The cadmium-phosphate relationship in brine: biological versus physical control over micronutrients in sea ice environments

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Abstract: Despite supporting productive ecosystems in the high latitudes, the relationship between macro- and micronutrients in sea ice environments and their impact on surface productivity is poorly documented. In seawater, the macronutrient phosphate and the micronutrient cadmium follow similar distributions, which are controlled by biological processes in surface waters. We investigated cadmium and phosphate in sea ice brine, and the biological and physical processes controlling their distribution. Cadmium concentrations in sea ice brine ranged from 0.09–2.4 nmol kg^{-1}, and correlated well with salinity. Our results show that micronutrients in sea ice are most probably sourced from the seawater from which it froze rather than external sources such as atmospheric deposition. The weak correlation between sea ice cadmium and phosphate, and the positive relationship between cadmium and biomass, suggests against biological uptake being a principal control over micronutrient distribution even in a highly productive setting. Instead, brine expulsion and dilution play a dominant role in cadmium distribution in sea ice. Nutrient dilution within brine channels during melting, and contrasting sea ice and open water phytoplankton populations, suggests that late spring sea ice is not a significant source of nutrients or biomass to seawater. We suggest that future changes in sea ice seasonality may impact nutrient distribution and Antarctic marine ecosystems.

Introduction

Sea ice plays a vital role in global climate systems, influencing the exchange of heat and atmospheric gases (including carbon dioxide, CO_2), deepwater formation, regional weather patterns, planetary albedo and ocean circulation (Stephens & Keeling 2000, Parkinson 2004). Biological primary productivity associated with Antarctic sea ice significantly impacts the global cycling of carbon, contributing to an estimated 10–28% of Southern Ocean production (Abelmann & Gersonde 1991, Lizotte 2001, Arrigo & Thomas 2004), as well as the availability of macro- and micronutrients (Sedwick & Di Tullio 1997). Sea ice algae may contribute significantly to the sinking of organic matter from surface waters to the seafloor (export production), due to flocculation, high silica content and repackaging in faecal pellets of small grazers such as copepods (Cadée *et al*. 1992, Shimmield *et al*. 1995, Nelson *et al*. 2002, Brierley & Thomas 2002). This rapid export of organic matter associated with sea ice reduces the time available for remineralization and, consequently, sea ice organic carbon burial may be a significant sink for atmospheric CO_2 (Abelmann *et al*. 2006).

Sea ice is a unique biological habitat that experiences extreme physical and chemical conditions. For example,

nutrient levels within sea ice show a high degree of spatial heterogeneity, and depend on physical factors, such as ice formation, consolidation and ablation (Thomas *et al*. 1998), and biological factors including community structure and bacterial activity (Kottmeier & Sullivan 1990). The nutrients may be sourced internally (e.g. bacterial activity, Kottmeier & Sullivan 1990) or externally from ice sheets or vertical eddy diffusion from underlying waters (Cota & Sullivan 1990, Lizotte 2001). The prevalence of nitrifying bacteria, regeneration of nutrients in a closed or semi-closed system and physical processes, results in elevated nitrite, dissolved organic matter, ammonium and phosphate (Clarke & Ackley 1984, Dieckmann *et al*. 1991, 1992, Thomas *et al*. 2001). Nutrient limitation may occur in sea ice (McConville *et al*. 1985, Dieckmann *et al*. 1991) although sea ice algae appear to have physiological adaptations and a sufficiently strong affinity for some nutrients, e.g. Si, to avoid limitation (Nelson & Tréguer 1992, Stapleford & Smith 1996, McMinn *et al*. 1999).

