Dissolved zinc in the subarctic North Pacific and Bering Sea: Its distribution, speciation, and importance to primary producers

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[1] The eastern subarctic North Pacific, an area of high nutrients and low chlorophyll, has been studied with respect to the potential for iron to control primary production. The geochemistry of zinc, a critical micronutrient for diatoms, is less well characterized. Total zinc concentrations and zinc speciation were measured in near-surface waters on transects across the subarctic North Pacific and across the Bering Sea. Total dissolved zinc concentrations in the near-surface ranged from 0.10 nmol L^{-1} to 1.15 nmol L^{-1} with lowest concentrations in the eastern portions of both the North Pacific and Bering Sea. Dissolved zinc speciation was dominated by complexation to strong organic ligands whose concentration ranged from 1.1 to 3.6 nmol L^{-1} with conditional stability constants ($K'_{ZnL/Zn'}$) ranging from $10^{9.3}$ to $10^{11.0}$. The importance of zinc to primary producers was evaluated by comparison to phytoplankton pigment concentrations and by performing a shipboard incubation. Zinc concentrations were positively correlated with two pigments that are characteristic of diatoms. At one station in the North Pacific, the addition of 0.75 nmol L^{-1} zinc resulted in a doubling of chlorophyll after 4 days.

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1. Introduction

[2] Surface macronutrient concentrations (nitrate, phosphorus, silicate) in the subarctic N. Pacific are not depleted by phytoplankton growth [*McAllister et al.*, 1960], leading to its characterization as a high nutrient, low chlorophyll (HNLC) region. Surface concentrations of iron (Fe) in this region are very low (e.g., 0.06 nmol L^{-1}) [*Martin et al.*, 1989]. Additions of Fe to both bottle incubations [*Martin and Fitzwater*, 1988; *Coale*, 1991; *Boyd et al.*, 1996; *Lam et al.*, 2001; *Crawford et al.*, 2003; *Leblanc et al.*, 2005] and mesoscale ocean patches [*Tsuda et al.*, 2003; *Boyd et al.*, 2004; *Marchetti et al.*, 2006] have demonstrated the ability of Fe to regulate primary production in this region.

[3] Zinc (Zn) concentrations are also very low in the surface waters of the subarctic N. Pacific [*Bruland et al.*, 1978; *Martin et al.*, 1989; *Lohan et al.*, 2002]. Though Zn is an important micronutrient for phytoplankton, the role of Zn in limiting marine primary production is not as clear as that of Fe. Low Zn concentrations can limit phytoplankton growth in cultures [*Anderson et al.*, 1978; *Brand et al.*, 1983; *Morel et al.*, 1991]. Though similarly low Zn concentrations are found in the open ocean, unlike Fe, Zn additions to bottle experiments generally have had little or no effect on total chlorophyll biomass [*Coale*, 1991; *Coale et al.*, 1996; *Scharek et al.*, 1997; *Gall et al.*, 2001; *Coale et al.*, 2003; *Crawford et al.*, 2003; *Franck et al.*, 2003; *Ellwood*, 2004; *Lohan et al.*, 2005; *Leblanc et al.*, 2005], with the exception of Fe-Zn (and Fe-Co) co-limitation observed at the Costa Rica Upwelling Dome [*Franck et al.*, 2003, Table 7; *Saito et al.*, 2005]. The few observations of a primary productivity increase in response to Zn addition is likely due in part to the ability of some phytoplankton to substitute cobalt (Co) and cadmium (Cd) for Zn in enzyme systems [e.g., *Lee et al.*, 1995; *Yee and Morel*, 1996]. Some phytoplankton can also substitute non-Fe containing proteins [*LaRoche et al.*, 1996] or copper containing proteins [*Peers and Price*, 2006] to alleviate Fe stress when Fe concentrations are low. The low solubility of Fe at oceanic pH precludes there being a large reservoir of Fe in deep waters in the same way that there is for classic 'nutrient-type' trace metals such as Zn. The reduced deep source of Fe compared to Zn likely contributes to the greater prevalence of observed Fe limitation in the world's oceans.

[4] Co is preferentially utilized over Zn by some phytoplankton species or vice versa [*Sunda and Huntsman*, 1995;

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Saito et al., 2002; *Xu et al.*, 2007; *Saito and Goepfert*, 2008], which suggests that the ratio of Zn to Co may influence species composition in the ocean [*Sunda and Huntsman*, 1995]. While this hypothesis has not been explicitly tested, the ability of Zn to influence species composition has been shown. In an incubation in the eastern subarctic N. Pacific, the addition of Zn and Fe together (+Zn/+Fe) resulted in a higher proportion of phytoplankton in the smaller size fraction (0.2–5 μm) compared to the addition of Fe alone [*Crawford et al.*, 2003]. The community in the +Zn/+Fe addition had a higher abundance of small diatoms and small flagellates and less coccolithophores and ciliates than the Fe alone addition [*Crawford et al.*, 2003]. Zn may influence not only which taxa dominate but which species within a taxa are most successful. In a bottle incubation experiment in the sub-Antarctic zone near New Zealand, the addition of Zn caused a community shift from a large colonial pennate diatom to a smaller, less-silicified, solitary pennate diatom species [*Leblanc et al.*, 2005].

[5] Zn deficiency can also affect the extent of calcification of *E. huxleyi*, a ubiquitous marine coccolithophore [*Schulz et al.*, 2004]. Under Zn limitation, *E. huxleyi* cells become more heavily calcified due to a slowing of growth rates with no corollary decrease in calcium carbonate ($CaCO_3$) production rate [*Schulz et al.*, 2004]. This effect, along with the potential of Zn to influence species composition, suggests that Zn may be an important determinant of the organic carbon:$CaCO_3$ rain ratio. At low Zn:Co, coccolithophores and small cyanobacteria would be expected to dominate over diatoms based on their growth rates at low Zn:Co [*Sunda and Huntsman*, 1995]. This community shift would decrease the organic carbon:$CaCO_3$ due to coccolithophores' $CaCO_3$ shells. In addition, the coccolithophores growing under low Zn would be more highly calcified than those experiencing replete levels of Zn, further decreasing the organic carbon:$CaCO_3$ rain ratio.

[6] Culture studies with the synthetic ligand ethylenediaminetetraacetic acid (EDTA) have shown that Zn bioavailability is related to the Zn free ion (Zn^{2+}) concentration rather than the total Zn concentration [e.g., *Anderson et al.*, 1978]. Natural organic ligands in the surface ocean strongly bind Zn [*Donat and Bruland*, 1990; *Bruland*, 1989; *Ellwood and van den Berg*, 2000; *Ellwood*, 2004; *Jakuba et al.*, 2008]. These ligands dominate the speciation of the total Zn pool, with Zn^{2+} typically accounting for 5% or less of the total dissolved Zn. The inventory of Zn binding ligands can be extremely dynamic with production and removal of ligands occurring on timescales of 1 day [*Lohan et al.*, 2005]. Zn speciation measurements of shipboard incubation experiments suggest that the phytoplankton community can survive at lower Zn^{2+} than is known to limit some large phytoplankton species in cultures [*Ellwood*, 2004; *Lohan et al.*, 2005]. However, smaller diatoms such as *Thalassiosira oceanica* are able to growth at Zn^{2+} abundances below those that limit larger phytoplankton species [*Sunda and Huntsman*, 1992, 1995] suggesting that low zinc could cause species composition effects or that diatoms under these conditions can meet their Zn requirement by substituting Co or Cd.

[7] This study examines total dissolved Zn concentrations and Zn speciation across the subarctic N. Pacific and Bering Sea and the potential influence of Zn on phytoplankton growth, species composition and nutrient utilization. The eastern part of the subarctic N. Pacific, the Gulf of Alaska, is characterized by low levels of chlorophyll and high nutrient concentrations. Fe fertilization experiments have demonstrated the ability of Fe to regulate primary production in this region [e.g., *Martin and Fitzwater*, 1988; *Boyd et al.*, 2004]. In the western part of the subarctic N. Pacific, there are relatively high rates of atmospheric deposition of Fe [*Duce and Tindale*, 1991] and a high seasonal export by diatoms [*Honjo*, 1997], though portions of Western Subarctic Gyre can also experience Fe limitation [*Suzuki et al.*, 2005]. In this area, the east-flowing North Pacific Current originates from the Kuroshio Extension in the central Pacific. Enhanced vertical mixing events associated with variability in the strength of the North Pacific Current and with eddies of the system can bring nutrient-rich waters to the surface [*Cummins and Freeland*, 2007; *Chu and Kuo*, 2010] which likely contributes to the observed gradient in Zn concentrations from east to west noted by *Fukuda et al.* [2000].

[8] The Bering Sea is split into a deep western basin whose surface waters are characterized by low summertime primary productivity and a wide continental shelf to the east that is highly productive, particularly at the shelf break with decreasing productivity toward the coast [*Springer et al.*, 1996]. There is evidence that the deep western portion of the Bering Sea is an HNLC limited by Fe [*Tyrrell et al.*, 2005; *Aguilar-Islas et al.*, 2007].

