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On the nonlinear relationship between dissolved cadmium and phosphate in the modern global ocean: Could chronic iron limitation of phytoplankton growth cause the kink?

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Abstract

I report two vertical profiles of dissolved cadmium (Cd) and phosphate (PO_4) from the Bering Sea: one from a high-nutrient, low-chlorophyll (HNLC) area, in which phytoplankton growth is limited by iron (Fe) availability, and one in highly productive waters near the continental shelf, where Fe is sufficient. At both stations, dissolved Cd and PO_4 display nutrient-like profiles and are strongly correlated with depth. The surface-water dissolved Cd : PO_4 ratio in the Fe-limited HNLC (0.21 ± 0.03 nmol μmol^{-1}) is significantly lower than the ratio in the productive Fe-replete station (0.31 ± 0.02 nmol μmol^{-1}). A simple model based on the results of previously published laboratory culture studies by others and field incubation experiments with natural phytoplankton assemblages is proposed relating the availability of Fe to the Cd : phosphorus content of phytoplankton, the dissolved Cd : PO_4 of ocean surface waters, and the slope of Cd : PO_4 in the nutricline. The model is consistent with available data and suggests that the nonlinearity or kink in the global dissolved Cd versus PO_4 relationship exists because of chronic Fe-limiting conditions in high-latitude HNLC areas in the modern ocean.

For almost 30 yr, oceanographers have been aware of the strong correlation of dissolved Cd concentrations with those of PO_4 in seawater (Boyle et al. 1976; Bruland et al. 1978; de Baar et al. 1994). The relationship between dissolved cadmium (Cd) and phosphate (PO_4) in the world ocean is well characterized and nonlinear, with a pronounced break in the slope, hereafter referred to as a "kink," at PO_4 concentrations of ~1.3 μmol L^{-1} (Table 1; Figs. 1, 2). The correlation implies that the vertical distribution of Cd is controlled by its uptake by phytoplankton in surface waters and sinking of particulate organic matter and subsequent remineralization at depth. The strength of the correlation has been applied along with records of Cd : calcium (Ca) ratios in fossil tests of foraminifera to reconstruct past deep-water nutrient distributions in the ocean (Boyle 1988). This approach was recently expanded to include surface waters in an attempt to elucidate how changes in upper ocean nutrient inventories, reflecting the efficiency of the biological pump, might relate to glacial–interglacial climate change (Elderfield and Rickaby 2000). One of the main criticisms of the accuracy of the above paleonutrient proxy is the extent to which one can be certain that the dissolved Cd versus PO_4 relationship in the ocean has remained constant in time and space (Saager and de Baar 1993; de Baar et al. 1994).

The global Cd versus PO_4 relationship in the modern ocean is generally described by two distinct linear relationships: one for North Atlantic Ocean data with PO_4 concentrations <1.3 μmol L^{-1} and, after the kink, one for the Indian–Southern–Pacific Ocean data (Löscher et al. 1997). Accepting the regional difference above, the ratio of dissolved Cd to PO_4 is quite constant in waters of >1,000 m; however, significant variability exists in surface-water ratios (de Baar et al. 1994; Rutgers van der Loeff et al. 1997), especially in areas in which phytoplankton growth is known to be iron limited (Martin et al. 1989, 1990). These observations have led to the suggestion that Cd might be preferentially removed from surface waters relative to PO_4 during uptake by phytoplankton (Saager and de Baar 1993; Löscher et al. 1998). At present, we lack a mechanistic explanation for these surface-water deviations in the dissolved Cd : PO_4 ratio and for the pronounced regional differences in Cd : phosphorus (P) cycling indicated by the kink in the global dissolved Cd versus PO_4 relationship.

Differences in the relative removal of dissolved Cd and PO_4 by phytoplankton during their growth in surface waters could help to explain the vertical and horizontal variation of seawater Cd : PO_4 ratios. Our understanding of the factors that control algal uptake of Cd and their Cd : P ratios are based largely on the results of laboratory studies with cultured phytoplankton grown in trace metal ion-buffered artificial seawater. These studies have demonstrated that the Cd content of marine phytoplankton is largely controlled by aqueous Cd ion concentrations and is inversely related to manganese (Mn) and zinc (Zn) ion concentrations (Lee and Morel 1995; Sunda and Huntsman 1998), as well as the concentration of aqueous carbon dioxide in the growth media (Lane and Morel 2000). The few field studies with natural algal assemblages tend to

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Table 1. A selection of dissolved cadmium and phosphate data compiled from the literature in de Baar et al. (1994), Löscher et al. (1997), and Abe (2004).