For over 20 years, it has been known that cadmium (Cd) exhibits a similar distribution to Dissolved Inorganic Phosphate (DIP or PO_4^{3-}) in seawater (reviewed by de Baar 1994, Elderfield & Rickaby 2000). The nature of this relationship, however, remains elusive, although there is
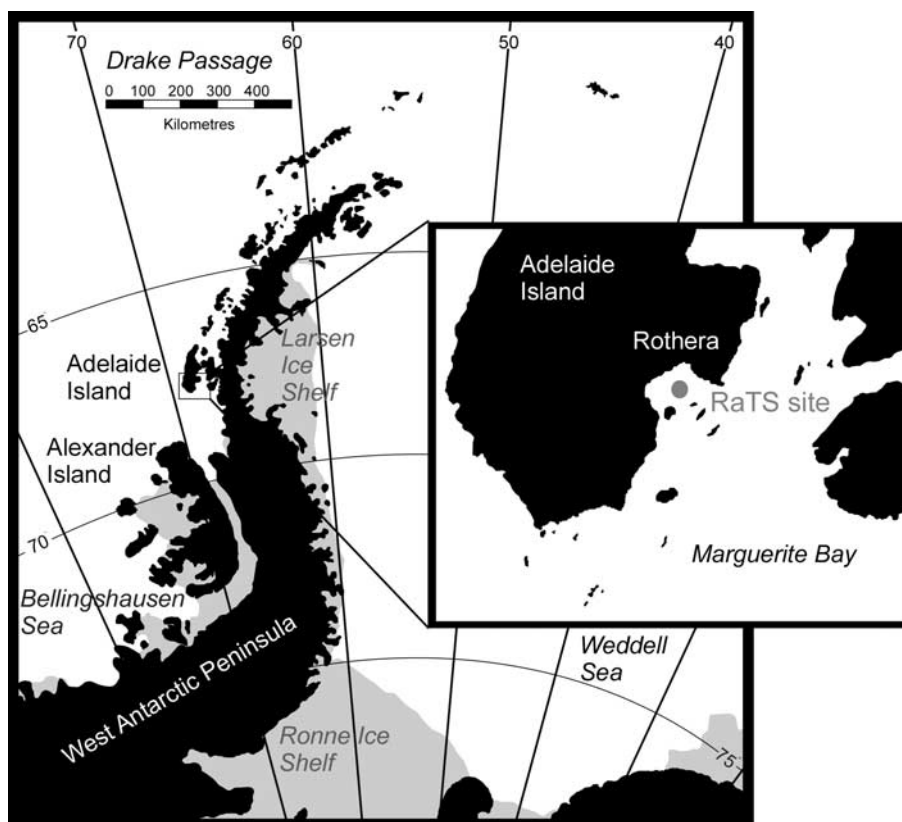
Fig. 1. A map of the study area showing Marguerite Bay sampling region. Samples were taken from near Rothera Research Station and from the Rothera Oceanographic and Biological Time-Series (RaTS) sampling site.

increasing evidence that Cd is a micronutrient actively taken up by phytoplankton, rather than being passively scavenged onto organic matter. Recent molecular work has shown the existence of a specific Cd metalloenzyme, Cd-carbonic anhydrase (Cd-CA), required for photosynthesis by phytoplankton (Lane & Morel 2000b, Xu *et al.* 2008). Further, Cd isotopic fractionation in surface water is highly indicative of biological uptake (Ripperger *et al.* 2007).

The departure from the quasi-linear relationship between Cd and PO_4^{3-} (de Baar 1994) in surface waters is also poorly understood, and may result from fractionation of Cd with respect to P into organic matter (Elderfield & Rickaby 2000), growth rate effects, population structure (Finkel *et al.* 2007), interactions with other trace metals (Fe, Zn), variations in pCO_2 and carbonic anhydrase activity (Cullen & Sherrell 2005, Cullen 2006, Hendry *et al.* 2008).

Although there is some limited data on macronutrients, there is currently no data on Cd concentrations in sea ice brine to act as a direct comparison to open water conditions. Here, we present Cd data from sea ice brine collected by sackhole drilling and analysed by ICP-MS using isotope dilution followed by magnesium hydroxide precipitation of filtered samples. Our results show that physical processes are probably as important, if not more so, than biological processes in controlling the distribution

of micronutrients in the sea ice environment. In the light of these results, we discuss the probable impact of sea ice melt on the surrounding seawater.