2. Methods

2.1. Sample Collection and Handling

[9] Samples were collected in the N. Pacific and Bering Sea aboard the R/V Kilo Moana in the summer of 2003 (Figure 1). Water samples were collected using 10 L Teflon-coated Go-Flos (General Oceanics) on a Kevlar hydrowire. Seawater was collected from the Go-Flo bottles by connecting Teflon tubing to both ports and over-pressuring the top port with filtered ultra-high purity nitrogen gas. Seawater passed directly from Teflon tubing through an all plastic sandwich filter rig with acid-cleaned 0.4 μm, 142 mm diameter polycarbonate membrane filters and into rigorously acid-washed (including sequential soaks in warm Citranox detergent, J.T. Baker Instra-analyzed HCl, J.T. Baker Instra-analyzed HNO_3, and pH 2 Seastar HCl) low density polyethylene (LDPE) or Teflon bottles. Samples for total dissolved Zn analysis (LDPE bottles) were acidified to approximately pH 2 by the addition of 2 mL HCl (Seastar) per liter of seawater. Samples for Zn speciation analysis (Teflon bottles) were stored refrigerated (4°C) until analysis (typically within 10 days). All manipulation of the samples occurred in a laminar flow bench inside clean laboratories.

2.2. Total Dissolved Zn Analysis

[10] Total dissolved zinc (Zn_T) concentrations were measured using isotope dilution and magnesium hydroxide preconcentration followed by analysis using inductively coupled plasma mass spectrometry (ICP-MS) after *Wu and Boyle* [1998] and *Saito and Schneider* [2006]. Centrifuge tubes (15 mL polypropylene, Globe Scientific) were cleaned by soaking in 2N HCl (J.T. Baker instra-analyzed) at 60°C for 48 h followed by rinsing 5 times with pH 2 HCl (J.T. Baker instra-analyzed) and once with pH 2 HCl (Seastar). Finally, tubes were filled to a positive meniscus with pH 2 HCl

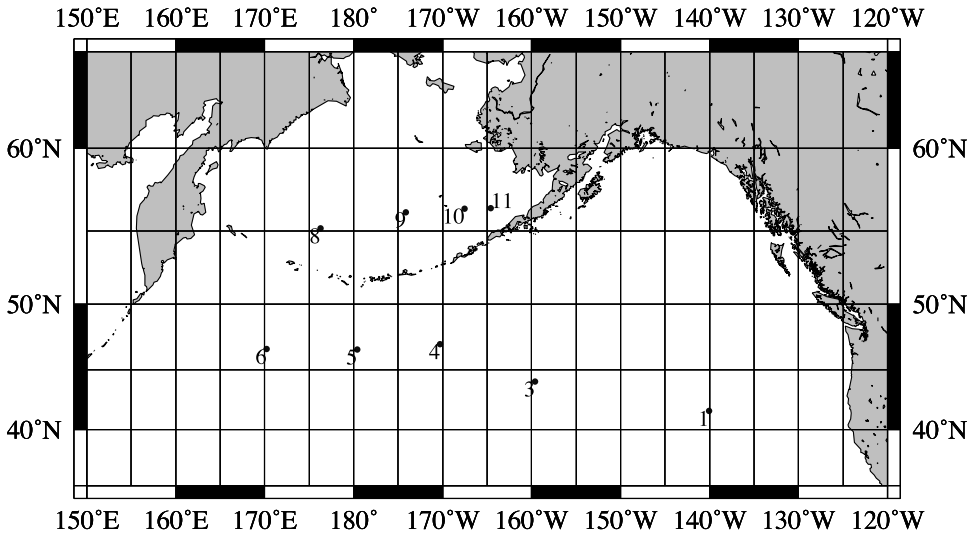

Figure 1. Map of station locations from the North Pacific and Bering Sea visited aboard the R/V *Kilo Moana* in June–August 2003.

(Seastar) and capped until use. At the time of analysis, tubes were rinsed once with sample and then filled to approximately 13.5 mL (exact volume determined gravimetrically). Samples were then spiked with ^{66}Zn (98.9% as ^{66}Zn, Cambridge Isotope Laboratories, Inc.) to an estimated ^{66}Zn:^{64}Zn ratio of 9. This ratio minimizes error magnification [*Heumann*, 1988]:

$$R_{optimum} = \sqrt{\left(\frac{^{66}Zn}{^{64}Zn}\right)_{sample} \times \left(\frac{^{66}Zn}{^{64}Zn}\right)_{spike}}. \quad (1)$$

The added ^{66}Zn spike was allowed to equilibrate with the samples overnight. The following day, 125 μL of ammonia (Seastar) was added to each tube. After 90 s, the tube was inverted and after an additional 90 s, tubes were centrifuged for 3 min at 3000 × g (3861 rpm) using a swinging bucket centrifuge (Eppendorf 5810R). The majority of the supernatant was carefully decanted. Tubes were then respun for 3 min to firm pellet and the remaining supernatant was shaken out. Pellets were dissolved on the day of ICP-MS analysis using 0.5–1.5 mL of 5% nitric acid (Seastar). Zn_T concentrations were calculated as

$$[Zn_T] = \frac{f_{64\,spike}}{f_{64\,natural}} \times [Zn_{spike}] \times \frac{spike\,volume}{sample\,volume} \times \left(\frac{R_{measured} - R_{spike}}{R_{natural} - R_{measured}}\right) \quad (2)$$

where f_{64} is the fraction of the abundance of ^{64}Zn over the abundance of all the Zn isotopes and R is the ratio of ^{66}Zn:^{64}Zn. To measure the procedural blank, 1 mL of low zinc surface seawater was treated the same as samples, and calculations were performed as though it was a 13.5 mL sample (Zn contribution from the 1 mL is considered negligible). The average blank value was 0.12 nmol L^{-1} with a detection limit of 0.09 nmol L^{-1} (calculated as three times the standard deviation of the blank). The daily procedural blank value was subtracted from measured sample values.

[11] The efficiency of the magnesium hydroxide precipitate at scavenging Zn was tested. One mL aliquots of acidified seawater (n = 3) were equilibrated with the radioisotope ^{65}Zn (approximately 0.5 μCi) for 2 h. Thirty μL of ammonia was added to each sample and after 1.5 min, the samples were centrifuged for 3 min. The amount of ^{65}Zn was quantified in the seawater before precipitation, in the precipitate, and in the supernatant using a sodium iodide detector. The percent of ^{65}Zn that was captured, on average, by the magnesium hydroxide pellet was 96% and the fraction remaining in the supernatant was 2%. The accuracy of the method was evaluated by measuring a NASS-5 seawater standard (National Research Council of Canada). The NASS standard has a certified value of 1.56 ± 0.60 nmol L^{-1} Zn. The value obtained by this method (1.00 ± 0.03 nmol L^{-1}) was within the specified range of the certified value.

[12] ICP-MS measurements were made using a Thermo Finnigan ELEMENT2 in medium resolution mode, which was sufficient to resolve ^{64}Zn from the potential interference peak due to Mg-Ar. Another potential interference at mass 64 is that of ^{64}Ni, which is a minor isotope of Ni (natural abundance of less than 1%). This interference was not measured explicitly. In many cases, the contribution of the mass 64 signal due to Ni will not be significant relative to ^{64}Zn, however at the lowest Zn concentrations measured here, the contribution due to Ni may be significant. Total dissolved Ni concentrations were measured in this study using voltammetric methods (see below). The potential influence of the ^{64}Ni on the Zn_T concentrations calculated here is discussed in the Results section.

2.3. Total Dissolved Ni Analysis

[13] Total dissolved nickel (Ni) was also measured here as described in *Saito et al.* [2005]. Briefly, a Metrohm 663 hanging mercury drop electrode stand with a Perfluoroalkoxy Teflon (PFA) sample vessel was interfaced with an Eco-chemie μAutolab system and GPES (General Purpose Electrochemical System, Eco Chemie) software. Dimethylglyoxime (DMG) from Aldrich was recrystallized in Milli-Q (Millipore) water in the presence of 10^{-3} ethylenediaminetetraacetic acid (EDTA; Sigma Ultra) to remove impurities, dried, and redissolved in high performance liquid

chromatography (HPLC)-grade methanol. We prepared 1.5 mol L^{-1} sodium nitrite (Fluka Puriss) purified by an overnight equilibration with prepared Chelex-100 beads (BioRad). An N-(2-hydroxyethyl)piperazine-N′-(3-propanesulfonic acid) (EPPS) buffer solution (Fisher) was purified by passing through a column with 3 mL of prepared Chelex-100 beads. For total dissolved nickel analyses, 8.50 mL of ultraviolet light irradiated filtered seawater was pipetted into the Teflon sample cup followed by 50 μL of 0.5 mol L^{-1} EPPS, 20 μL 0.1 mol L^{-1} DMG, and 1.5 mL of 1.5 mol L^{-1} sodium nitrite. The μAutolab protocol involved a 3-min 99.999% N_2 gas purge at 120 kPa, a 90-s deposition time at −0.6 V, a 15-s equilibration period, and a high-speed negative scan from −0.6 to −1.4 V at 10 V s^{-1}. A linear sweep waveform was used on drop size three (0.52 mm^2) and a stirrer speed of five. Total nickel concentrations were determined with three standard additions of 1 nmol L^{-1} using a $NiCl_2$ solution prepared in pH 2 Milli-Q water.

2.3. Zn Speciation Determinations

[14] Zn speciation was determined using an anodic stripping voltammetry method [*Jakuba et al.*, 2008] that was adapted from that of *Fischer and van den Berg* [1999] for the measurement of total lead and cadmium. Measurements were made using a 663 VA stand (Metrohm) consisting of a glassy carbon rotating disc working electrode (2 mm diameter), a glassy carbon rod counter electrode, and a double junction Ag, AgCl, saturated KCl reference electrode. The electrode was interfaced to a PC (IBM Thinkpad) using an IME663 and μAutolab I (Eco Chemie). Before each day of speciation analysis, the glassy carbon rotating disc electrode (RDE) was manually polished with aluminum oxide. Then, a cyclic voltammetry step was performed cycling the voltage between −0.8 V and 0.8 V 50 times. Reagents used included 4-(2-Hydroxyethyl)-1-piperazinepropanesulfonic acid (EPPS), ammonium thiocyanate, and mercuric chloride. The pH of the EPPS buffer was adjusted to 8.1. EPPS and thiocyanate reagents were run through a pre-cleaned chelex column [*Price et al.*, 1989] to remove trace metal contamination. The thiocyanate reagent is added to improve the reproducibility of the mercury film and to ensure full de-plating of the film between samples [*Fischer and van den Berg*, 1999].

