

# Decoupling of zinc and silicic acid in the subarctic northeast Pacific interior

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## ABSTRACT

Zinc (Zn) is an essential micronutrient for marine phytoplankton that plays a role in regulating community composition and may limit primary productivity in localized regions. Depth profiles of dissolved Zn throughout the world ocean are tightly correlated with dissolved silicic acid (Si). New and previously published data from the subarctic northeast Pacific show a decoupling of dissolved Zn and Si. Waters above 400–500 m depth are characterized by elevated Zn compared to Si and the global average. The oxygen deficient zone of the subarctic northeast Pacific is characterized by a dissolved Zn:Si trend with slopes below the global average. The deficit of Zn relative to Si in the oxygen-depleted water column is consistent with a specific removal process for dissolved Zn in the subarctic northeast Pacific oxygen deficient zone. We propose that this data adds to a growing body of evidence implicating the formation of solid Zn sulfides in low oxygen, particle-associated microenvironments as an important loss term in the oceanic Zn budget. Time series data indicate that dissolved oxygen concentrations are diminishing in the ocean interior, expanding and intensifying oxygen deficient zones, and model results predict this trend will continue in the future. An oxygen-sensitive removal process affecting dissolved Zn may impact global ocean productivity and carbon cycling due to the role of Zn in regulating community composition and even total primary productivity in select regions.

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## 1. Introduction

Zinc (Zn) is a biologically important trace metal with a nutrient type distribution and a strong correlation to dissolved silicic acid (Si) concentration in seawater (Bruland et al., 1978; Bruland and Lohan, 2006). As with other nutrient type trace metals, dissolved Zn is depleted and strongly complexed in surface waters by a dynamic pool of organic ligands (~98%) (Bruland, 1989) that can exhibit production and consumption cycles on time scales less than one day (Lohan et al., 2005). The sources, sinks and lability of these ligands are poorly understood (Bruland and Lohan, 2006). While laboratory-based experiments with phytoplankton isolates maintained in culture have shown that Zn may act as a limiting nutrient (Anderson et al., 1978; Brand et al., 1983; Tortell and Price, 1996; De La Rocha et al., 2000; Shaked et al., 2006), field evidence of Zn limitation in marine microalgae is scarce, with only a few clear examples of community composition regulation (Crawford et al., 2003) and total primary productivity limitation (Franck et al., 2003; Jakuba et al., 2012) in the literature.

Zinc correlates strongly with Si, generally showing a deeper remineralization signal than the other macronutrients nitrate ( $\text{NO}_3^-$ ) and phosphate ( $\text{PO}_4^{3-}$ ) as well as other biologically utilized trace metals

like cadmium (Cd) (Bruland et al., 1978; cf. GEOTRACES, 2014). The reasons for this Zn–Si correlation are not entirely clear and while some Zn may be found associated with diatom frustules (i.e. ‘hard parts’), the vast majority of Zn in biological particles is found associated with nitrogen (N) and phosphorus (P) in organic tissues (i.e. ‘soft parts’) in marine algae (Ellwood and Hunter, 2000; Twining et al., 2003; Twining and Baines, 2004). As Zn is associated with N and P intracellularly, it would follow that remineralization of organic matter would release Zn in concordance with macronutrients  $\text{NO}_3^-$  and  $\text{PO}_4^{3-}$  and trace metals such as Cd rather than the observed deeper remineralization signal of Zn matching ‘hard part’ associated elements like Si. John and Conway (2014) have recently shown that while Zn is remineralized from the particulate phase to the dissolved pool concurrently with Cd in cultured plankton, Zn is reversibly re-adsorbed onto particles, temporarily re-entering the particulate phase. This may explain the incongruity between the intracellular co-location of Zn and other organic phase macro- and micro-nutrients and their disparate respective oceanic depth profiles. Deeper apparent remineralization of Zn may also reflect an association with more refractory organic matter that degrades more slowly than average cellular organic matter (Lohan et al., 2002), or the coupling may be driven by some other currently unidentified mechanism.