Methods and materials

Sea ice brine sampling was carried out in Marguerite Bay, Adelaide Island, from June 2005 to December 2006 in collaboration with the British Antarctic Survey Rothera Oceanographic and Biological Time-Series (RaTS; Fig. 1). The study site is described fully elsewhere (Clarke *et al.* 2008, Meredith *et al.* 2008).
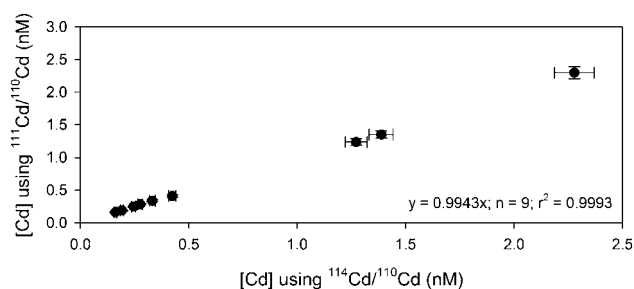

Fig. 2. Comparison of sample concentrations calculated using $^{111}Cd/^{110}Cd$ and $^{114}Cd/^{110}Cd$. Error bars show $\pm 1\sigma$.

Table I. Collection day, temperature, biomass, macro- and miconutrient results for sea ice brines. All macro- and micronutrient data were corrected for density and reported per kg (a maximum correction of approximately 5%), which was calculated from brine or underlying water temperatures and brine salinity calculated from Na concentrations, using CSGNetwork Water Density Calculator version 1.6.4. (http://www.csgnetwork.com/h2odenscalc.html).

Date	Temp (°C)	Total chl a (mg m^{-3})	Si(OH)$_4$ (μmol l^{-1})	NO$_3^-$ (μmol l^{-1})	PO$_4^{3-}$ (μmol l^{-1})	Cd (nmol l^{-1}) SA[a]	Cd (nmol l^{-1}) ID[b]	Na (mmol kg^{-1})	Calculated salinity	Density (g l^{-1})	Si(OH)$_4$ (μmol kg^{-1})	NO$_3^-$ (μmol kg^{-1})	PO$_4^{3-}$ (μmol kg^{-1})	Cd (nmol kg^{-1}) SA[a]	Cd (nmol kg^{-1}) ID[b]
17/09/05		4.53	95.8	13.5	0.4	0.891		1095	63.5	1052	91.1	12.8	0.4	0.85	
13/10/05		0.64	30.0	1.7	0.3	0.222		233	13.5	1011	29.7	1.7	0.3	0.22	
21/11/05	-3.8	2.76	22.0	2.1	0.4	0.414		347	20.1	1016	21.6	2.1	0.4	0.41	
23/11/05	-1.5	1.66	11.7	9.1	0.2	0.765		340	19.7	1016	11.5	8.9	0.2	0.75	
28/11/05	-2.7	1.33				0.216		182	10.6	1008				0.21	
01/12/05	-2.0			3.8	0.6	0.284		191	11.1	1009		3.8	0.6	0.28	
06/12/05	-1.8	1.17		1.1	0.3	0.290		185	10.7	1008		1.0	0.3	0.29	
09/12/05	-0.9	0.91	4.0	1.0	0.2	0.250		196	11.4	1009	3.9	1.0	0.2	0.25	
20/12/05	-1.1	1.77	6.3	1.1	0.3	0.162		146	8.5	1007	6.3	1.1	0.3	0.16	
31/07/06	-1.8*	0.65	113.1	72.5	3.2	1.524	1.25	842	48.8	1039	108.8	69.8	3.1	1.47	1.25
22/08/06			156.2	129.6	7.2	2.268		1506	87.3	1071	145.8	121.0	6.7	2.12	
31/08/06	-1.8*	1.04	131.0	111.0	3.0	2.562	2.11	1314	76.2	1062	123.4	104.5	2.8	2.41	2.11
18/09/06	-1.8*	0.50	50.8	21.8	2.1	0.248	0.27	157	9.1	1007	50.5	21.7	2.1	0.25	0.27
27/09/06	-1.8*	1.26	143.0	108.4	3.2	1.778	1.39	1139	66.1	1054	135.7	102.9	3.1	1.69	1.39
09/10/06	-1.7*	8.77	121.9	13.3	0.6	0.369		673	39.0	1031	118.2	12.9	0.6	0.36	
02/11/06		2.31	13.3	3.3	0.1	0.060		63	3.6	1003	13.3	3.3	0.1	0.06	
03/11/06	-1.4*	0.97	15.9	1.7	0.1	0.117	0.19	52	3.0	1002	15.8	1.7	0.1	0.12	0.19
09/11/06	-1.3*	0.46	26.6	1.9	0.2	0.205	0.24	132	7.6	1006	26.4	1.9	0.2	0.20	0.24
10/11/06	-1.3*	1.41	32.7	0.1	0.3	0.216	0.16	168	9.7	1008	32.5	0.1	0.3	0.21	0.16
15/11/06	-1.4*	0.70	22.3	1.9	0.7	0.274	0.03	116	6.7	1005	22.2	1.9	0.7	0.27	0.33
21/11/06	-1.4*	0.80	39.4	2.2	0.2	0.506	0.41	244	14.1	1011	38.9	2.1	0.2	0.50	0.41
02/12/06	-1.4*	1.33	18.1	0.7		0.210		165	9.59	1001	18.1	0.7		0.21	
07/12/06	0.5	0.41	15.4		0.1	0.060		115	6.6	1000	15.4		0.1	0.06	