[15] Zn speciation titrations were set up in 15 mL Teflon vials (Savillex). In order to prevent wall loss, Teflon vials were equilibrated with specific concentrations of Zn before use and each vial was always used for the same concentration of Zn. Before a titration, the vials were rinsed with 12 mL of sample. Then, 12 mL of sample was added into each vial, along with 1.7 mmol L^{-1} EPPS. For each sample aliquot, the appropriate concentration of Zn was allowed to equilibrate with the sample in the sample vial for 10 min. Then, the sample aliquot was poured into the voltammetric cell and 4.2 mmol L^{-1} ammonium thiocyanate and 10.4 μmol L^{-1} mercuric chloride were added. Each sample aliquot was purged with ultra-high purity nitrogen gas for 5 min to remove oxygen. A conditioning potential of 0.6 V was held for 60 s. The mercury film and Zn′ were then deposited at a potential of −1.5 V for 180 s. After a 10 s equilibration time, the voltage was ramped in square wave mode from −1.3 V to 0.6 V. A frequency of 50 Hz was used and the step potential and modulation amplitude were 4.95 mV and 49.95 mV, respectively. A peak in current was evident at −1.1 V representing the concentration of inorganic Zn species (Zn′). The total ligand concentration ($[L_T]$) and conditional stability constant ($K'_{cond,Zn'}$) with respect to Zn′ were calculated by performing a linearization of the titration data [*Ružić*, 1982; *van den Berg*, 1982], where [Zn′]/[ZnL] is plotted versus [Zn′]. The equation for the resulting line is

$$\frac{[Zn']}{[ZnL]} = \frac{[Zn']}{[L_T]} + \frac{1}{\left(K'_{cond,Zn'} \times [L_T]\right)} \quad (3)$$

Hence, $[L_T]$ can be calculated as $\frac{1}{slope}$ and $K'_{cond,Zn'}$ as $\frac{1}{([L_T] \times \text{y-intercept})}$. The Zn^{2+} concentrations in Table 1 were calculated based on the relationships:

$$K'_{cond,Zn'} = \frac{[ZnL]}{[Zn'][L']} \quad (4)$$

$$[Zn'] = \alpha_{Zn} \times \left[Zn^{2+}\right] \quad (5)$$

$[Zn']$ was calculated from equation 3, assuming that $[L]_T - [Zn]_T = [L']$ and that $[ZnL] = [L]_T - [L']$. A value of 2.2 was used for α_{Zn} [*Turner et al.*, 1981].

2.4. Shipboard Incubation

[16] Trace metal clean water was collected with an air-driven Teflon pump that pumped water from approximately 15 m depth directly into an acid-washed HDPE carboy, housed in a trace-metal free bubble constructed of a HEPA filter and plastic sheeting. Acid-washed polycarbonate bottles were filled with unfiltered seawater from the carboy. A time zero sample for chlorophyll *a* was also collected from the carboy. Additions were made to duplicate polycarbonate bottles as follows: control (no addition), +Fe (2.5 nmol L^{-1} $FeCl_3$), +Zn (0.75 nmol L^{-1} $ZnCl_2$), +Zn/+Fe (0.75 nmol L^{-1} $ZnCl_2$, 2.5 nmol L^{-1} $FeCl_3$). Bottles were tightly capped and placed in an on-deck water bath supplied with flowing seawater for temperature control. Sunlight was attenuated with bluegel shading (Roscolux 65: Daylight Blue, Stage Lighting Store) to mimic 15 m irradiances. On days 2 and 4, one bottle was removed from the incubator and sampled for chlorophyll. In order to avoid potential contamination by Zn, which is a highly contamination prone element, bottles were sacrificed upon sampling. Samples for analysis of dissolved nutrients from select bottles were also collected, filtered, and frozen.

2.5. Chlorophyll, Nutrients, and HPLC Pigments

[17] For chlorophyll *a* analysis, seawater was passed through a GF/F filter. Filters were extracted in 90% acetone overnight at −20°C. Chlorophyll *a* (Chl*a*) concentrations were corrected for the interference of phaeophytin by the addition of acid. All samples for nutrient analysis were filtered through the trace metal filtration rig described above into acid-cleaned polypropylene tubes and stored frozen until analysis. Analysis was performed by the Ocean Data Center (ODC) at the Scripps Institution of Oceanography for nitrate, nitrite, ammonium, silicic acid, and phosphate. In addition, phosphate analyses were run on board at select

Table 1. Dissolved Zn, SRP, and Ni Data[a]

Station	Dates Occupied	Latitude	Longitude	Depth (m)	Zn_T (nmol L^{-1})	Ni_T (nmol L^{-1})	SRP (μmol L^{-1})	Chl*a* (μg L^{-1})	L_T (nmol L^{-1})	$logK'_{ZnL/Zn'}$	Zn^{2+} (nmol L^{-1})
1	24 Jun–28 Jun 2003	41°60′N	140°06′W	15	0.10 (0.02)[b]	3.3	0.29	0.14	1.1	10.0	0.005
				50	0.35 (0.01)	3.6	**0.33**	0.99			
				75	0.10 (0.02)		**0.48**	0.27	1.6	10.0	0.003
				150	1.99 (0.02)	3.5					
				300	2.80 (0.10)						
				500	6.82 (0.03)	8.3					
				1000	8.89 (0.03)						
				1500	10.30 (0.17)	12.4					
3	4 Jul–5 Jul 2003	44°02′N	159°59′W	20	0.20 (0.03)[b]	4.2	**1.10**	0.37	1.8	10.5	0.002
4	7 Jul–8 Jul 2003	47°01′N	170°30′W	13	0.56 (0.10)	4.0	1.34	0.72			
				26	0.71 (0.06)	5.6	1.35	1.01	2.2	10.5	0.007
				40	0.89 (0.08)	8.0	1.47	0.41	2.3	11.0	0.003
				60	1.24 (0.11)	5.9	**1.63**[c]	0.16			
				100	1.51 (0.01)	6.6	1.57	0.03	2.6	10.1	0.048
				150	5.10 (0.07)	6.1	**2.08**	0.01			
				300	8.57 (0.59)	10.6	2.86				
				500	8.84 (0.14)	9.1	2.23[c]				
				1000	7.95 (0.13)	8.9	2.86				
				1500	10.70 (0.06)	11.9	3.17				
				3000	13.51 (0.04)[d]	11.8	2.20[c]				
5	12 Jul–13 Jul 2003	46°59′N	179°58′W	25	0.65 (0.02)	6.2	1.40	0.81	2.3	10.5	0.006
6	15 Jul 2003	46°60′N	170°20′E	20	0.78 (0.11)	7.5	1.40	0.56	2.5	9.8	0.033
				40	1.66 (0.09)	6.4	1.45		2.7	10.1	0.059
				50	2.39 (0.29)		**1.64**	0.65			
				80	2.73 (0.01)	5.9	**1.74**[c]	0.13			
				150	5.26 (0.02)	7.5	2.33	0.02			
				300	8.52 (0.02)	10.9	3.13				
				500	8.71 (0.10)	13.4					
				1000	9.76 (0.10)		2.23[c]				
				1500	9.58 (0.27)		3.03				
				3000	12.27 (0.19)[d]		2.77[c]				
8	21 Jul–22 Jul 2003	55°18′N	176°31′E	20	0.89 (0.01)	8.2	1.46	0.86	3.6	9.3	0.071
9	24 Jul 2003	56°19′N	174°15′W	20	1.15 (0.02)						
10	26 Jul 2003	56°43′N	167°50′W	14	0.42 (0.05)		**0.31**	0.63			
11	27 Jul 2003	56°45′N	164°60′W	16	0.29 (0.02)[b]	5.1	**0.24**	1.21			

[a]Values in parentheses represent the standard deviation of duplicate or triplicate analyses for Zn_T. The majority of the SRP values were measured from sub-samples collected from Go-Flo bottles. Where sub-samples from Go-Flo bottles were unavailable, values are reported from samples collected from Niskin bottles and measured on-board (bold values).

[b]Potentially high level of Ni interference, see section 3 for details.

[c]Samples where the SRP values measured from the Go-Flo sub-samples did not match expected oceanographic depth trend. When available these values were replaced by SRP measured on-board from Niskin bottles. See section 3 and Figure 4a.

[d]Contamination suspected, see section 3 for details.

stations using the molybdate blue method [*Murphy and Riley*, 1962]. In general, analyses from ODC are used here, except on several occasions where frozen nutrient values were not oceanographically consistent due to preservation problems [*Maher and Woo*, 1998, and references therein] and shipboard analyses were substituted. Besides these few outliers, shipboard and frozen samples compared well. Samples were collected for phytoplankton pigment analysis from Niskin bottles on a CTD rosette frame. Analysis of HPLC pigments was performed after *Bidigare* [1991] and *Bidigare and Trees* [2000].

