Croot, 2011). In the marginal seas, although there are few studies, relatively high total ligand concentrations and relatively low conditional stability constants ( $K'_{ZnL,Zn^{2+}}$ ) reveal in the surface waters of the Black Sea (Muller et al., 2001) and Bering Sea (Jakuba et al., 2012) compared with those in the open ocean. The main source of Zn complexing ligands could be humic substances (Campbell et al., 2002), phytoplankton and bacteria-excreted organic

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substances (Bruland, 1989) and pore waters from estuarine marine sediments (Skrabal et al., 2006). However, more Zn speciation studies are needed to unravel sources and identities of Zn ligands.

This study presents total dissolved Zn concentrations and Zn speciation in the western subtropical and subarctic North Pacific and the adjacent Sea of Okhotsk and Sea of Japan (East Sea), using competitive ligand equilibration–adsorptive cathodic stripping voltammetry (CLE–ACSV) to characterize organic Zn complexing ligands and their influence on the chemical speciation of Zn.

## 2. Methods

### 2.1. Sample collection and storage

Seawater samples were collected in the western subarctic North Pacific, Sea of Okhotsk and Sea of Japan (East Sea) during R/V Hakuho-maru research cruises KH-10-2 (in June and July 2010, at stations CR-27, CR-30 and CR-47) and R/V Hakuho-maru research cruise KH-12-4 (from August to October 2012, at stations BD-7 and BD-11). Additional samples were collected in the western subtropical North Pacific (in December 2011, at Stn. 2) during R/V Hakuho-maru research cruise KH-11-10. Locations of the sampling stations are indicated in Fig. 1.

Detailed sampling methods are described elsewhere (Kim et al., 2015). Briefly, seawater samples were collected using acid-cleaned Teflon-coated X-type Niskin samplers. O-rings, inside the Niskin samplers, and spigots were replaced with Viton ones and Teflon ones, respectively. X-type Niskin bottles were cleaned using a 1% alkaline surfactant (Extran MA01), 0.1 M HCl (Special Grade, Wako Pure Chemical Industries) and Millipore Milli-Q water (MQW). The acid-cleaned Teflon-coated X-type Niskin bottles were then deployed on a conductivity–temperature–depth carousel multi-sampling system (CTD–CMS, SBE-911plus and SBE-32 water sampler, Sea Bird Electronics, Inc.), on which a Zn sacrificial anode was replaced with an Al one to avoid the possibility of Zn contamination from the frame. For sub-sampling from the Niskin-X bottles, the bottles were detached from the CTD–CMS frame and carefully moved into a clean space (filled with air that had

been passed through a HEPA filter) in the onboard laboratory of the research vessel. Seawater samples were filtered using an acid-cleaned (0.1 M HCl) 0.2- $\mu\text{m}$  Acropak filter cartridge (PALL Co.) directly connected to the Niskin-X Teflon spigot. Filtered samples were stored in acid-cleaned 500-mL low-density polyethylene (LDPE) bottles (Nalgene Co., Ltd.) after rinsing at least three times with filtered seawater. Samples were then acidified to achieve a pH of <1.8 by using ultra pure HCl (Tamapure AA-100, Tama Chemicals) and then placed in storage for later measurement of total dissolved Zn concentration. The filtered samples for Zn speciation analysis were frozen immediately after collection and kept frozen until just before analysis.

### 2.2. Total dissolved Zn analysis

Total dissolved Zn ( $C_{\text{Zn}}$ ) concentrations in seawater were determined using cathodic stripping voltammetry (CSV) (Donat and Bruland, 1990; Ellwood and Van den Berg, 2000; Kim et al., 2015; Lohan et al., 2002; Van den Berg, 1985). In this study, the 757 VA Computrace (Metrohm) voltammetric system was used. The reference electrode was Ag/saturated AgCl, 3 M KCl. The counter electrode was made of glassy carbon, and the working electrode was a hanging mercury drop electrode (HMDE). To decompose interfering dissolved organic matter (DOM) and metal complexing organic ligands, which occur naturally in seawater (Van den Berg, 1985), a UV irradiation system was used (Kim et al., 2015). In this study, seawater samples were UV-irradiated over 40 min to ensure the full break down of naturally occurring DOM using a high-pressure mercury vapor UV lamp (UM-453B-A, USHIO). The sample solution was kept cold using ice to prevent water evaporation during the UV-irradiation.

Following UV-irradiation, 10 mL of seawater was added into a Teflon cell with 100  $\mu\text{M}$  ammonium 1-pyrrolidinedithiocarbamate (APDC), and 2 mM buffer solution piperazine-1,4-bis (2-ethanesulfonic acid) (PIPES). The pH values of the samples were adjusted to 7.0 by adding ultra pure  $\text{NH}_3$  (Tamapure AA-100, Tama Chemicals). In the Teflon cell, Zn was complexed with APDC (Zn–PDC) and absorbed onto the HMDE. The potential of the electrode was scanned in the negative

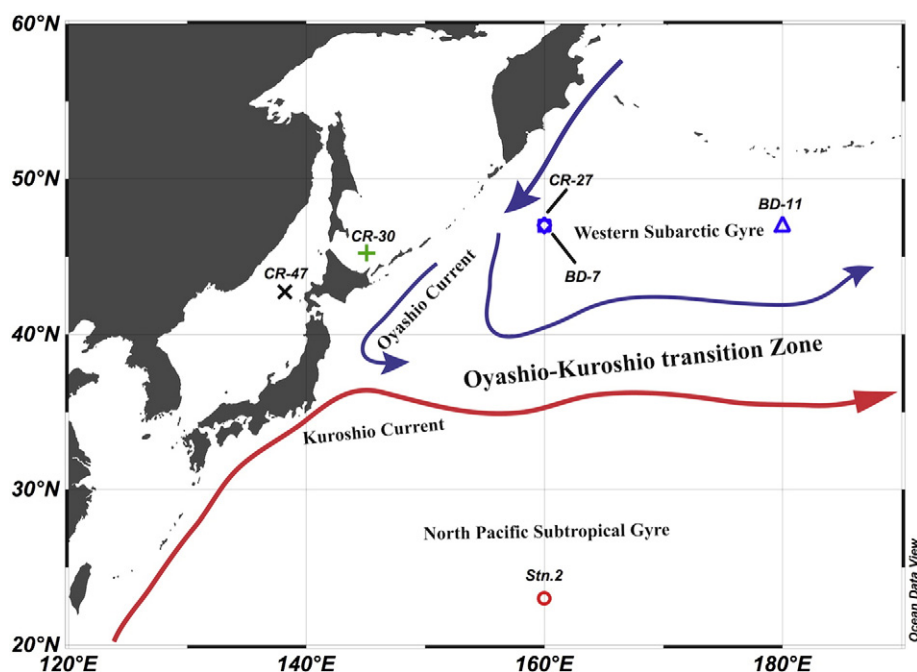


Fig. 1. Location of sampling stations in the subtropical North Pacific (Stn. 2, red), subarctic North Pacific (CR-27, BD-7 and BD-11, blue), Sea of Okhotsk (CR-30, green) and Sea of Japan (East Sea) (CR-47, black). Schematic illustration of the near-surface current is described based on Yasuda (2003).

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