*Temperature data are only available for underlying seawater. If no temperature data are available, temperature was estimated from previous value.

[a] Cadmium concentrations measured using Standard Addition (SA).

[b] Cadmium concentrations measured using co-precipitation followed by Isotope Dilution (ID).

The brine was collected using sackhole drilling. Snow was removed from the surface of the sea ice, and the sea ice surface cleaned with a plastic edge. Partial holes were drilled into the sea ice, ensuring not to penetrate the water-ice interface, scraped with a plastic edge and covered for five minutes to one hour. The brine drained into the holes and was collected into clean HDPE containers. Water samples were collected from below sea ice near Rothera Research Station into clean containers. Chlorophyll a (chl a) was determined by extracting pigments from filtered subsamples using chloroform/methanol, before analysis by fluorometry (Clarke et al. 2008). However, it should be noted that sackhole drilling is not suitable for accurate determination of particulate concentrations, so the chl a concentrations are only an approximate measure of biomass (Weissenberger 1992). The brine and water were filtered under clean conditions in the Bonner Laboratories, Rothera Research Station using 0.2 micrometer polycarbonate membranes (Whatman). The filtrate was acidified using 1 ml sub-boiling distilled HNO_3 per litre of brine and transported back to the UK for analysis. All plasticware and filter membranes were trace metal clean. Additional samples were filtered for silicic acid ($Si(OH)_4$) and PO_4^{3-} analysis. Glass fibre filters (Whatman GF/F) are routinely used to filter seawater for NO_3^- and PO_4^{3-} analysis. Silica free polycarbonate 0.2 µm filter membranes (Whatman) were used to filter seawater for $Si(OH)_4$ analysis to avoid contamination by any Si released from the glass fibres of the GF/F membranes.

Approximate Cd concentrations were measured initially on a Perkin Elmer Elan 6100DRC Quadrupole Inductively Coupled Plasma Mass Spectrometer (Q-ICP-MS) using a standard addition method based on a protocol for analysing trace metals (~ppb) in high matrix solutions (Hendry et al. 2008). Laboratory blanks of Milli-Q water were measured by standard addition and were found to be below detection level (~1 ppt). Brine sodium concentrations were also measured using Q-ICP-MS measured against an In internal standard. Internal reproducibility using the In standard is excellent (<0.1%) and external reproducibility was estimated at between 0.05 and 1.12% using repeat dilutions.

Precise and accurate Cd concentrations were then measured using an isotope dilution method, followed by magnesium hydroxide co-precipitation (Wu & Boyle 1997, Ripperger & Rehkamper 2007, Hendry et al. 2008). Briefly, approximately 13 ml of acidified seawater or brine was weighed in 15 ml polypropylene centrifuge tubes (5 point balance ± 0.01 mg), spiked with 400 µl enriched ^{110}Cd spike (Ripperger & Rehkamper 2007). FEP distilled aqueous NH_3 (500–2000 µl) was added to precipitate $Mg(OH)_2$; the amount added was determined empirically to allow ~7% Mg to precipitate to minimize matrix effects during analysis (Mg ~ 1000 ppm). After the NH_4OH is added, the sample is left before centrifugation at 6000 rpm for 4 min. For seawater samples this precipitation process

took two minutes. However, for sea ice brine, the precipitation process takes longer and the samples are left for 30 minutes prior to centrifugation. The supernatant is discarded and the precipitate is redissolved in 0.5 ml 5% HNO_3 (sub-boiling quartz-distilled HNO_3 in Milli-Q water), diluted with 0.5 ml Milli-Q and analysed for Cd by ICP-MS. All precipitation processes were carried out under Class 100 clean conditions.