3. Results

3.1. Total Dissolved Zn

[18] Zn_T was measured in the near-surface at 5 stations in the N. Pacific and 4 stations in the Bering Sea. Zn_T concentrations in the near-surface ranged from 0.10 to 1.15 nmol L^{-1} (Table 1). Concentrations increased from east to west in the North Pacific, in agreement with reports of integrated Zn_T in the upper 100 m of this region [*Fukuda et al.*, 2000]. The Zn_T value at Station 1 (0.10 nmol L^{-1}) is within the range reported for the near-surface in that vicinity (0.06–0.25 nmol L^{-1}) [*Martin et al.*, 1989]. During the SEEDS Fe enrichment experiment, which was performed further west of Station 6 (48.5°N, 165°W), near-surface Zn_T concentrations were even higher than those observed at Station 6 (1.18–2.35 nmol L^{-1}) [*Kinugasa et al.*, 2005], which may indicate that the east–west trend of increasing Zn_T continues beyond our study region.

[19] Near-surface Zn_T concentrations in the Bering Sea were high ($\sim$1 nmol L^{-1}) in the deep western portion of the basin and low in the eastern waters over the Bering shelf. Previous studies of Zn in the Bering Sea have shown elevated Zn_T concentrations at depth (3.5 nmol L^{-1} at 30 m and 20 nmol L^{-1} at 3000 m) in the western Bering Sea [*Fujishima et al.*, 2001], but low surface Zn_T concentrations (<0.41 nmol L^{-1}) [*Fujishima et al.*, 2001; *Leblanc et al.*,

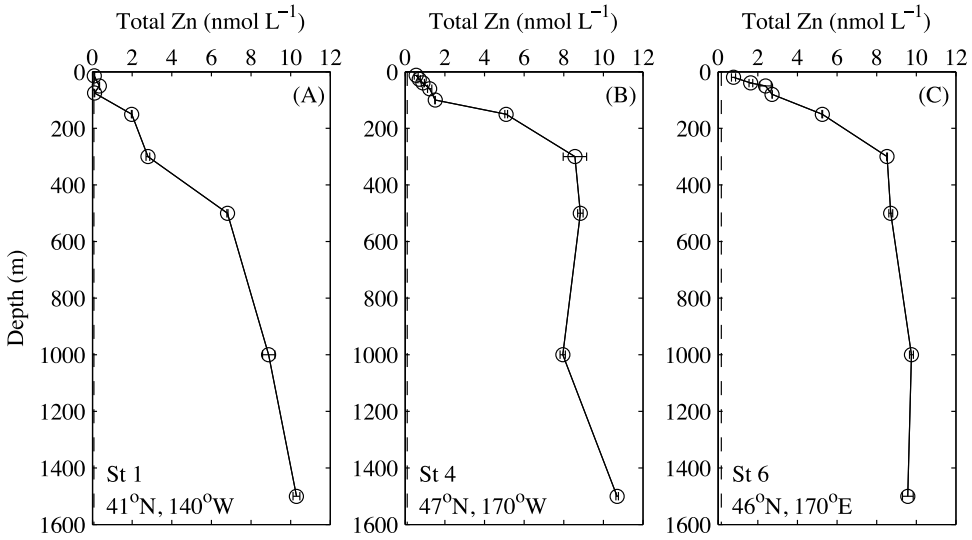

Figure 2. Depth profiles down to 1500 m of total dissolved Zn concentrations from (a) stations 1, (b) 4, and (c) 6. Error bars represent the standard deviation of duplicate or triplicate analyses. Dashed line represents the detection limit.

2005]. At Station 8, the mixed layer was only 15 m, and the SRP concentration at 20 m was 1.56 μmol L^{-1} compared with only 1.25 μmol L^{-1} at the surface. Thus, the high Zn_T at Station 8 is likely a result of sampling below the mixed layer. The mixed layer at Station 9 is about 18–20 m and the near-surface sample from this station was taken from 20 m. Unfortunately, nutrient data is not available for Station 9 to confirm that the high Zn_T value was collected from a depth of active nutrient remineralization. The western Bering Sea can experience high dust inputs from Asian deserts, which may contribute to relatively high Zn concentrations in this area [*Boyd et al.*, 1998; *Nishioka et al.*, 2003]. Lower Zn_T was observed in the eastern Bering Sea on the Bering Shelf where Chl*a* concentrations were high, possibly reflecting biological uptake.

[20] As mentioned in the Methods section, the possible interference of ^{64}Ni contributing to our calculated Zn_T concentrations was not measured explicitly. The Ni_T concentrations in those near-surface samples measured ranged from 3.3 to 8.2 nmol L^{-1} (Table 1). While this Ni_T technique has somewhat variable precision due to Ni's slow kinetic properties and the small mercury drop surface of the Metrohm 663 hanging drop mercury electrode, the surface and deep water values reported here were generally consistent to that reported by *Bruland* [1980] for the Central North Pacific. These Ni concentrations could cause an overestimation of our Zn_T values that was generally less than 10% of Zn_T values; however at the lowest Zn_T values the potential for the Ni interference is more significant. For example, in the near-surface at Station 1, the ^{64}Ni concentration was

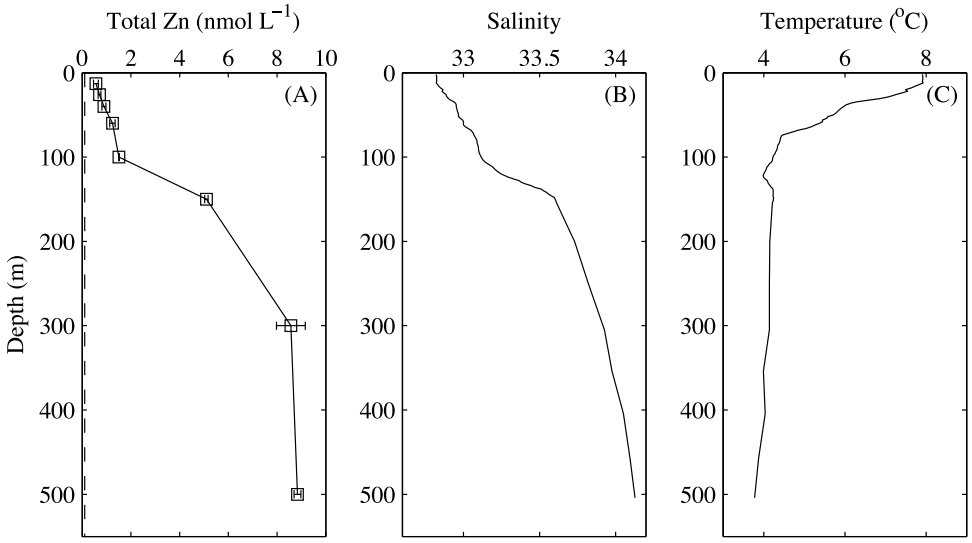

Figure 3. Comparison of (a) total dissolved Zn concentrations with (b) salinity and (c) temperature profiles in the upper 500 m at Station 4. Dotted line and error bars in Figure 3a as in Figure 2.

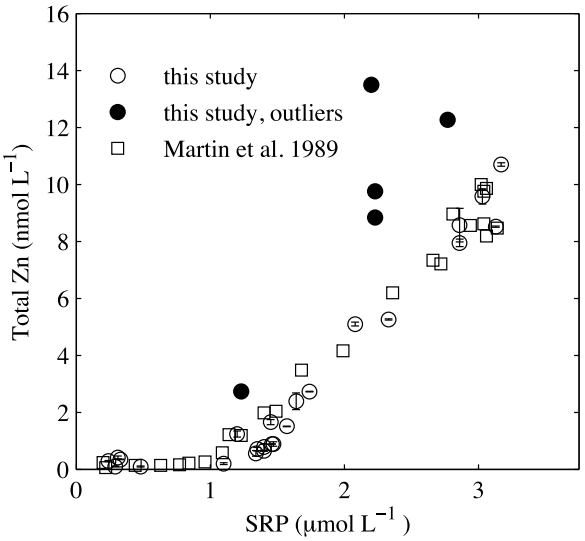

Figure 4a. Total dissolved Zn concentrations versus soluble reactive phosphorus (SRP) concentrations from all stations. Open squares represent data from VERTEX stations T-5 and T-6, which are in close proximity to Station 1 [*Martin et al.*, 1989]. Both open and closed circles are data from this study. The closed circles represent data where the SRP values are suspected outliers. Zinc error bars as in Figure 2.

30 pmol L^{-1}, which could account for approximately 30% of the Zn_T measured at this depth. The three samples where the ^{64}Ni could account for over 10% of the Zn_T concentration are noted in Table 1. The potential contribution of Ni_T to the deeper Zn_T values was generally very low (average possible contribution of less than 3%).

[21] Profiles of 8–11 depths were collected at three stations in the N. Pacific (Figure 2). Zinc profiles exhibited nutrient-like behavior, in agreement with previous studies in the region [*Bruland et al.*, 1978; *Bruland*, 1980; *Martin et al.*, 1989; *Bruland et al.*, 1994; *Lohan et al.*, 2002]. At the majority of stations, the near-surface samples collected were close to the base of the surface mixed layer (e.g., Station 4, Figure 3). In the N. Pacific, the seasonal thermocline extended down to roughly 40–150 m. In the Bering Sea, the thermocline occurred over shallower depths (25–50 m).