Zinc is one of several ‘class B’ metals (following the distinction of Jacobs and Emerson, 1982) which form highly insoluble sulfides (approximate  $K_{sp}$  for ZnS (sphalerite) =  $10^{-18.47}$ ,  $\text{ZnS} + \text{H}_2\text{S} \leftrightarrow \text{Zn}^{2+} + 2\text{HS}^-$

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(Daskalakis and Helz, 1993)). These metals (including Cd, copper (Cu), and silver (Ag) in addition to Zn) are known to be depleted below oxic–anoxic boundaries of fjords, inlets, and seas with restricted circulation and ventilation due to the formation of solid metal sulfides (Jacobs and Emerson, 1985). While sulfidic regions are not generally observed in the open ocean – though measurable hydrogen sulfide has been found in the oxygen-depleted waters of the eastern tropical South Pacific (ETSP) (Schunck et al., 2013) – large volumes of oxygen depleted water, called oxygen deficient zones (ODZs), exist in the ocean interior. Although there is generally still measurable oxygen ( $O_2$ ) and no measurable free sulfide in these ODZs, a complex and active community of sulfate reducing and sulfide oxidizing bacteria exists in water column ODZ environments presenting a sulfide source (Canfield et al., 2010; Stewart, 2011; Wright et al., 2012; Podlaska et al., 2012; Johnston et al., 2014). Regions with less than  $50 \mu\text{mol kg}^{-1}$  dissolved  $O_2$  account for approximately 1.0–4.6% of the ocean's volume (Bianchi et al., 2012). These ODZs are found at nearly basin-wide scales in the eastern tropical Pacific, the subarctic northeast Pacific, and the Indian Ocean and in localized upwelling regions off the coast of Mauritania as well as Namibia and Angola in the eastern Atlantic. Time series data show that oxygen depleted regions are expanding spatially while the degree of  $O_2$  depletion itself is intensifying (Whitney et al., 2007; Stramma et al., 2010; Keeling et al., 2010) and model projections predict that this will continue in the future (Shaffer et al., 2009; Keeling et al., 2010).

We report data from Line P, a time series transect beginning at  $48.5^\circ\text{N}$   $125.5^\circ\text{W}$  and extending westward off of the continental shelf of Vancouver Island, BC to Ocean Station PAPA/P26 ( $50^\circ\text{N}$   $145^\circ\text{W}$ ) in the subarctic northeast Pacific (Fig. 1). Surface waters in this region are influenced by the North Pacific Current, having both subtropical and subarctic components (Whitney et al., 2007). Isopycnal surfaces along Line P shoal slightly heading westward (offshore) along the transect and a permanent halocline is observed at around 100–150 m depth (Crawford et al., 2007). Density surfaces found at depths  $\sim 200$  m along the Line P transect may outcrop periodically in the subarctic northwest Pacific in the East Kamchatka and Oyashio Currents but depths below do not ventilate in the open North Pacific (Ono et al., 2001; Shcherbina et al., 2003; Mecking et al., 2006; Whitney et al., 2007). The density range corresponding with North Pacific Intermediate Water (NPIW,  $\sigma_\theta = 26.5\text{--}27.0$ , Talley, 1993) is found at  $\sim 150\text{--}500$  m depth; however the Line P transect lies near the eastern extent of

NPIW (Talley, 1993) and a prominent salinity minimum is not observed along the transect (Line P hydrographic data has been made by the Institute of Ocean Sciences (Sidney, BC) at <https://www.waterproperties.ca/linep/index.php>). Below this depth range, the subarctic North Pacific has a pronounced ODZ which is strongest along the eastern margin and weakens heading westward (Whitney et al., 2007). At a depth of approximately 400 m [ $O_2$ ] falls below  $50 \mu\text{mol kg}^{-1}$ , reaching minimum values of  $<10\text{--}20 \mu\text{mol kg}^{-1}$  near 900–1000 m depth before increasing, reaching  $50 \mu\text{mol kg}^{-1}$  again near 1900 m depth. At more coastal stations, the transect receives the northern reach of the California Undercurrent (Thomson and Krassovski, 2010). Surface and near-surface waters ( $\leq 200$  m depth) of the Line P transect have previously been sampled for Zn, providing information about seasonal and onshore–offshore trends in Zn in the upper water column (Lohan et al., 2002). Additionally, the VERTEX T transect, intersecting the Line P transect at station T7/Ocean Station Papa/P26, has been sampled for Zn to a depth of  $\sim 1500$  m (T5, T6, T8 and T9) and 3910 m (T7/P26) (Martin et al., 1989).