The standards and samples were analysed for Cd isotopes using an Element II ICP-MS (Thermo Finnigan), introduced via a Cetac ASX-100 microautosampler. The full procedure is detailed elsewhere (Hendry et al. 2008). Uncertainties are estimated to be ~3% using repeat measurements and comparison to external standards (NASS4). Concentrations calculated using $^{111}Cd/^{110}Cd$ and $^{114}Cd/^{110}Cd$ agree well (Fig. 2). However, a previous study has shown that concentrations calculated using measured $^{114}Cd/^{110}Cd$ are more precise and accurate than those from $^{111}Cd/^{110}Cd$, and will be quoted here in the results section (Hendry et al. 2008).

NO_3^-, PO_4^{3-} and $Si(OH)_4$ were measured on brine samples using a Skalar Auto analyser (Kirkwood 1996). The PO_4^{3-} concentrations have an estimated uncertainty of 5%, and error propagation thus yields an uncertainty of ~5.5% for the Cd/PO_4^{3-} ratios. All macro- and micronutrient data (Table I) were corrected for density and reported per kg (a maximum correction of approximately 5%), which was calculated from brine temperatures and salinities, using CSGNetwork Water Density Calculator version 1.6.4. (http://www.csgnetwork.com/h2odenscalc.html). Where brine temperatures were not recorded, temperatures from the underlying water were used. This introduces minimal uncertainty because salinity is the primary control on density at these low temperatures.

Sampling contamination

The sampling of brine is far more susceptible to contamination than seawater given the need to use a metal drill to penetrate the sea ice. In December 2006, sequential samples were taken from a sackhole at five minute intervals
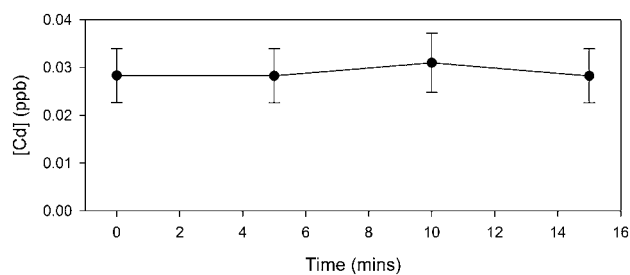

Fig. 3. Results of contamination experiment. Brine samples were taken at time intervals after ice drilling, filtered, acidified and analysed for Cd. There is no decrease in Cd content through time, suggesting that contamination from the drill is negligible. Error bars show ± 2σ.
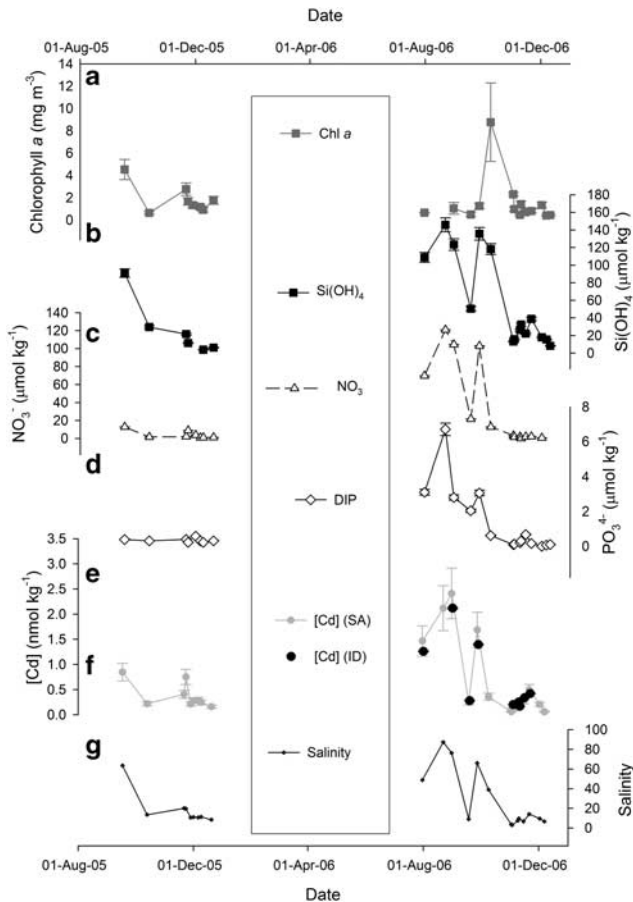
Fig. 4. Macro- and micronutrient results from sea ice brine samples collected by sackhole drilling. **a.** Total unfractionated chl *a* (data courtesy of British Antarctic Survey), **b.** $Si(OH)_4$, **c.** NO_3^-, and **d.** PO_3^{4-} concentrations, **f.** Cd concentrations measured by standard addition (light grey circles) and isotope dilution (black circles), and **g.** salinity, calculated from Na concentrations measured by Q-ICP-MS. Error bars show ± 2σ.