[22] A plot of Zn_T versus soluble reactive phosphorus (SRP), shows good agreement between this study and *Martin et al.* [1989] from the N. Pacific in the vicinity of Station 1 (Figure 4a), with a few exceptions. At high SRP and Zn, four data points fall above the trend (Station 4, 500 m; Station 4, 3000 m; Station 6, 1000 m; Station 6, 3000 m). They occur at depths in the profile (1000–3000 m) where SRP concentrations are expected to remain relatively constant with depth, yet the SRP in these samples is significantly lower than the two depths surrounding it or the depth above it in the case of the 3000 m points. SRP was measured on board the ship and on frozen samples for this depth. The shipboard value of 1.7 μmol L^{-1} SRP is significantly higher than the frozen sample of 1.2 μmol L^{-1} and is a value that matches the trend. The anomalously low SRP values suggest that in some cases SRP may have been lost during storage before analysis by ODC, a potential problem of sample storage [*Maher and Woo*, 1998, and references therein]. If the SRP values for these four data points are replaced with the average value for the two surrounding depths or the value above it in the case of 3000 m, the two shallower samples (Station 4, 500 m; Station 6, 1000 m) fall back in line with the expected trend (Figure 4b). The final two data points (Station 4, 3000 m; Station 6, 3000 m) fall closer to the line but still seem to have higher than expected Zn_T concentrations. The 3000 m samples were collected with Go-Flo bottles attached to the ship's CTD rosette frame, so they may have been contaminated. A final point that seems to fall somewhat off the trend is that at 1.2 μmol L^{-1} SRP and 2.7 nmol L^{-1} Zn_T (Station 6, 80 m). Once again, when the ODC SRP value is replaced with the shipboard SRP value, the data point conforms with the trend.

[23] A tight correlation was observed between silicic acid (Si) and Zn_T concentrations (Figure 5, R^2 = 0.93). The highest Zn values again fall above the trendline–the likely contamination of these samples has already been noted. The Zn/Si relationship is generally linear, but data from both this study and *Martin et al.* [1989] trend slightly above the linear relationship in the mid-values.

[24] Zinc concentrations reached maximum concentrations in deep waters of 10–10.5 nmol L^{-1} (excluding the presumably contaminated 3000 m data) in agreement with *Martin et al.* [1989] who reported similar concentrations at 1500 m for VERTEX stations T-5 thru T-8 and *Fujishima et al.* [2001] who found deep water Zn_T concentrations across the subarctic N. Pacific to be 10–11 nmol L^{-1}. In the central North Pacific, between 20–30°N, Zn_T concentrations reached maximums of only about 9.5 nmol L^{-1} [*Bruland et al.*, 1978; *Bruland*, 1980; *Bruland et al.*, 1994]. The higher deep Zn values in the subarctic N. Pacific relative to the central N. Pacific are consistent with the increasing time for remineralized Zn to accumulate in deep waters as

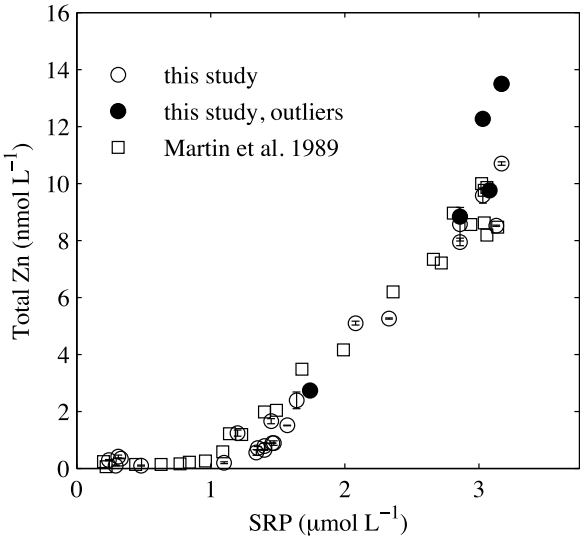

Figure 4b. Total dissolved Zn concentrations versus soluble reactive phosphorus (SRP) concentrations from all stations. Suspect SRP values (closed circles) have been replaced with average values from surrounding depths or with SRP values measured at sea (see section 3 for more detail). Zinc error bars as in Figure 2.

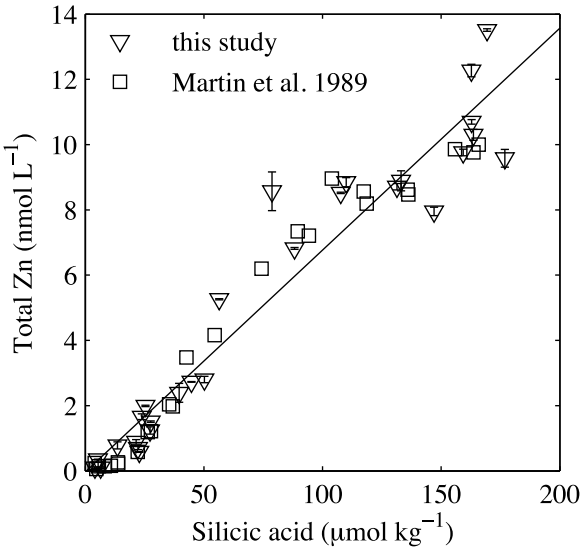

Figure 5. Total dissolved Zn concentrations from stations 1, 4, and 6 compared to silicic acid taken from the WOCE archive from stations close to these stations (triangles). Squares are data taken from VERTEX stations T-5 and T-6, which are in close proximity to Station 1 [*Martin et al.*, 1989]. Line is a least squares fit line for the Zn_T concentrations from this study and the WOCE silicic acid data (R^2 = 0.93). Zn error bars as in Figure 2.

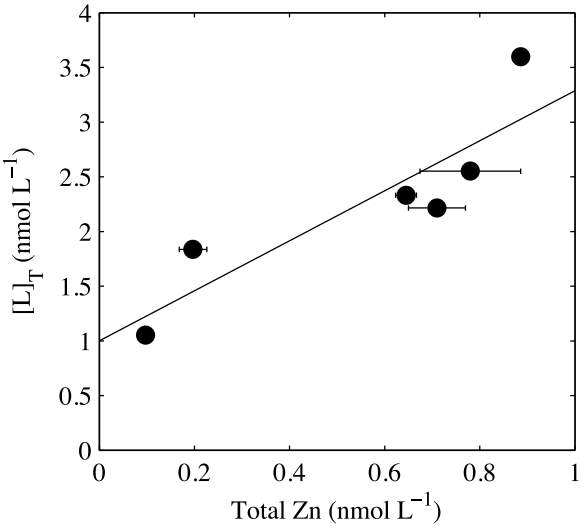

Figure 6. Concentration of Zn binding ligands (L_T) in the near surface shown in relation to the total dissolved Zn concentration. Line is a least squares fit line (R^2 = 0.79, $p < 0.05$).

they move northward. At Station 4, Zn_T concentrations from the same profile were also measured using isotope dilution, magnesium hydroxide pre-concentration coupled with an anion exchange resin, and the results from that method showed excellent agreement with this study [*John*, 2007].

3.2. Zn Speciation

[25] Zn speciation titrations were performed on near-surface samples for stations 1–8. The concentration of Zn binding ligands (L_T) ranged from 1.1 to 3.6 nmol L^{-1} in the near-surface with an average concentration of 2.3 nmol L^{-1} (Table 1). The concentration of L_T followed a general trend of increasing concentrations from east to west in the N. Pacific, similar to Zn_T concentrations (Figure 6). The highest concentration of L_T was observed at Station 8 in the western Bering Sea. The $K'_{cond,Zn'}$ of the natural organic ligands ranged from $10^{9.3}$ to $10^{11.0}$ with an average value of $10^{10.2}$ (Table 1). The resultant Zn^{2+} concentrations ranged from 2–71 pmol L^{-1}, which represented 3% on average of the total Zn concentration. Where multiple depths of a profile were analyzed for speciation, the Zn binding ligands had similar concentrations and conditional stability constants at each depth (Table 1). Free Zn^{2+} concentrations in the near-surface were very low at the eastern North Pacific stations (2–7 pmol L^{-1}), similar to previous studies in this area [*Bruland*, 1989; *Donat and Bruland*, 1990; *Lohan et al.*, 2005]. The Zn^{2+} concentrations at the westernmost station in the North Pacific and in the Bering Sea were much higher at 33 and 71 pmol L^{-1}, respectively.

[26] The lowest Zn^{2+} concentrations were observed in the eastern portion of the subarctic N. Pacific where the majority of previous studies have focused. Ligand concentrations of 1.0–2.2 nmol L^{-1} that had $K'_{cond,Zn'}$'s of $10^{10.6}$–$10^{11.2}$ were observed in the central and northeast North Pacific by these workers. However, the ligand concentrations were higher and the $K'_{cond,Zn'}$'s lower here than those reported by *Bruland* [1989]. The differences cancel out when determining free Zn^{2+}, hence the agreement. $K'_{cond,Zn}$ and $[L_T]$ observed in this study are more similar to those in subantarctic waters near New Zealand where the $[L_T]$ ranged from

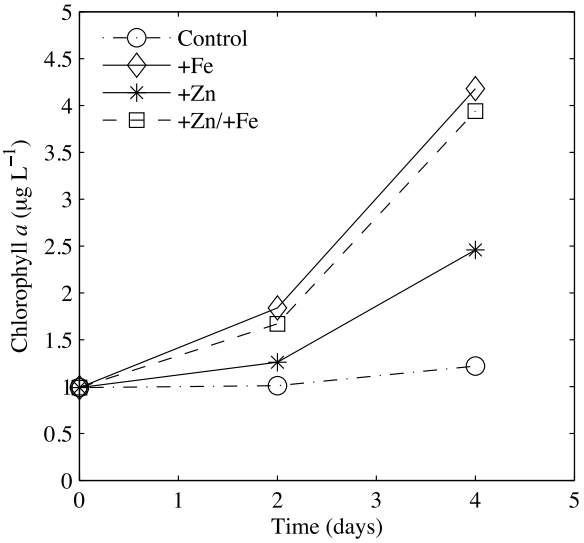

Figure 7. Results from a bottle incubation experiment examining the influence of Zn and Fe on phytoplankton biomass. The incubation was performed at Station 5 in the North Pacific. Chlorophyll *a* concentrations are shown over the 4 days of the experiment. One bottle was sacrificed at each time point. Additions were: Control (no addition), +Fe (2.5 nmol L^{-1} $FeCl_3$), +Zn (0.75 nmol L^{-1} $ZnCl_2$), +Zn/+Fe (0.75 nmol L^{-1} $ZnCl_2$, 2.5 nmol L^{-1} $FeCl_3$).