Location	Reference	Latitude	Longitude	Location	Reference	Latitude	Longitude
Bering Sea	This study	55°0.17′N	178°59.59′W	Southern Ocean	Löscher et al. (1998)	57°45.00′S	06°29.00′W
Southern Ocean	Fitzwater et al. (2000)	72°0.50′S	178°0.47′W	Southern Ocean	Löscher et al. (1998)	55°59.00′S	06°4.00′ W
SW Pacific	Boyle et al. (1976)	52°30.00′S	178°0.00′W	Southern Ocean	Löscher et al. (1998)	55°1.00′S	06°0.00′ W
Southern Ocean	Fitzwater et al. (2000)	76°0.50′S	175°0.04′W	Southern Ocean	Löscher et al. (1998)	54°0.00′S	06°0.00′ W
Southern Ocean	Fitzwater et al. (2000)	72°0.50′S	174°0.00′W	Southern Ocean	Löscher et al. (1998)	53°0.00′S	06°0.00′ W
Bering Sea	This study	56°19.97′N	171°36.02′W	Southern Ocean	Löscher et al. (1998)	52°0.00′S	06°0.00′ W
NE Pacific	Martin et al. (1989)	58°40.80′N	147°57.00′W	Southern Ocean	Löscher et al. (1998)	51°0.00′S	06°0.00′ W
NE Pacific	Martin et al. (1989)	55°30.00′N	147°30.00′W	Southern Ocean	Löscher et al. (1998)	50°0.00′S	06°0.00′W
NE Pacific	Martin et al. (1989)	50°0.00′N	145°0.00′W	Southern Ocean	Löscher et al. (1998)	49°0.00′S	06°0.00′W
NE Pacific	Martin et al. (1989)	45°0.00′N	142°52.20′W	Southern Ocean	Löscher et al. (1998)	48°0.00′S	06°0.00′W
NE Pacific	Martin et al. (1989)	39°36.00′N	140°46.20′W	Southern Ocean	Löscher et al. (1998)	47°0.00′S	06°0.00′W
NE Pacific	Bruland (1980)	35°0.00′N	130°0.00′W	Southern Ocean	Löscher et al. (1998)	46°52.00′S	06°0.00′W
NE Pacific	Jones and Murray (1984)	47°0.00′N	130°0.00′W	Southern Ocean	Löscher et al. (1998)	49°0.00′S	06°0.00′W
NE Pacific	Jones and Murray (1984)	47°0.00′N	126°0.00′W	N NE Atlantic	Nolting et al. (1987)	67°0.00′N	02°0.00′W
Northeast Pacific	Bruland et al. (1978)	12°0.00′N	115°0.00′W	Atlantic (Zaire)	Nolting et al. (unpubl. data)	06°18.00′S	08°11.40′E
Gulf of Mexico	Boyle et al. (1984)	24°6.00′N	84°30.00′W	Arctic Atlantic	Danielsson and Westerlund (1983)	82°18.60′N	43°34.20′E
Sargasso Sea	Sakamoto-Arnold et al. (1987)	36°22.80′N	73°28.20′W	Upwelling	Saager et al. (1992)	22°18.00′N	60°24.00′E
Sargasso Sea	Sakamoto-Arnold et al. (1987)	35°23.40′N	71°31.80′W	Upwelling	Saager et al. (1992)	22°18.00′N	60°24.00′E
NW Atlantic	Bruland and Franks (1983)	34°3.60′N	66°4.20′W	Indian Ocean	Bordin et al. (1987)	54°24.00′S	63°3.60′E
NW Atlantic	Sakamoto-Arnold et al. (1987)	40°0.00′N	65°0.00′W	Indian Ocean	Bordin et al. (1987)	61°3.00′S	66°12.00′E
Drake Passage	Martin et al. (1990)	60°27.60′S	63°15.60′W	NW Indian Ocean	Saager et al. (1992)	14°18.00′N	67°0.00′E
NW Atlantic	Yeats and Campbell (1983)	50°0.00′N	50°0.00′W	NW Indian Ocean	Saager et al. (1992)	14°18.00′N	67°0.00′E
Antarctic Atlantic	Nolting et al. (1991)	57°0.00′S	49°0.00′W	Southern Ocean	Frew (1995)	65°6.00′S	84°18.00′E
Southern Ocean	Nolting and de Baar (1994)	57°0.00′S	49°0.00′W	SE Indian Ocean	Nolting et al. (1989)	10°42.00′S	112°0.00′E
Southern Ocean	Nolting and de Baar (1994)	62°0.00′S	49°0.00′W	South China Sea	Chen et al. (2005)	18°0.00′N	115°30.00′E
Southern Ocean	Löscher et al. (1998)	56°59.00′S	38°51.00′W	South China Sea	Chen et al. (2005)	15°42.00′N	116°42.00′E
Southern Ocean	Löscher et al. (1998)	56°59.00′S	30°27.00′W	South China Sea	Chen et al. (2005)	18°0.00′N	117°42.00′E
Southern Ocean	Löscher et al. (1998)	57°0.00′S	23°19.00′W	South China Sea	Chen et al. (2005)	20°15.00′N	118°34.80′E
NE Atlantic	JGOFS (04 Jun 1990; PMS)	58°18.00′N	20°18.00′W	South China Sea	Chen et al. (2005)	21°25.20′N	119°28.20′E
N NE Atlantic	Danielsson et al. (1985)	59°0.00′N	20°0.00′W	Northwestern Pacific	Abe (2002*b*)	24°18.00′N	124°0.00′E
NE Atlantic	Danielsson et al. (1985)	50°0.00′N	20°0.00′W	Northwestern Pacific	Abe (2002*b*)	34°18.00′N	125°0.00′E
NE Atlantic	Danielsson et al. (1985)	48°18.00′N	20°0.00′W	Northwestern Pacific	Abe (2002*b*)	33°18.00′N	126°0.00′E
NE Atlantic	JGOFS (25 Sep 1989; PMS)	33°0.00′N	20°0.00′W	NW Pacific	Matsunaga and Abe (1985)	33°33.60′N	143°13.80′E
NE Atlantic	JGOFS (27 Apr 1990; RFN-NIOZ)	33°0.00′N	20°0.00′W	Northwestern Pacific	Abe (2002*a*)	45°25.00′N	145°5.00′E
NE Atlantic	JGOFS (10 Jun 1990; PMS-A'dam)	47°0.00′N	20°0.00′W	Western Equatorial Pacific	Abe (2001)	00°0.00′N	146°0.00′E
NW Atlantic	Olafsson (1983)	60°18.00′N	17°0.00′W	NW Pacific	Matsunaga and Abe (1985)	42°17.40′N	155°0.00′E
NW Atlantic	Nolting et al. (1987)	50°0.00′N	17°0.00′W	Northwestern Pacific	Abe (2002*a*)	44°0.00′N	155°0.00′E
Southern Ocean	Löscher et al. (1998)	56°9.00′S	15°26.00′W	Western Equatorial Pacific	Abe (2001)	00°0.00′N	162°0.00′E
NE Atlantic	Statham et al. (1985)	03°0.00′N	12°30.60′W	Tasman Sea	Hunter and Ho (1991)	35°30.00′S	162°24.00′E

Table 1. Continued.

Location	Reference	Latitude	Longitude	Location	Reference	Latitude	Longitude
Off Gibraltar	Boyle et al. (1985)	36°0.00′N	07°0.00′W	Southern Ocean	Fitzwater et al. (2000)	76°0.50′S	163°0.86′E
				Puyseger Tr.	Frew and Hunter (1992)	48°3.00′S	164°18.00′E
				Southern Ocean	Fitzwater et al. (2000)	76°0.56′S	167°0.49′E
				NE Pacific	Boyle et al. (1976)	30°20.40′N	170°21.60′E
				Tasman Sea	Hunter and Ho (1991)	34°18.00′S	171°25.20′E
				Southern Ocean	Fitzwater et al. (2000)	72°0.52′S	172°0.52′E
				Southern Ocean	Fitzwater et al. (2000)	76°0.50′S	173°0.34′E
				Southern Ocean	Fitzwater et al. (2000)	72°0.50′S	177°0.00′E
				Southern Ocean	Ellwood (2004)	47°0.00′S	178°0.00′E
				Western Equatorial Pacific	Abe (2001)	00°0.00′N	179°0.00′E
				Southern Ocean	Fitzwater et al. (2000)	76°0.50′S	179°0.65′E

support the controlling factors identified in culture (Cullen et al. 1999; Cullen and Sherrell 2005).

Evidence is increasing that Fe limitation of algal growth rates can lead to the preferential uptake of Cd relative to P by marine phytoplankton (Sunda and Huntsman 2000; Cullen et al. 2003). Sunda and Huntsman (2000) demonstrated that Fe limited populations of the oceanic diatom *Thalassiosira oceanica* had significantly elevated cellular Cd content relative to Fe-replete treatments. The authors suggested high cellular Cd : P ratios were related mostly to depletion of ambient Zn free ion concentrations [Zn^{2+}] in response to Fe-limitation and partly from a reduced growth rate. The latter idea of growth rate or biodilution has been extensively developed by Sunda (2001), and at steady state, relates the cellular Cd pool and specific growth rate according to the equation

$$\rho = \mu Q$$

where ρ is the normalized cellular uptake rate (mol Cd cell^{-1} time^{-1}), μ is the specific growth rate (time^{-1}), and Q is the cellular quota (mol Cd cell^{-1}). The effect of growth rate dilution can be described as a constant accumulation of metals combined with varying rates of accumulation of nonmetal biomass. Cullen et al. (2003) performed shipboard incubation studies with natural assemblages of Fe-limited phytoplankton from the Southern Ocean and determined that the Cd : P composition of the cells varied in response to Fe supplements in a manner consistent with the idea of growth rate dilution. Unlike Sunda and Huntsman (2000), this preferential removal of dissolved Cd relative to PO$_4$ occurred despite high total dissolved and calculated free ion Zn concentrations in the surrounding seawater. Taken together, this evidence suggests that Fe-limited phytoplankton remove Cd preferentially to PO$_4$ in ocean surface waters.

Herein, I report two of the first vertical profiles of dissolved Cd and PO$_4$ from two stations in the Bering Sea: one from a classic Fe-limited, high-nutrient, low-chlorophyll (HNLC) area and the other from a highly productive Fe-replete station. A simple model relating Fe bioavailability, the Cd : P composition of marine phytoplankton, and the dissolved Cd : PO$_4$ of surface waters is constructed by synthesizing laboratory studies of phytoplankton Cd uptake (Sunda and Huntsman 2000) with shipboard incubation studies (Cullen et al. 2003) that is consistent with the Bering Sea data and with previously reported data in the literature. The results suggest that previously reported regional differences in the cycling of Cd and P and the pronounced nonlinearity of the global dissolved Cd versus PO$_4$ relationship might reflect hyperaccumulation of Cd by Fe-limited phytoplankton in high-latitude HNLC regions. The implications for the accurate application of the emerging planktonic Cd : Ca paleonutrient proxy are discussed.