to show that contamination of brine with Cd from the drill is negligible (Fig. 3).

Results

In order to quantify algal activity and trace metal uptake, we report our Cd results relative to the dilution curve of seawater (Thomas & Papadimitriou 2003). Salinity, calculated from [Na], decreased during the season as a result of progressive melting from 60 to less than 10. Brines exhibit a wide range of macronutrient concentrations with $Si(OH)_4$, NO_3^- and PO_4^{3-} ranging from <10 to 150, <1 to 120 and <0.1 to 6.7 $\mu mol\,kg^{-1}$ respectively (Fig. 4, Table I). Cd concentrations varied from 0.06–2.4 $nmol\,kg^{-1}$ (Fig. 4, Table I). Cd concentrations in seawater underlying the sea ice near Rothera (winter–spring 2005) are 0.7–0.8 $nmol\,kg^{-1}$, and are approximately constant throughout the sampling period.
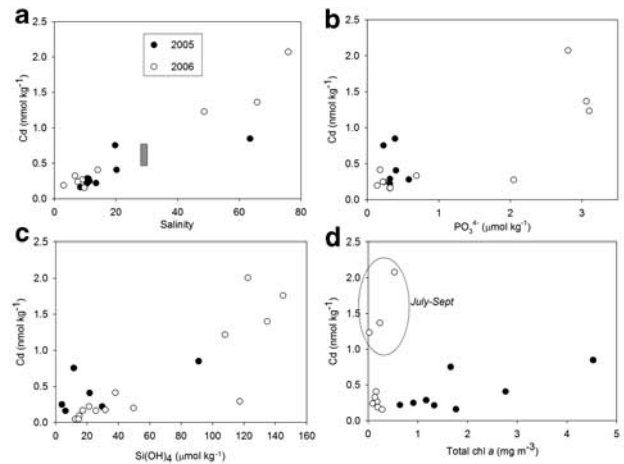

Fig. 5. Correlation between Cd concentrations and **a.** salinity (grey bar shows typical seawater composition from Hendry *et al.* 2008), **b.** PO_3^{4-}, **c.** $Si(OH)_4$, and **d.** chl *a*. The early season (July–September) sea ice results are highlighted by the circle. Note the 2005 Cd concentrations were measured only by standard addition; the 2006 samples were also measured by isotope dilution.

Discussion

Sea ice forms from the freezing of seawater, producing a network of brine channels in a variety of textures (reviewed by Brierley & Thomas 2002). Marguerite Bay sea ice is a mixture of congelation and granular ice, with a predominance of granular ice as in other regions of Antarctica. The granular ice comprises both snow ice (15%) and frazil ice and can, thus, be classified as the "warm end member" of Antarctic sea ice (Perovich *et al.* 2004). As a comparison, Weddell Sea granular ice comprises near 100% snow ice as a result of rapid snow ice formation at the surface and rapid basal melting as a result of upwelling warm water (Dieckmann *et al.* 1991). The sea ice in Marguerite Bay can be above the porosity threshold, especially in late winter/spring, resulting in rapid flushing and early algal growth (Perovich *et al.* 2004). Sea ice brine channels are semi-closed or closed systems that are very different environments to open seawater, and may exhibit distinct biogeochemical cycling. Here, we investigate how trace metals behave during brine formation and subsequent dilution and biological uptake. We then discuss the implications of our results on the impact of sea ice melt on seawater nutrient distribution.