Table 2. Time Final (Day 4) Nutrient Concentrations and Nutrient Drawdown Ratios From the Shipboard Incubation Performed at Station 5 in the North Pacific

Treatment	NO_3 (μmol L^{-1})	SRP (μmol L^{-1})	Si (μmol L^{-1})	ΔSi/ΔNO3	ΔSi/ΔSRP
Time Zero	14.3	1.3	14.5		
Control	13.0	1.2	12.4	1.62	21.0
+Fe	7.4	0.8	9.2	0.77	10.6
+Zn/Fe	7.9	0.9	9.5	0.78	12.5
+Zn	10.6	1.0	11.4	0.84	10.3

1.3–2.5 nmol L^{-1} and $K'_{cond,Zn'}$ was between $10^{9.7}$ and $10^{10.4}$ [*Ellwood*, 2004].

[27] Culture studies have shown that *E. huxleyi* can exude Zn binding ligands [*Vasconcelos et al.*, 2002]. In this study, though the concentrations of L_T followed a trend similar to Chl*a*, there was not a significant relationship between Chl*a* and [L_T] ($R^2 = 0.51$, $p > 0.1$).

[28] The [L_T] at Station 8 in the Bering Sea (3.6 nmol L^{-1}) is the highest reported value of Zn binding ligands in the open ocean measured by voltammetric methods to the authors' knowledge. Ligand concentrations as high as 6 nmol L^{-1} have been reported in bottle incubations after the addition of Zn [*Lohan et al.*, 2005], and much higher concentrations (>20 nmol L^{-1}) have been observed in coastal waters and phytoplankton cultures [*van den Berg*, 1985; *Vasconcelos et al.*, 2002]. Station 8 had the highest Zn_T concentrations of any station where Zn speciation measurements were performed (0.89 nmol L^{-1}). The pool of Zn binding ligands is dynamic and can change on short timescales in response to the addition of Zn [*Lohan et al.*, 2005]. The high L_T concentrations may reflect a phytoplankton community that is well adapted to synthesizing additional ligands in response to atmospheric dust, which can be deposited to the Bering Sea from Asian deserts [*Duce and Tindale*, 1991].

3.3. Shipboard Incubations

[29] Results from the shipboard incubation that began at Station 5 are presented (Figure 7). At time zero of the incubation, total Chl*a* concentrations were 0.99 μg L^{-1}. The dominant phytoplankton pigments at Station 5 were hexanoyloxyfucoxanthin, fucoxanthin, chlorophyll *c*, and chlorophyll *b.* This pigment signature is consistent with an initial phytoplankton community dominated mainly by diatoms, prymnesiophytes, and green algae [*Mackey et al.*, 1998]. The near-surface Zn_T concentration at Station 5 was 0.65 nmol L^{-1}. Chlorophyll *a* values remained constant in the control treatment over 4 days (Figure 7). In the +Zn treatment, Chl*a* concentrations increased over the control by 25% on day 2 and reached twice the value in the control on day 4. An even more pronounced effect was seen in the treatments where Fe was added (+Fe, +Zn/+Fe). In these treatments, Chl*a* increased by between 60 and 80% over the control on day 2 and reached over 3 times the Chl*a* values observed in the control on day 4. At the end of the experiment, nutrients were most depleted in the treatments where Fe was added. Nutrient concentrations in the +Zn treatment were intermediate between those of the control and the Fe additions. The drawdown of nutrients in the incubation bottles matched the Chl*a* trend (Table 2). Incubation experiments that included Zn additions were performed at 7 other stations. No increase in response to Zn addition was observed at any other station (Table 3). Previous shipboard incubations in the N. Pacific have shown little effect on total Chl*a* concentration due to the addition of Zn [*Coale*, 1991; *Crawford et al.*, 2003] or no effect [*Lohan et al.*, 2005; *Leblanc et al.*, 2005]. There is no obvious explanation for the anomalous result at Station 5. Near-surface Zn_T concentrations at Station 5 were relatively high, and the concentration of Zn^{2+} was not particularly low at 7 pmol L^{-1}. The pigment distribution at Station 5 was very similar to that at Station 6, where Zn addition had no effect. Fe contamination is a possible explanation for the positive result to Zn addition at this site. However, no growth was observed in the control bottles or in a treatment of 500 pmol L^{-1} added Co (M. Saito et al., unpublished data, 2003). Thus it seems unlikely that contamination would have randomly occurred in the two +Zn bottles that

Table 3. Summary Table of Incubation Experiments Performed in the North Pacific and Bering Sea During the Summer of 2003[a]

Station	Location	+Zn	+DIP	+N	+Zn/N	+Fe	+Zn/Fe
1	41.60°N, 140.06°W	–	–	+	+		
3	44.02°N, 159.59°W	–	–	–	–		
4	47.01°N, 170.30°W	–	–	–	–		
5	46.59°N, 179.58°W	+				+	+
6	46.60°N, 170.20°E	–				+	+
Station	**Location**	**+Zn**	**+DIP**	**+Zn/DIP**	**+Fe/DIP**	**+Fe**	**+Zn/Fe**
8	55.18°N, 176.31°E	–				+	+
10	56.43°N, 167.50°W	–	–	–	–	–	
11	56.45°N, 164.60°W	–	–	–		–	

[a]Stations 1–6 are the subarctic North Pacific; stations 8–10 are the Bering Sea. An + indicates that a treatment resulted in an increase in chlorophyll *a* above a no-addition control, whereas a – indicates no increase observed. Where spaces are empty, the treatment was not performed at that station. +Fe additions were performed by Saito et al. (unpublished data, 2003) at stations 1, 3 and 4. A chlorophyll *a* increase due to Fe addition was observed at stations 3 and 4 but not at station 1.

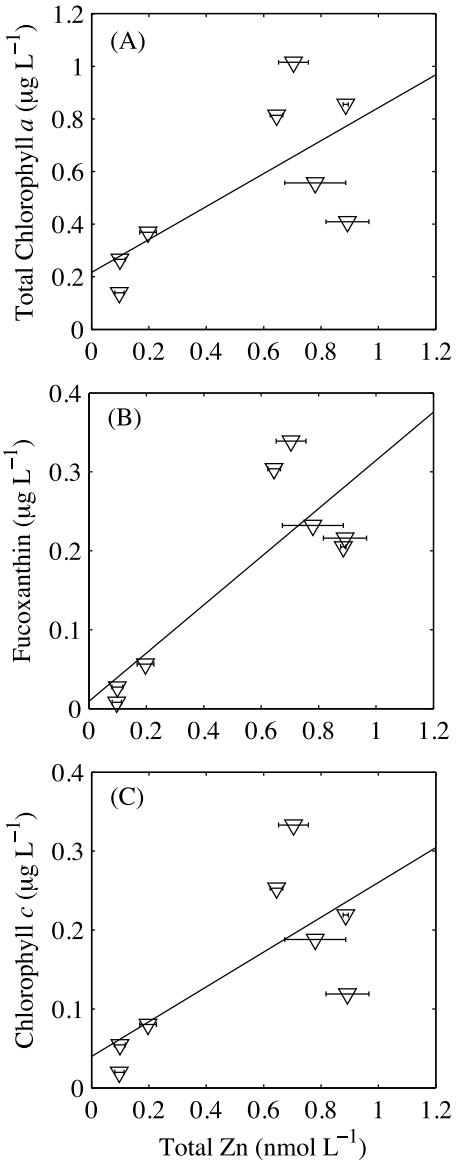

Figure 8. Comparison of total Zn concentrations and several phytoplankton pigments (as determined by HPLC). (a) The apparent positive relationship between total chlorophyll *a* and Zn is not significant ($R^2 = 0.49$, $p > 0.05$); however, there is a significant positive correlation between Zn and the relative contribution of two pigments found in diatoms: (b) fucoxanthin ($R^2 = 0.70$, $p < 0.01$) and (c) chlorophyll *c* ($R^2 = 0.50$, $p < 0.05$). Error bars as in Figure 2. Lines are least squares fit lines.

were sacrificed at successive time points and not in any of the control or +Co bottles.

3.4. Chlorophyll, Nutrients, and HPLC Pigments

[30] In the N. Pacific, near-surface SRP was lowest in the east and increased significantly between Station 1 and Station 3 and then remained relatively constant (Table 1). In the Bering Sea, SRP was highest in the west and decreased significantly on the Bering shelf. There were twelve samples where SRP was measured both by the Popp group at sea and from frozen samples by the ODC. When the SRP values from both analysts are plotted against one another, the vast majority of the samples fall within 10% of the 1:1 line (data not shown). Two exceptions are the samples from Station 4, 60 m and Station 6, 80 m. In both cases, the values measured by the ODC (1.20 μmol L^{-1}, 1.23 μmol L^{-1}) were significantly lower than those measured at sea (1.63 μmol L^{-1}, 1.74 μmol L^{-1}). The ODC SRP values for these two samples were also lower than would be expected based on the SRP concentrations from the shallower depths of the same profile. For both these samples, the values measured at sea are used in Table 1 and in Figures 4 and 9.