Methods

Oceanographic data were collected at two stations in the Bering Sea on 12 Aug and 16 Aug 2003 aboard the R/V

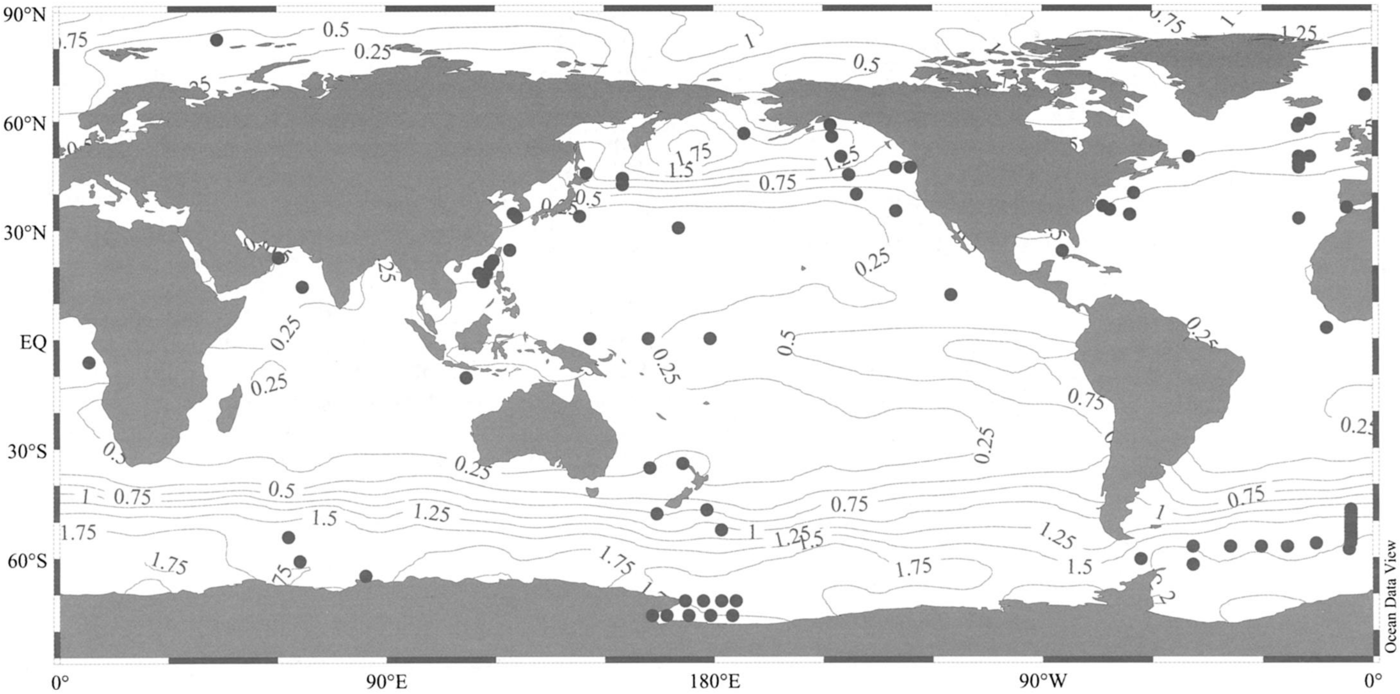

Fig. 1. Global map indicating where dissolved Cd and PO_4 vertical profiles were obtained by various investigators over the time period 1976–present. Data were compiled from de Baar et al. (1994), Löscher et al. (1997), and Abe (2004). Contours represent surface dissolved PO_4 concentrations (μmol L^{-1}) from Conkright et al. (2002). References for individual points are listed in order of increasing longitude from (−180) in Table 1. Note that this compilation is not comprehensive.

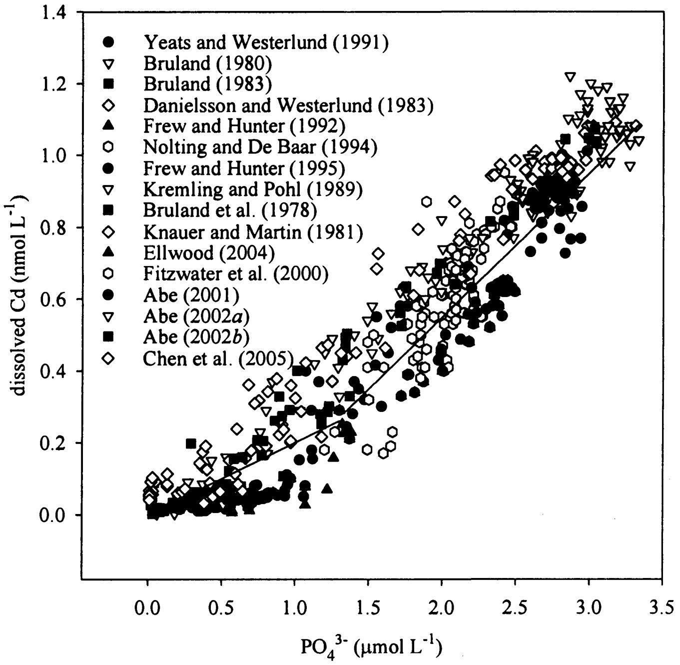

Fig. 2. Selected dissolved Cd versus PO_4 compiled from the global database. Lines represent the two distinct relationships for $[PO_4] < 1.3$ μmol L^{-1}, primarily Atlantic waters, and for $[PO_4] > 1.3$ μmol L^{-1}, primarily Indian–Southern–Pacific Ocean waters, as defined by Boyle (1988). Note that data presented in this figure have not been subjected to any quality control or selection criteria and do not represent the dataset used to reconstruct deep-water paleonutrient distributions.

Kilo Moana. A Seabird CTD system was used to obtain hydrographic data for the two stations. Throughout sampling and handling of samples, rigorous contamination control and trace metal clean technique were used. All laboratory apparatuses contacting the samples were cleaned with a detergent wash for 1 week (2% v/v, Micro; International Products), followed by soaking for 1 week each in 50% (v/v) HCl and then in 50% (v/v) HNO_3. Equipment was rinsed with Milli-Q Water (18 MΩ cm) and quartz subboiling distilled water before drying on a clean bench and placed in resealable plastic bags. All critical handling steps onboard ship and onshore were carried out in either a class 100 laminar flow hood or a clean room.

Water samples for the determination of cadmium were collected by two distinct methods. Samples from subsurface waters were obtained with 30-liter Teflon™-coated GO-Flo™ bottles (General Oceanics) suspended from a Kevlar™ hydroline (Bruland et al. 1979). A trace metal clean surface sampling system consisting of an all-Teflon diaphragm pump (Bruiser™, Osmonics) connected to PFA (perfluoroalkoxy) Teflon tubing mounted on a polyvinyl chloride (PVC) depressor vane above a 20-kg PVC torpedo was used to collect surface water (<10 m).

Seawater samples were filtered through either acid-cleaned 0.45-μm pore size Teflon membrane polypropylene capsule filters (Calyx™, MSI) or through acid-cleaned 142-mm-diameter, 0.4-μm cutoff polycarbonate filters (Nuclepore™) housed in PTFE (polytetrafluoroethylene) Teflon filter sandwiches (Millipore).