## 2. Methods

### 2.1. Sample collection and sampling site

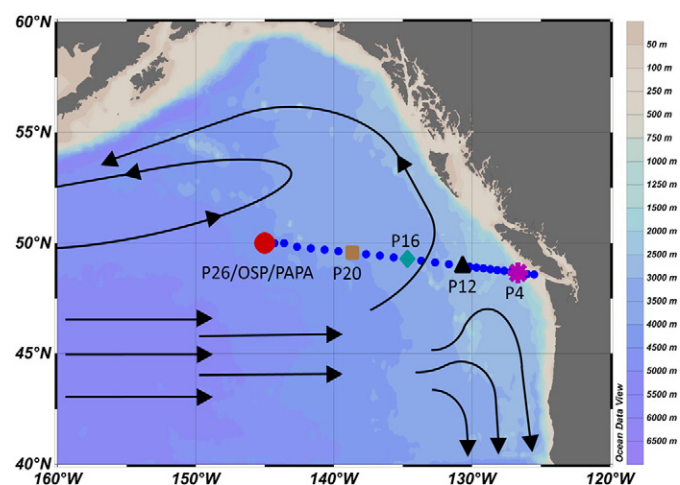
The Line P transect (Fig. 1) was sampled between August 14th and 30th 2012 (cruise 2012–13) on board the CCGS *J.P. Tully*. Sample and reagent bottles were cleaned according to GEOTRACES protocols. Samples for Zn determination were collected using a 12 bottle powder coated trace metal clean rosette system modified according to Measures et al. (2008) equipped with 12 L Teflon-coated GO-FLO (General Oceanics, FL USA) bottles. The GO-FLO bottles were gravity filtered through  $0.2 \mu\text{m}$  AcroPak filters (Pall Corporation). Samples were acidified to  $\text{pH} = 1.7$  with  $12 \text{ mol L}^{-1}$  HCl (SeaStar Chemical) after collection and stored for at least 6 h before analysis. Unfiltered samples for Si,  $\text{NO}_3^-$  and  $\text{PO}_4^{3-}$  were analyzed according to Barwell-Clarke and Whitney (1996). Dissolved  $O_2$  data was obtained with a Seabird SBE43 dissolved oxygen sensor calibrated against Winkler titrations. Nutrient and  $O_2$  data are courtesy of the Line P Program (Chief Scientist Marie Robert, Institute of Ocean Sciences, Canada).

### 2.2. Zinc analysis

Zinc samples were analyzed at sea with a flow injection method, shown in Fig. 2, based on Nowicki et al. (1994) utilizing the fluorescent binding ligand p-tosyl-8-aminoquinoline (p-taq) (Chemica Inc., Los Angeles CA, USA). The methodology of Nowicki et al. (1994) was followed with the following modifications: pre-acidification and on-line buffering of samples, changing the chelating resin to a commercially available resin which eliminates Cd interference, and minor changes in the p-taq buffer solution and elution acid strength.

Reagents and samples were pumped using an eight channel peristaltic pump (Rainin Dynamax) at a pump speed of 9.50 RPM and flow was directed using 6 and 12 port injection valves (Valco Instruments Co. Inc., Cheminert). FlowZf software (Global FIA) was used to control the injection sequence and record fluorescence. Fluorescence was measured using a Shimadzu RF-535 fluorometer connected to a data acquisition module (Omega). PVC 2 stop pump tubing (Fisher) was used as follows: sample line, rinse line and p-taq buffer lines coded yellow–blue (1.52 mm id), elution line coded orange–orange (0.89 mm id), on-line buffer line coded black–black (0.76 mm id).

Acidified samples ( $\text{pH} = 1.7$ ) were buffered online to  $\text{pH} = 4.3$  using an  $0.50 \text{ mol L}^{-1}$  ammonium acetate ( $\text{NH}_4\text{Ac}$ ) buffer and an 80 cm mixing coil (type KOT2 from Selavka et al., 1987) and loaded onto a 2 cm mini column (Global FIA) of NTA Superflow resin (Qiagen). Samples below 150 m depth were loaded for 2 min and samples above 150 m were loaded for 4 min. Previous applications of this method were susceptible to a Cd interference via a fluorescent p-taq complex with



**Fig. 1.** The Line P transect. The Line P transect, extending westward off of Vancouver Island, British Columbia Canada is shown with all stations in blue and with major stations for which trace metal data was collected labeled and in larger colored symbols (P4 as a purple star, P12 as a black triangle, P16 as a light blue diamond, P20 as a brown square and P26/OSP as a red dot). Surface currents are adapted from Whitney et al. (2007) and Freeland (2007). The small scale structure of the currents near the margins and the degree to which subtropical origin North Pacific Gyre water reaches the Line P transect is variable year to year (e.g. Cummins and Freeland, 2007; Freeland, 2006).

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