[31] Nitrate plus nitrite values in the near-surface were also very low at Station 1 (<0.1 μmol L^{-1}) and much higher and more consistent over the western half of the N. Pacific transect (~15 μmol L^{-1}). Silicic acid followed the same trend (Station 1: 0.5 μmol L^{-1}; Sts. 4–6: 14 μmol L^{-1}).

[32] Total Chl*a* concentrations in the near-surface were lowest in the eastern N. Pacific (Table 1). Chlorophyll *a* increased moving west from Station 1 to Station 5. Moderate Chl*a* values were observed for stations 6 through 10 in the western N. Pacific and Bering Sea, and the highest Chl*a* concentration encountered was at Station 11 on the Bering Shelf. The most abundant phytoplankton marker pigments (i.e., non-Chl*a*) were hexanoyloxyfucoxanthin, fucoxanthin, chlorophyll *c*, and chlorophyll *b.* The pigment signatures agree with previous examinations of phytoplankton pigments in the North Pacific and are consistent with phytoplankton communities containing prymnesiophytes, diatoms, pelagophytes, and green algae. In the northeast subarctic Pacific at Ocean Station Papa (50°N, 145°W), the phytoplankton community is typically dominated by small prymnesiophytes (such as *E. huxleyi*), pelagophytes, small diatoms, and cyanobacteria, with larger diatoms and other large phytoplankton contributing 10–30% of the total Chl*a* [e.g., *Boyd and Harrison*, 1999; *Thibault et al.*, 1999]. The waters of the northwest subarctic Pacific often host phytoplankton communities with abundant prasinophytes and a higher relative abundance of diatoms than in the eastern subarctic North Pacific [e.g., *Suzuki et al.*, 2002; *Obayashi et al.*, 2001]. Hexanoyloxyfucoxanthin was the most abundant marker pigment at Sts. 1, 2, 3, and 10, while fucoxanthin was dominant at Sts. 4, 5, 6, 8, and 11. This pattern meshes with the above studies and indicates that at the eastern North Pacific stations the community was likely dominated by prymnesiophytes, while at the western North Pacific stations, diatoms were more likely to dominate. The higher concentrations of fucoxanthin at the western North Pacific stations is consistent with the proliferation of diatoms in waters containing relatively high levels of macro- and micronutrients.

[33] Phytoplankton pigment concentrations were compared to Zn concentrations from those samples in the upper thermocline where Zn speciation data were available. This criterion excludes data from St 6, 40 m and St 4, 100 m, where significant mixing with deep waters is evidenced by the more than doubling of the total Zn concentrations relative to mixed layer values. There was not a significant relationship ($p > 0.05$) between Zn_T concentration and total Chl*a* (Figure 8a). However, for two major pigments found in diatoms, fucoxanthin ($p < 0.01$) and chlorophyll *c* ($p < 0.05$), positive relationships were observed with Zn_T (Figures 8b and 8c), which may indicate the relative importance of Zn

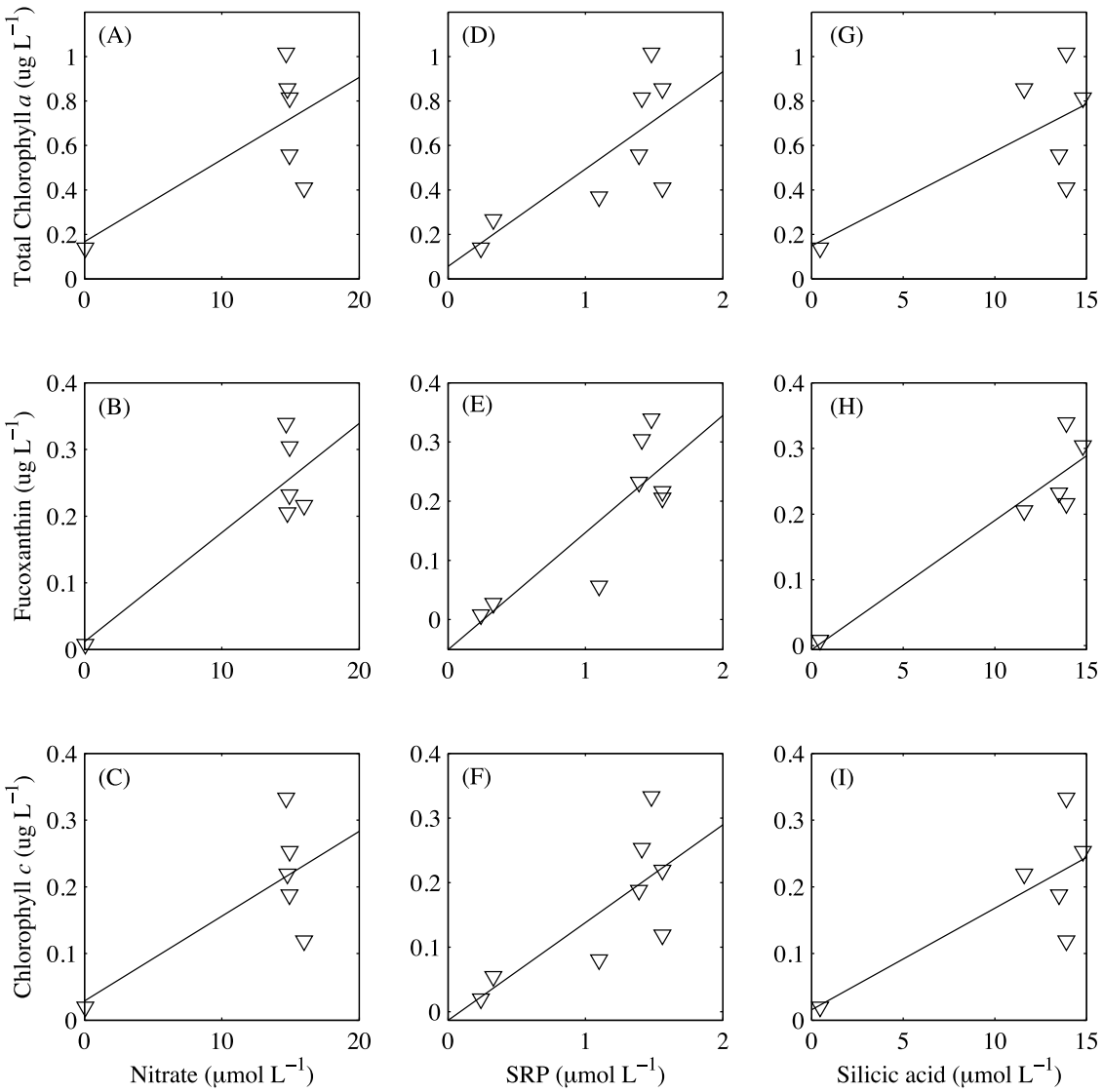

Figure 9. Comparison of total NO_3, SRP, and silicic acid concentrations with several phytoplankton pigments (as determined by HPLC). There are not significant correlations between the concentration of NO_3 and the concentration of (a) total chlorophyll *a* ($R^2 = 0.49$, $p > 0.1$) or (c) chlorophyll *c* ($R^2 = 0.51$, $p > 0.1$). There was a significant correlation between the concentration of NO_3 and the concentration of (b) fucoxanthin ($R^2 = 0.76$, $p < 0.05$). There are significant correlations between the concentration of SRP and the concentration of (d) total chlorophyll *a* ($R^2 = 0.58$, $p < 0.05$), (e) fucoxanthin ($R^2 = 0.72$, $p < 0.01$), and (f) chlorophyll *c* ($R^2 = 0.58$, $p < 0.05$). Similar to NO_3, there are not significant correlations between the concentration of silicic acid and the concentration of (g) total chlorophyll *a* ($R^2 = 0.51$, $p > 0.1$) or (i) chlorophyll *c* ($R^2 = 0.58$, $p > 0.05$). There was a strong correlation between the concentration of silicic acid and the concentration of (h) fucoxanthin ($R^2 = 0.86$, $p < 0.01$). Lines are least squares fit lines.

to this fraction of the phytoplankton community. Diatoms have high Zn quotas relative to other taxa [*Sunda and Huntsman*, 1995]. The relationship observed here is consistent with Zn being an essential micronutrient for diatoms.

[34] Significant correlations ($p < 0.01$) were also observed between both SRP and silicic acid and fucoxanthin (Figure 9) but nitrate was not as strongly correlated. When pigment concentrations were compared to the free Zn^{2+} concentration rather than total Zn concentration, no significant correlations were observed (Figure 10). Instead, aside from two high points, most of the data were below 10 pmol L^{-1}, regardless of pigment concentration, suggesting that at very low concentrations, free Zn^{2+} is relatively invariant with biology within the capabilities of this methodology.