Instrumentation and analysis—Total dissolved Cd was measured with differential pulse anodic stripping voltammetry after preconcentration of Cd at a thin mercury film, glassy carbon rotating disk electrode (TMF-GCRDE) (Bruland 1992). The voltammetric system consisted of an Eco Chemie GCRDE interfaced with a computer-controlled μAutolabII potentiostat/galvanostat (Eco Chemie). The electrochemical cell comprised the TMF-GCRDE; a double-junction, Ag/AgCl, KCl (3 mol L^{-1}) saturated AgCl reference electrode; and a platinum wire counter electrode. The thin mercury film was prepared at the beginning of each analytical day and as required thereafter according to Bruland (1989). Cadmium standards were prepared in 0.05% HCl (Baseline, SeaStar Chemical) by serial dilution of a 1,000 mg mL^{-1} standard (in 2% HNO_3; High Purity Standards). Seawater samples were stored at 4°C in acid-cleaned PTFE or low-density polyethylene bottles and were analyzed within 24 h of collection.

Duplicate seawater samples for dissolved Cd analysis were transferred to either 60- or 120-mL PTFE Teflon cups (Savillex) with modified quartz window lids and were ultraviolet (UV) digested with the use of a high-pressure mercury lamp (28 mW cm^{-2}, λ = 254 nm; Jelight) for at least 90 min. UV digestion is necessary to break down interfering organic substances and metal complexing organic ligands, which occur naturally in seawater (Achterberg and van den Berg 1994). After UV digestion, 20 mL was deoxygenated with high-purity N_2 gas and transferred to the electrochemical cell. A deposition potential of −0.9 V was applied for a period of at least 3 min while the electrode rotated at 4,000 rpm to concentrate Cd in the mercury film. The motor was stopped, and after a 30-s equilibration period, the working electrode potential was scanned from −0.9 to −0.2 V in differential pulse mode with a modulation amplitude of 50 mV and a scan rate of 40 mV s^{-1}. The height of the Cd oxidation peak (at −0.69 V vs. Ag/AgCl reference electrode) was then recorded. After duplicate scans, the procedure was repeated for each of two standard additions of Cd, in which the amount of Cd added was adjusted to be approximately equal to the concentration of the sample. Procedural blanks were performed on a daily basis. The detection limit calculated from three times the standard deviation of 10 analyses of the blank (25 pmol L^{-1}) was 20 pmol L^{-1}. To assess the accuracy of the entire analytical procedure, the open-ocean reference material NASS-5 (National Research Council of Canada) was analyzed in triplicate.

Phosphate concentrations were measured with a Lachat Quick Chem 8000™ flow injection analysis system according to Parsons et al. (1984). For [PO_4] > 0.3 μmol L^{-1}, the precision or reproducibility was <3% and analyses were accurate to within 5% given typical uncertainties in blanks.

Results

Dissolved Cd and PO_4—Stations at which dissolved Cd and PO_4 profiles were measured are indicated on a bathymetric map of the Bering Sea in Fig. 3. Hydrographic data and dissolved Cd and PO_4 for the various depths sampled at the stations are summarized in Table 2. Station 1 (55°0.168′N, 178°59.589′W) was located in the HNLC region of the open Bering Sea, whereas Sta. 2 (56°19.966′N, 171°36.016′W) was located in the highly productive "green belt" (Springer et al. 1996), a persistent zone of high algal biomass thought to arise from the mixing of trace nutrient–rich shelf waters and macronutrient-rich HNLC waters at the energetic shelf–slope break (Bruland pers. comm.) southwest of the Pribilof Islands.

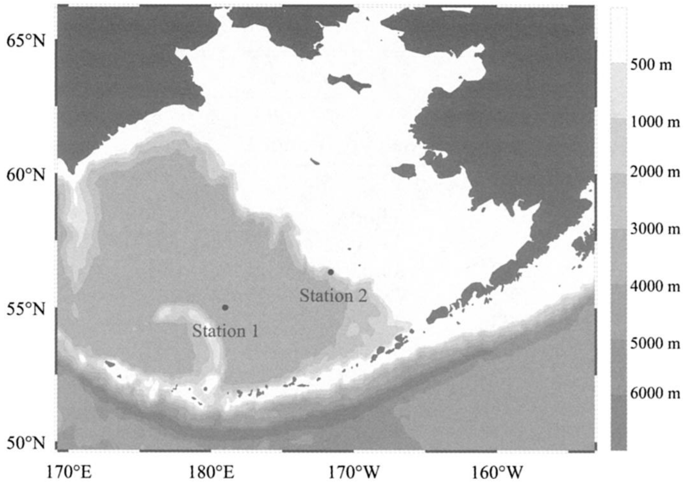

Fig. 3. Bathymetric map of the Bering Sea indicating stations for which dissolved Cd and PO_4 were determined as part of this study. Station 1 is in classic HNLC waters, whereas Sta. 2 is located in highly productive shelf–slope waters. Figure produced using Ocean Data View (Schlitzer 2004).

Dissolved Cd and PO_4 data for Sta. 1 and Sta. 2 are reported in Figs. 4 and 5, respectively. As in previous studies, Cd displayed a nutrient-like profile at both stations with depleted surface concentrations that increased below the mixed layer (Boyle 1976; Bruland et al. 1976; de Baar et al. 1994). At HNLC Sta. 1, dissolved Cd concentrations were lowest in surface waters with 0.25 ± 0.02 nmol L^{-1} at 5 m depth and reached a maximum concentration of 0.99 ± 0.03 nmol L^{-1} at 300 m. The concentration of PO_4 covaried with that of Cd with surface-water concentrations of 1.07 μmol L^{-1} at 6 m and a maximum concentration of 2.94 μmol L^{-1} at 500 m depth.

As at Sta. 1, dissolved Cd at Sta. 2 displayed a nutrient-like vertical distribution (Fig. 5). However, the surface concentrations of dissolved Cd and PO_4 at Sta. 2 were approximately half as large as those observed at HNLC Sta. 1. Dissolved Cd was depleted in surface waters to concentrations of 0.13 ± 0.002 nmol L^{-1} at 15 m and increased to a maximum of 0.87 ± 0.03 nmol L^{-1} at 300 m. As at Sta. 1, the vertical distribution of dissolved PO_4 was similar to that of Cd. A minimum PO_4 concentration of 0.36 μmol L^{-1} was detected at 8 m, and a maximum of 2.28 μmol L^{-1} occurred at 307 m.

Dissolved Cd : PO_4 ratio—The dissolved Cd : PO_4 ratio for Sta. 1 and Sta. 2 were calculated assuming a conservative error of 5% for dissolved PO_4 concentrations. Results of these calculations are presented in Fig. 6. At HNLC Sta. 1, dissolved Cd : PO_4 was lowest in surface waters (<50 m) with a minimum ratio 0.17 ± 0.01 nmol μmol^{-1} at 40 m. Waters below the mixed layer were typified by dissolved

Table 2. Hydrographic, nutrient, and dissolved cadmium data for two stations in the Bering Sea.

CTD bottle data						GO-Flo bottle data					
Depth (m)	Temperature (°C)	Salinity	PO_4 (μmol L^{-1})	NO_3 (μmol L^{-1})	Si (μmol L^{-1})	Depth (m)	Dissolved Cd (nmol L^{-1})	SD	PO_4 (μmol L^{-1})	NO_3 (μmol L^{-1})	Si (μmol L^{-1})
Sta. 1 (55.0028°N, 178.99°W)											
6	10.7	33.00	1.15	14.8	4.5	5	0.25	0.02	—		
26	7.23	33.10	1.72	22.0	26.0	15	0.29	0.00	1.31	17.7	22.0
53	3.32	33.23	2.15	31.1	53.4	25	0.30	0.01	1.26	16.7	13.3
78	2.82	33.24	2.21	31.5	56.8	40	0.31	0.02	1.82	24.2	32.0
102	2.75	33.27	2.27	31.5	56.8	70	0.58	0.01	2.09	30.9	50.5
153	2.99	33.40	2.29	33.0	65.4	100	0.67	0.02	2.06	31.8	49.3
204	3.57	33.63	2.79	38.0	84.0	200	0.82	0.01	2.59	41.5	81.3
253	3.73	33.76	2.90	40.2	93.0	300	0.99	0.03	2.83	44.7	96.8
304	3.73	33.86	2.83	42.0	105	500	0.92	0.02	2.94	46.0	118
403	3.67	34.01	2.91	43.8	114	900	0.93	0.03	3.04	45.3	152
504	3.54	34.09	3.02	43.4	124	2,200	0.95	0.02	2.90	42.3	205
804	3.09	34.27	3.02	43.4	139	2,700	0.87	0.04	2.86	38.9	207
1,005	2.84	34.35	2.92	44.0	156						
1,254	2.51	34.43	2.92	44.0	172						
1,507	2.24	34.50	2.91	44.0	187						
1,758	2.02	34.55	2.88	43.5	197						
2,007	1.88	34.58	2.89	42.2	209						
2,258	1.77	34.61	2.83	42.1	219						
2,510	1.70	34.62	2.79	40.4	220						
2,761	1.64	34.64	2.83	40.0	220						
3,012	1.61	34.65	2.92	38.6	212						
3,513	1.60	34.66	2.80	37.7	220						
Sta. 2 (56.33°N, 171.6°W)											
3	10.44	32.39	0.47	1.56	2.0	15	0.13	0.00	0.42	3.3	2.9
9	10.49	32.38	0.39	1.40	1.7	25	0.35	0.01	1.03	11.3	18.5
14	9.67	32.47	0.47	2.71	3.4	40	0.50	0.00	1.66	22.4	38.7
18	9.15	32.46	0.57	3.67	5.0	50	0.54	0.04	1.95	27.6	49.2
23	9.39	32.61	0.82	6.98	11.3	75	0.60	0.02	1.93	27.9	49.8
28	8.57	32.62	0.94	8.65	14.7	100	0.65	0.04	2.04	29.9	53.9
36	6.32	32.72	1.56	18.88	34.6	150	0.70	0.02	2.08	31.3	58.4
40	5.22	32.76	1.73	23.72	41.1	200	0.73	0.04	2.12	31.9	59.8
46	5.11	32.79	1.88	25.77	45.3	300	0.87	0.03	2.44	37.7	82.0
54	4.84	32.90	1.92	27.16	49.3						
65	4.71	32.93	1.93	27.91	49.8						
85	4.58	32.98	1.99	29.21	52.0						
105	4.71	32.93	2.04	29.86	53.9						
154	4.18	33.24	2.08	31.26	58.4						
205	3.77	33.32	2.12	31.91	59.8						
255	3.74	33.44	2.28	34.70	70.4						
307	3.87	33.61	2.44	37.67	82.0						

Cd : PO_4 ratios that were higher and more similar to the average Pacific deep-water ratio (de Baar et al. 1994), falling between 0.28 ± 0.02 and 0.35 ± 0.03 nmol μmol^{-1}. In contrast, at green belt Sta. 2, the dissolved Cd : PO_4 was more uniform throughout the water column. Despite more acute surface depletion of both Cd and PO_4, the concentration ratio of these dissolved constituents fell within a narrow range between 0.28 ± 0.03 nmol μmol^{-1} at 50 m and 0.36 ± 0.05 nmol μmol^{-1} at 300 m.

Discussion

Mesoscale Fe enrichment experiments and shipboard incubation studies demonstrate that Fe availability limits the growth rate and can affect the species composition of phytoplankton in both oceanic (Martin et al. 1994; Coale et al. 1996) and coastal waters (Bruland et al. 2001; Hutchins et al. 2002). Evidence is also increasing that in addition to affecting physiological rate processes, Fe limitation can effect the elemental composition of natural phytoplankton assemblages (Hutchins and Bruland 1998; Twining et al. 2004). Here, we synthesize results from laboratory studies with field incubations to construct a simple model relating the effects of Fe limitation of phytoplankton physiology and growth rates on the Cd : P ratio of the particulate and Cd : PO_4 ratio of the dissolved phase. Building on the work of Sunda and Huntsman (2000), we speculate that the nonlinearity or kink in the global dissolved Cd : PO_4 relationship exists because of the systemic Fe limitation of phytoplankton growth rates in the modern ocean.

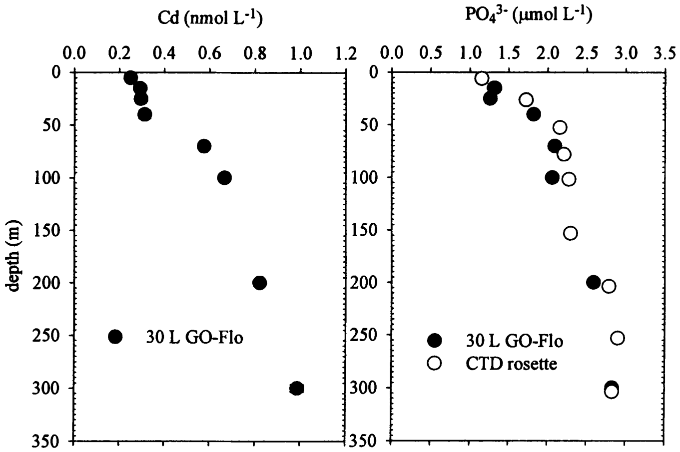

Fig. 4. Vertical profiles of dissolved Cd and PO_4 at Sta. 1 in HNLC waters of the Bering Sea. Open symbols represent analyses carried out on samples recovered from Niskin bottles on the R/V *Kilo Moana*'s CTD rosette, and solid symbols represent analyses carried out on samples collected from 30-liter Teflon-coated GO-Flo bottles. Error bars on the dissolved Cd analyses represent the standard deviation of duplicate determinations.

Algal uptake of bioactive metals appears to be highly regulated at the cellular level (Morel and Price 2003), and as a result, the cellular quotas (normalized to P) of these metals only vary by a factor of ~20 in marine plankton (Ho et al. 2003). Conversely, the uptake of Cd seems to be less specific, and resulting quotas are observed to vary by factors of 100–1,000 (Sunda and Huntsman 2000; Ho et al. 2003; Cullen and Sherrell 2005). Results from laboratory studies with the oceanic diatom *T. oceanica* (Sunda and Huntsman 2000) in chemically defined growth media and incubation studies with natural phytoplankton assemblages from the Southern Ocean (Cullen et al. 2003) suggest that, like Si : nitrogen (N) ratios, the Cd : P composition of marine phytoplankton can be affected by the bioavailability of Fe. Experiments with an Fe-limited isolate of the oceanic diatom *T. oceanica* (Sunda and Huntsman 2000) have indicated that cellular Cd content increases with decreasing Fe availability. At [Zn^{2+}] typical of open ocean surface waters, Cd : P ratios for Fe-limited cells were ~2.5-fold higher than Fe-replete cells. For the laboratory isolate, the Fe-related effect on Cd content was only significant when ambient log([Zn^{2+}]) was below at least −12.0 (Sunda and Huntsman 2000). The single experiment with a natural assemblage of phytoplankton from the Southern Ocean demonstrated that, like in the laboratory study, Fe-limited cells had lower growth rates and Cd : P ratios that were 3.6-fold higher than Fe-replete phytoplankton (Cullen et al. 2003). Unlike the study of Sunda and Huntsman (2000), the effect of Fe limitation of the Cd : P of the phytoplankton occurred independent of Zn availability, with significantly higher ratios in Fe-limited versus Fe-replete cells at calculated log([Zn^{2+}]) as high as −8.2 (Cullen et al. 2003).