[35] Two minor pigments, alloxanthin and chlorophyllide *a*, also exhibited positive correlations with Zn_T (data not shown). Alloxanthin is a marker for cryptomonads and was found in very low quantities (average relative contribution to total Chl*a* ~1%). Chlorophyllide *a* is a degradation product of Chl*a* and was observed in somewhat higher concentrations (average relative contribution to Chl*a* < 9%). Degradation of

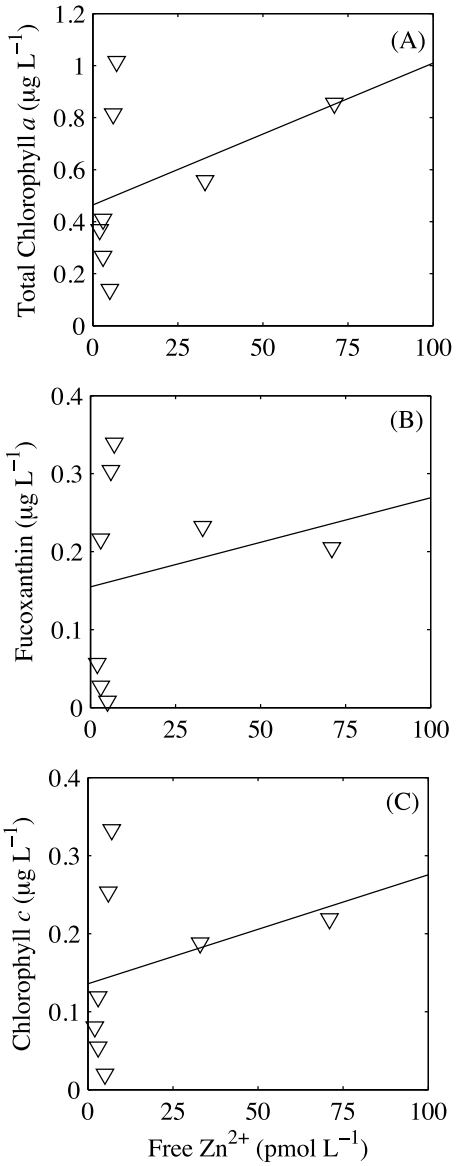

Figure 10. Comparison of free Zn^{2+} concentrations and several phytoplankton pigments (as determined by HPLC). There are not significant correlations between (a) the concentration of Zn^{2+} and the concentration of total chlorophyll *a* ($R^2 = 0.05$, $p > 0.1$) and the relative contribution of two pigments found in diatoms: (b) fucoxanthin ($R^2 = 0.05$, $p > 0.1$) and (c) chlorophyll *c* ($R^2 = 0.10$, $p > 0.1$). Lines are least squares fit line.

Chl*a* to chlorophyllide *a* can occur during copepod grazing and during the filtration of some diatoms [*Klein and Sournia*, 1987, and references therein]. These relationships are based on limited data, and interpreting pigment data can be difficult because organisms contain multiple pigments and the pigment composition of field organisms does not accurately match those of cultured organisms.

4. Discussion

[36] A prominent feature of the data presented here is the strong gradient in zinc concentration and zinc speciation in surface waters on the east–west transect. Increasing zinc concentrations toward the west were matched by increasing ligand concentrations, leading to relatively little variability in free Zn^{2+} in the mixed layer until the westernmost station (Station 6). Zn_T at Station 6 is higher in surface waters, and free Zn^{2+} increases to values seen only in the subsurface further east. Together, these results show an emerging picture of a large region in the central and eastern N Pacific where mixed layer free Zn^{2+} is less than 10 pmol L^{-1}. This region is bounded by waters underlying the mixed layer, where Zn_T and free Zn^{2+} are much higher, and by nutrient-rich surface waters in the west. Increasing Zn levels toward the west are associated with an increase in biomass and diatoms, as indicated by Chl*a* and fucoxanthin data. These increasing zinc abundances may be one of the factors, with the increased macronutrients, that contributes to this trend toward higher primary productivity in the west. Establishing a causal relationship between Zn and biological activity is premature, since Zn additions to bottle incubations resulted in a positive response at only one station.

[37] Free Zn^{2+} is presumed to be the biologically available form [*Sunda and Huntsman*, 1992, 1995] so the observation that total dissolved Zn has a stronger correlation with pigment parameters is surprising. However, for acquisition of some micronutrients like Fe and Co, some phytoplankton appear to be capable of accessing the organically complexed forms [*Maldonado and Price*, 1999; *Saito et al.*, 2002], hence free ion concentrations may be less relevant than total concentrations for some species because of these high affinity uptake systems that render organically complexed forms biologically available. Correlations here also reflect the fact that Zn_T can be measured much more precisely than the scarcer free Zn^{2+}, making it difficult to look for correlations between the latter and other parameters.

[38] In spite of these limitations, our free Zn^{2+} data enable us to compare field data with culture studies, which are typically carried out using metal ion buffers like EDTA, where effects (e.g., specific growth rates, cellular Zn quota) are reported as a function of free Zn^{2+}. Comparison of our free Zn^{2+} data with phytoplankton culture studies suggest that Zn is a limiting micronutrient for some phytoplankton, in particular larger diatoms [*Sunda and Huntsman*, 1995], and is low enough to induce biochemical responses such as substitution of Co for Zn [*Yee and Morel*, 1996; *Xu et al.*, 2007; *Saito et al.*, 2008].

[39] *Sunda and Huntsman* [1992, 1995] demonstrated a robust relationship between free Zn^{2+} and Zn:C in phytoplankton cultures, building on earlier studies [*Sunda and Guillard*, 1976; *Anderson et al.*, 1978]. Using a Redfieldian-type analysis, they estimated Zn:P ratios in phytoplankton biomass through analysis of the dissolved Zn:P data in the upper 1000 m of the North Pacific reported in *Martin et al.* [1989]. While Zn shows the strongest correlation with Si over the entire water column, the strong correlation with P in the upper water column indicates a close coupling of Zn and nutrient remineralization. Therefore, *Sunda and Huntsman* [1992] argue that these dissolved ratios presumably reflect the Zn:P of remineralized phytoplankton biomass, and using their data for Zn:C in culture, they estimated the corresponding free Zn^{2+} concentration required to produce a sufficiently large Zn:P ratio. Their calculations suggest that the Zn:P ratio from the nutricline

could only arise from diatoms growing with a free zinc abundance of ~1000 pmol L^{-1}. The estimated "nutricline value" for free Zn^{2+} is an order of magnitude higher than the highest value reported here and in *Lohan et al.* [2002]. The only source of nutrient-rich, high Zn water to lead to such conditions is substantially deeper than 100 m, yet the mixed layer does not penetrate that depth in this region, even during the winter [*Anderson et al.*, 1969]. Therefore, the Zn must come from elsewhere. One possibility is that episodic deep mixing events, perhaps within boundary regions, lead to conditions with elevated Zn. A major shortcoming of all Zn studies, including ours, is that they do not examine the dynamics of Zn injection and drawdown during bloom periods. For instance, it is possible that deep mixing events preceded the SEEDS experiment in the western North Pacific, when surface Zn was extremely high [*Kinugasa et al.*, 2005].

[40] The Zn:P ratio calculated from data between 50 to 150 m is much smaller, and yields a smaller cell quota and free Zn^{2+} abundance of 0.8 to 2 pmol L^{-1}. The free Zn^{2+} abundances estimated from the shallow dissolved Zn:P ratios are quite similar to that measured in this study in the low picomolar range (Table 1), suggesting that much less bioavailable Zn is in the photic zone and which also is within the range of what would affect phytoplankton species composition [*Sunda and Huntsman*, 1995].

[41] In summary, data from a variety of sources, including culture work and measurements of remineralized Zn:P inferred from dissolved Zn and phosphate abundances, provide a mechanism for Zn cycling that is consistent with the free ion model. A principal, if accidental role of organic ligands is to act as a natural Zn buffer. Complexation decreases the rate of "luxury" uptake or non-biological scavenging under conditions of high particle scavenging, leaving a residual concentration available for organisms with high affinity transport systems. From Sunda and Huntsman's work, this would appear to include small diatoms, but not larger ones. Zn limitation will probably induce community shifts to species or biochemistries with lower Zn requirements before total Zn is completely removed. Thus organic complexation provides a useful natural service to organisms with a small, but nonzero Zn requirement.

[42] The inter-replacement of Co and Zn as micronutrients has been shown in phytoplankton cultures [*Saito et al.*, 2008, and references therein]. Therefore, Co distributions should also be considered in evaluating the biological implications of our data, particularly for station 5, the only location where we had evidence for Zn limitation. A strong depletion in near-surface Co concentrations was observed at Station 5, with some of the lowest Co values observed on this transect (~30 pmol L^{-1}; M. Saito, manuscript in preparation, 2012). The low concentration of Co is consistent with the biochemical substitution of Co for Zn under low Zn conditions and with the observation that Co draw down in the North Pacific typically occurs when Zn concentrations are depleted relative to SRP concentrations [*Sunda and Huntsman*, 1995].

[43] Much of the region we surveyed exhibits Fe limitation to varying degrees [*Martin and Fitzwater*, 1988; *Kinugasa et al.*, 2005]. The relationship between Fe and Zn limitation has been studied previously in cultures and deckboard incubations. In cultures of the diatom *T. weissflogii*, Fe and Zn deficiency resulted in cells with higher Si contents, and Zn-stressed cells had a significantly higher $Si:NO_3$ than Zn replete diatoms [*De La Rocha et al.*, 2000]. *Franck et al.* [2003] performed a series of incubation experiments in Fe-limited upwelling regions and observed a decrease in the $Si:NO_3$ utilization ratio when Fe or Fe and Zn together were added, due to a greater stimulation of NO_3 uptake versus Si uptake. In contrast to the Fe addition results, the $Si:NO_3$ utilization ratio increased when Zn was added as a result of either a decline in NO_3 uptake (Costa Rica and Point Conception, CA stations) or enhanced Si uptake (Big Sur, CA) [*Franck et al.*, 2003]. In this study, a similar decrease in the $Si:NO_3$ utilization ratio was observed in all the metal treatments relative to the control (Table 2), which is consistent with previous Fe addition experiments in the subarctic North Pacific [*Takeda*, 1998]. The mechanism for the alteration of the nutrient ratios was not explored; however, our results support previous observations that both Zn and Fe limitation may influence a phytoplankton cell's ability to compete for Si [*De La Rocha et al.*, 2000; *Franck et al.*, 2003].

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