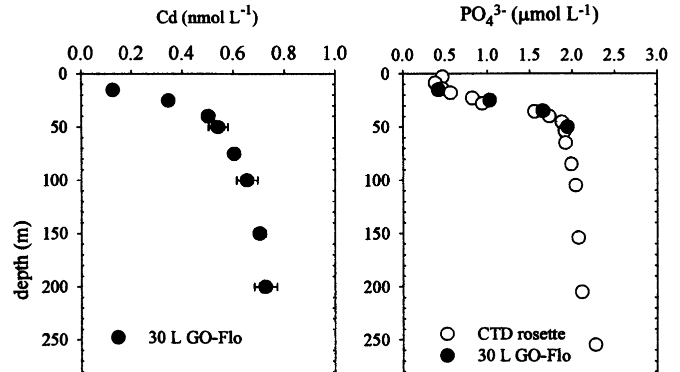

Fig. 5. Vertical profiles of dissolved Cd and PO_4 at Sta. 2 in the productive green belt waters of the Bering Sea. Open symbols represent analyses carried out on samples recovered from Niskin bottles on the R/V *Kilo Moana*'s CTD rosette, and solid symbols represent analyses carried out on samples collected from 30-liter, Teflon-coated GO-Flo bottles. Error bars on the dissolved Cd analyses represent the standard deviation of duplicate determinations.

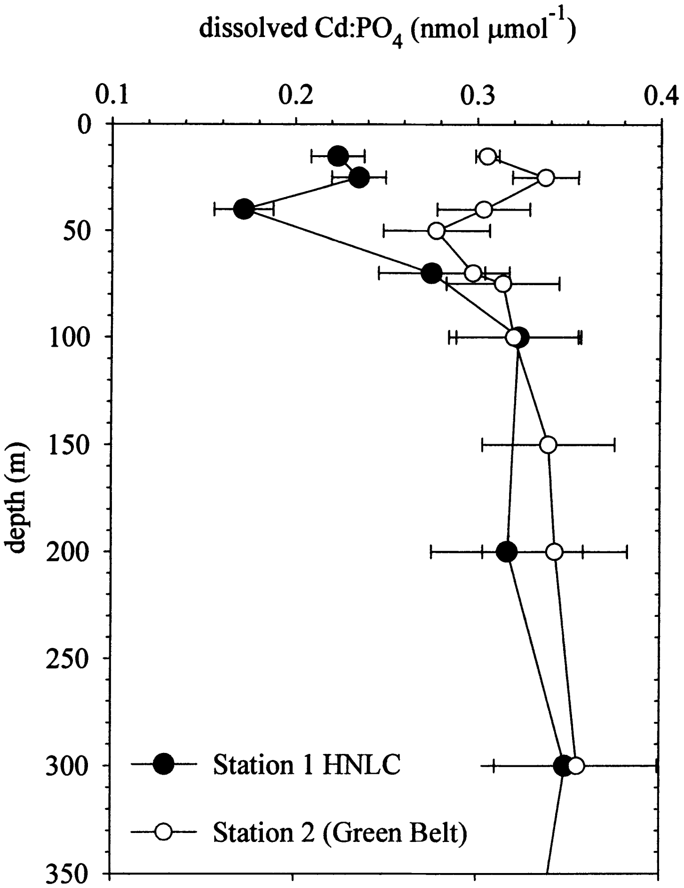

Fig. 6. Dissolved Cd : PO_4 ratios in the upper 350 m at Sta. 1 and Sta. 2 in the Bering Sea. Error bars represent the propagated standard deviation of the ratios assuming a 5% error for PO_4 analyses.

Although other factors are known to modulate Cd accumulation in marine algae (Lee and Morel 1995; Sunda and Huntsman 1998), a synthesis of the laboratory study of Sunda and Huntsman (2000) and the shipboard

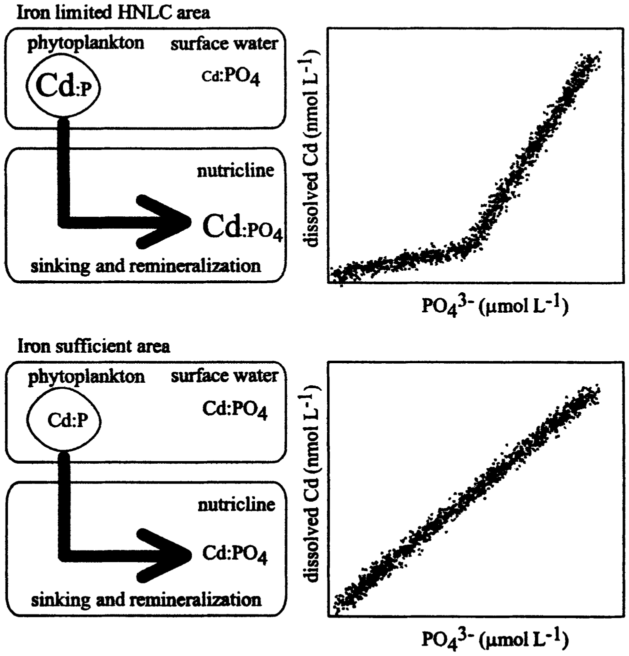

Fig. 7. A simple schematic diagram summarizing the proposed influence of Fe availability on the Cd : P composition of marine phytoplankton and the resulting effects on the dissolved Cd : PO_4 ratio of surface waters and the main nutricline.

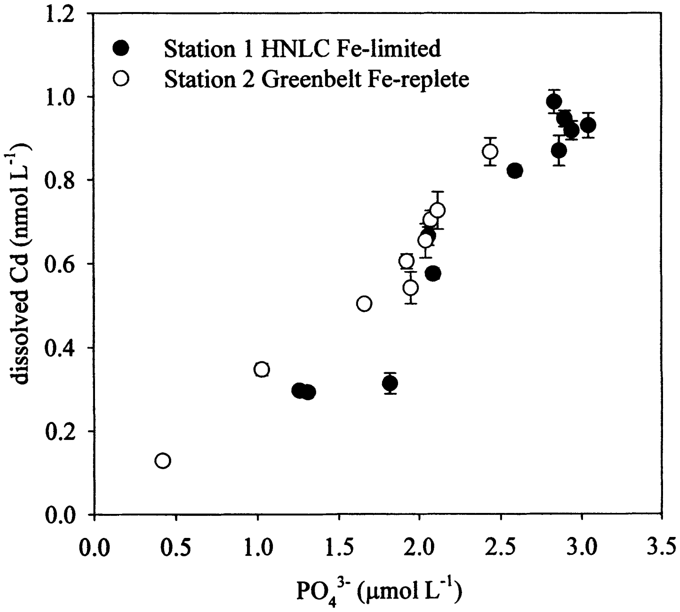

Fig. 8. Relationship between dissolved Cd versus PO_4 at Stas. 1 and 2 in the Bering Sea.

incubation study of Cullen et al. (2003) allows the construction of a simple model that relates the Fe nutrition of marine phytoplankton to their growth rate, their Cd : P composition, and the dissolved Cd : PO_4 ratio of the seawater in which they reside. In areas of the ocean in which steady-state Fe concentrations are sufficiently low, large diatoms that are thought to dominate the particulate export flux will grow only slowly, limited in a Monod sense by the bioavailability of Fe. As observed in laboratory cultures and shipboard incubations with field populations of phytoplankton, this slow growth and concomitant physiological adaptation accumulates Cd preferentially in cells driving the Cd : P ratio of the algae up to sixfold higher than the dissolved Cd : PO_4 of the surrounding seawater. The preferential uptake of Cd and export of high Cd : P particulate matter from Fe-limited surface waters will leave the mixed layer with a lower dissolved Cd : PO_4 ratio compared with subsurface and deep-water dissolved Cd : PO_4 ratios. In contrast, in surface waters in which Fe bioavailability is high and phytoplankton grow at near maximal rates, we expect lower Cd : P in the cells as they accumulate more PO_4 while Cd content remains relatively constant or does not increase as significantly as does cellular P (Cullen et al. 2003). Under Fe-replete conditions, we expect the export of cells with lower Cd : P ratios at or near to the dissolved Cd : PO_4 in the waters where they grow (Cullen et al. 2003). Under these conditions, surface waters in which Cd and PO_4 are drawn down by phytoplankton in Fe-replete areas will have dissolved Cd : PO_4 ratios that are equal to or greater than the ratio of subsurface and deep waters. This model makes very simple qualitative predictions about the relationship between Fe availability to the phytoplankton and the dissolved Cd : PO_4 ratio in ocean surface waters and the nutricline (Fig. 7). We will evaluate the model by comparing its predictions with the observed Cd and PO_4 concentrations in Fe-limited and Fe-replete surface waters of the Bering Sea and with previously published results in the literature.

The new dissolved Cd and PO_4 data from the Bering Sea are consistent with the simple model formalized herein (Fig. 8). At both stations, the vertical distribution of both Cd and PO_4 were nutrient-like with depleted surface concentrations as a result of biological uptake by phytoplankton in the mixed layer. Station 1 was a classic HNLC location with surface dissolved Fe concentrations of 0.01 nmol L^{-1} (Bruland et al. pers. comm.) and clear evidence of Fe limitation of phytoplankton growth rates, as demonstrated by shipboard incubation experiments (Hurst et al. pers. comm.). The Fe-limited, slow-growing phytoplankton community at Sta. 1 left surface dissolved Cd : PO_4 ratios as low as 0.17 ± 0.01 nmol μmol^{-1} with an average ratio of 0.23 ± 0.04 nmol μmol^{-1}. Surface-water dissolved ratios at HNLC Sta. 1 were significantly lower than in waters below the mixed layer, in which Cd : PO_4 averaged 0.33 ± 0.04 nmol μmol^{-1}. Station 2 was located in the highly productive green belt (Springer et al. 1996). Surface-water dissolved Fe concentrations were higher at Sta. 2, and the biomass was dominated by large diatoms. The phytoplankton community at this site was not Fe limited because their growth rates were not affected by Fe amendments to shipboard incubation bottles. The phytoplankton bloom observed at the Fe-replete Sta. 2 had depleted dissolved Cd and PO_4 concentrations to 0.13 ± 0.002 nmol L^{-1} and 0.39 $\mu mol\ L^{-1}$, respectively. Although these concentrations were lower than those at Fe-limited Sta. 1, the dissolved Cd : PO_4 ratio of the surface waters at Sta. 2 were significantly higher (0.33 ±

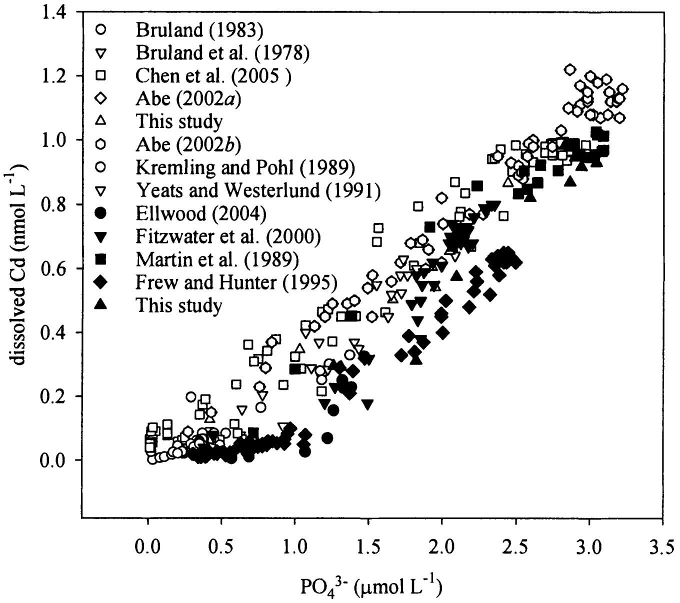

Fig. 9. Relationship between dissolved Cd versus PO_4 for selected stations in the global dataset (Table 1). Solid symbols represent stations from high-latitude HNLC areas for which the growth of phytoplankton is thought to be limited by Fe availability, and open symbols are from stations in which surface [PO_4] has been drawn down to <0.3 μmol L^{-1} by the growth of phytoplankton. Note that this criterion for identifying HNLC areas is somewhat arbitrary and includes stations, for example those near to the subtropical convergence zone in the Southern Ocean, for which Fe limitation might be relieved seasonally.

0.02 nmol μmol^{-1} in the upper 75 m) and similar to waters below the mixed layer (0.36 ± 0.02 nmol μmol^{-1} below 75 m). The data suggest that the preferential uptake of Cd relative to PO_4 and the resulting kink in the dissolved Cd versus PO_4 relationship observed in the HNLC waters of the Bering Sea (Fig. 8) might result from the effects of Fe limitation on the growth rate of the resident phytoplankton community.

Indeed, an examination of previously reported data in the literature supports the idea that the preferential uptake of dissolved Cd relative to PO_4 by phytoplankton observed in surface waters of the ocean and the kink in the global dissolved Cd versus PO_4 relationship could be direct consequences of systemic Fe limitation of algal growth physiological rate processes in the modern ocean. A compilation in which data from high-latitude HNLC regions are compared with data from areas of the oceans in which phytoplankton growth is not thought to be limited by Fe availability is presented in Fig. 9. Many studies have documented significant excursions from linearity in the global dissolved Cd versus PO_4 relationship in high-latitude HNLC regions of the Southern Ocean (Frew and Hunter 1995; Löscher et al. 1998; Ellwood, 2004). This nonlinearity manifests itself as higher than average slopes in subsurface waters, significant negative *y*-intercepts, and an unusual kink in the dissolved Cd versus PO_4 relationship at [PO_4^{3-}] ~1.3 μmol L^{-1} (de Baar et al. 1994). The kink occurs at PO_4 concentrations that are typical for surface waters in HNLC areas in which phytoplankton grow at submaximal rates because of Fe limitation (Fig. 9). Indeed, the extremely low bioavailable Fe concentrations, low temperature, and vigorous vertical mixing that reduces light levels in surface waters of the Southern Ocean all conspire to suppress phytoplankton community growth rates (Sunda and Huntsman 1997). We can speculate that under these conditions, the preferential uptake of Cd by the biota and the resulting reduction of the dissolved Cd : PO_4 ratio of surface waters would be most pronounced (Sunda and Huntsman 2000; Cullen et al. 2003). The export and subsequent remineralization of this high–Cd : P particulate matter elevates the dissolved Cd : PO_4 ratio in the subsurface nutricline, accentuating the nonlinearity of vertical profiles from Fe-limited regions of the Southern Ocean (Fig. 9). Thus the effects of Fe limitation and the growth rate dilution model presented here (Sunda and Huntsman 2000; Cullen et al. 2003) represent a plausible mechanism in which to explain the kink in the global dissolved Cd versus PO_4 relationship.

An outstanding question related to the model presented here is whether or not Fe-limited export production in HNLC areas is significant enough to drive observed surface depletions of Cd relative to PO_4. For the main thesis of this manuscript to hold, there must be an appreciable flux of organic matter out of HNLC surface waters associated with the export of high–Cd : P, Fe-limited phytoplankton. The following calculation for ocean Sta. PAPA (OSP) indicates that, with reasonable assumptions for Fe-stressed phytoplankton Cd : P composition and export production estimates, one can drive the low–surface-water dissolved Cd : PO_4 ratios observed in HNLC areas. At OSP, there is a seasonal biological drawdown of nitrate in the mixed layer of 7 μmol L^{-1} that we will assume is equal to export production (Whitney and Freeland 1999). Even during the most productive spring and summer months, measurements of photosynthetic competency and cellular-level molecular markers indicate that resident phytoplankton in this HNLC area are Fe-stressed (LaRoche et al. 1996; Suzuki et al. 2002). If we assume Redfield stoichiometry (N : P = 16 : 1), this corresponds to a removal of ~0.44 μmol L^{-1}, which agrees well with the seasonal change in the mixed-layer PO_4 concentration of 1.3 μmol L^{-1} in the winter down to 0.8 μmol L^{-1} in the late summer reported by (Harrison 2002). To calculate the effect on the dissolved Cd : PO_4 ratio, let us assume that the seasonal PO_4 drawdown can be attributed to the growth of Fe-limited phytoplankton with a Cd : P ratio of 1.3 nmol μmol^{-1}, as was observed in the Southern Ocean (Cullen et al. 2003). Assuming that the winter dissolved Cd : PO_4 ratio at Sta. P is similar to the deep-water ratio in the Pacific (0.35 nmol μmol^{-1}), then initial dissolved concentrations are [Cd] = 0.9 nmol L^{-1} and [PO_4] = 1.3 μmol L^{-1}. After the removal of 0.5 μmol L^{-1} PO_4 by Fe-limited phytoplankton (Cd : P = 1.3 nmol μmol^{-1}) over the course of the growing season, the late summer dissolved [Cd] would be 0.25 nmol L^{-1} and the surface-water dissolved Cd : PO_4 ratio would be reduced to ~0.3 nmol μmol^{-1}. This rough calculation is consistent with observations in HNLC areas. Note that the Cd : P of 1.3 nmol μmol^{-1} assumed for Fe-limited phytoplankton is a conservative value. Cells with Cd : P ratios of up to 6 nmol μmol^{-1} (Cullen et al. 1999) have been measured in coastal upwelling areas known to experience Fe limitation (Hutchins and Bruland 1998). Adopting a higher Cd : P for Fe-limited phytoplankton would drive the residual dissolved Cd : PO_4 ratio of the surface water even lower and more similar to values observed as part of this study in the Bering Sea (Cd : PO_4 = 0.21 nmol μmol^{-1}). Therefore, the export of Fe-limited cells with total flux values within accepted ranges can explain the anomalous Cd : PO_4 ratios observed for HNLC surface waters.

To date, only three other mechanistic explanations of observed nonlinearity in the global relationship are known to the author. The first suggests that the Cd in sinking organic matter is regenerated at greater depths than is P (Boyle 1988). This explanation is difficult to reconcile with the virtual coincidence of subsurface Cd and PO_4 concentration maxima. The second mechanism is based on the synthesis of results from laboratory experiments with marine phytoplankton isolates in ion-buffered artificial seawater and direct measurements of Cd and Zn speciation from the North Pacific (Sunda and Huntsman 2000). Controlled laboratory studies demonstrate that the Cd uptake and content of marine phytoplankton is largely controlled by aqueous Cd ion concentrations and is inversely related to Mn and Zn ion concentrations (Lee and Morel 1995; Sunda and Huntsman 1998). Modeled oceanic diatom Cd : P based on variations in [Cd^{2+}] and [Zn^{2+}] tend to agree well with existing measurements of the Cd : P ratio of suspended particulate matter and the slope of dissolved Cd versus PO_4 in different oceanic regimes (Sunda and Huntsman 2000). The kink in the global dissolved Cd versus PO_4 ratio was attributed to the export of high Cd : P phytoplankton growing in waters with depleted [Zn^{2+}] resulting from the high rates of Zn uptake by Fe-limited phytoplankton. Only a minor contribution to the kink was attributed to the direct effects of elevated Cd : P in the alga from lowered, Fe-limited growth rates. At present, regional application of kinetic models like Sunda and Huntsman (2000) are limited only by the lack of speciation data for Cd and Zn at appropriate spatial and temporal scales in the various oceanic regimes. The third explanation for the kink involves the formation of Antarctic bottom water from high–Cd : PO_4 surface waters close to the Antarctic continent (Frew 1995). Although the ventilation of this high preformed Cd : PO_4 water helps to explain elevated ratios in the deep ocean, it is unclear how this mechanism can account for the low ratios and variability in dissolved Cd : PO_4 observed in oceanic surface waters.

The model and data presented here are consistent with Sunda and Huntsman (2000) but do not necessarily acknowledge the singular importance of Zn bioavailability as the primary cause of elevated phytoplankton Cd : P in Fe-limited areas of the world ocean. The hypothesis that Fe limitation of algal growth rates leads to the nonlinear relationship between dissolved Cd and PO_4 in the modern ocean can be tested by examining the effects of Fe supplementation on the biological uptake of dissolved Cd and PO_4 and the Cd : P composition of natural phytoplankton assemblages in chronically Fe-limited areas of the ocean. Whether in shipboard incubation experiments or as part of planned mesoscale Fe fertilization experiments, the problem should be surrounded by a comprehensive study of dissolved trace metal concentrations and speciation (primarily Cd and Zn), changes in the particulate trace metal pool, and the biological response to Fe additions. Important questions about how and why changes in Fe bioavailability might affect the degree of coupling between Cd and P in surface waters remain. For instance, do changes in Fe availability affect the relative uptake of Cd and PO_4 by inducing cellular-level changes in the chemical composition of individual phytoplankton as has been observed for Si : N ratios (Hutchins and Bruland 1998; Takeda 1998)? Does Fe fertilization alter the surface dissolved Cd : PO_4 ratio by shifting the structure of the phytoplankton community from groups with higher Cd : P quotas, like coccolithophorids, to diatoms that have lower Cd : P quotas (Ho et al. 2003)? Perhaps large-scale input of Fe simply allows "excess" PO_4 to be converted to biomass, as is observed in shipboard incubation studies.

The correlation of Fe-limited growth rates with elevated Cd : P in the phytoplankton, decreased dissolved Cd : PO_4 in the mixed layer, and elevated dissolved Cd : PO_4 slopes in the nutricline cannot be taken as unequivocal support for the simple growth–dilution model outlined here. Underlying physiological mechanisms could exist that cause Fe-limited phytoplankton in HNLC regions to accumulate higher levels of Cd relative to their biomass than phytoplankton growing in Fe-sufficient waters. For example, in addition to the two Fe permeases of the high-affinity Fe transport system identified in the genome of the diatom *T. pseudonana* (Armbrust et al. 2004), these organisms might have less specific metal transporters, in which Cd and Fe compete for the binding site. Whether or not a nonspecific Cd : Fe metal transporter might exist in marine phytoplankton is presently unknown but would represent a compelling molecular-level mechanism to explain the high Cd : P ratios observed in Fe-limited phytoplankton and the low dissolved Cd : PO_4 ratios in surface waters in HNLC regions (Fig. 9).

The idea that Fe limitation of phytoplankton growth might be the root cause for the kink in the dissolved Cd : PO_4 relationship carries important implications for the use of Cd : Ca ratios in planktonic foraminifera to infer past changes in the efficiency of the biological CO_2 pump (Sunda and Huntsman 2000; Cullen et al. 2003). The possibility that phytoplankton in the Southern Ocean experienced reduced Fe limitation during the last glacial maximum (LGM) has been advanced to explain how the efficiency of the biological pump could be increased and account for a portion of lowered atmospheric CO_2 (Martin 1990). Increased Fe bioavailability during the LGM, according to the argument advanced here, could fundamentally change the nature of the dissolved Cd : PO_4 ratio in surface waters and the main nutricline. The use of the modern dissolved relationship to infer surface nutrient inventories during the LGM from paleorecords of dissolved Cd in this case would, a priori, carry large uncertainties.

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