Our results show that Cd followed a simple trend for both 2005 and 2006 that, although there is scatter, behaved conservatively and falls approximately along the dilution curve of seawater from Marguerite Bay (Cd vs salinity $r^2 = 0.86$, $n = 21$; Fig. 5a). Hence, seawater and ice can be considered as a closed system with respect to Cd, i.e. Cd in brine is sourced only from the seawater from which it froze, as opposed to atmospheric or meteoric input. Other field studies have shown that macronutrients only correlate with

salinity in regions of low biological activity (Dieckmann et al. 1991). However, sea ice in Marguerite Bay is relatively productive with biomass, measured using the algal pigment chl a, in sea ice brine ranging up to 8 mg m^{-3} in brine during winter (Fig. 4). This suggests that either biological uptake of Cd is negligible with respect to supply, or regeneration of micronutrients is rapid within the sea ice system.

Although there is scatter, sea ice brine exhibits a similar Cd and PO_4^{3-} fractionation behaviour to open marine seawater (Fig. 5b). As for seawater, there was a positive relationship between Cd and PO_4^{3-} in the brine samples ($r^2 = 0.75$, $n = 19$; Fig. 6). Compared to Cd, PO_4^{3-} concentrations are less well correlated with salinity ($r^2 = 0.62$, $n = 20$), which could be indicative of some biological uptake of PO_4^{3-}. This possible decoupling between Cd and PO_4^{3-} could be responsible for the scatter in the Cd-PO_4^{3-} relationship. $Si(OH)_4$ appears to behave more conservatively than PO_4^{3-} ($Si(OH)_4$ vs. salinity $r^2 = 0.85$, $n = 20$; Fig. 5c), which suggests that Si variations in sea ice are also driven mainly by physical processes, rather than diatom productivity.

There is a positive relationship between Cd and biomass (approximated by chl a) in sea ice brine, which further suggests Cd concentrations are not controlled primarily by biological uptake (Fig. 5d). Physical processes, such as brine rejection and dilution through melting are more likely to be the dominant controls on the distribution of Cd (and other metals) in sea ice. Despite this, there was variability in the relationship between chl a concentration and micronutrients within a sea ice season, which could represent a biological signature (Fig. 5d). During the early sea ice season (July–September), there was a lower biomass supported for a given concentration of micronutrients compared to spring (November–December). This is consistent with greater demand for Cd in spring relative to early winter, for example due to higher carbonic anhydrase (Cd-CA) activity in spring relating to higher growth rates (due to warmer temperatures, higher irradiance and longer photoperiods) and CO_2 availability from melting sea ice (Lane & Morel 2000a, 2000b, Morel et al. 1994, Sunda & Huntsman 2005). Further work establishing the relationship between other important trace metals, such as zinc, and Cd concentrations in sea ice brine may shed light on possible micronutrient limitation during winter. There may also be other factors limiting biomass accumulation in the early season, for example grazing pressure, light or temperature limitation.

The melting of sea ice is thought to promote productivity by 1) providing macro- and micronutrients and seeding for the phytoplankton blooms, and 2) changing water column stratification favouring net phytoplankton growth (Sedwick & Di Tullio 1997). However, observations of natural communities show sea ice diatom assemblages are significantly different to open water assemblages, and sea ice algal cells released from ice can be in a "poor physiological state" (Scharek et al. 1994, Boyd et al. 1995). Further, the degree of stratification in the melt zone is highly dependent on prevailing wind conditions, local hydrographic conditions and degree of surface mixing (Savidge et al. 1995, Whitehouse et al. 1995, Suzuki et al. 2001).

Here, differences between the diatoms present in sea ice (filtered samples examined under SEM appear to be dominated by Fragilariopsis spp. and Navicula spp.) and seawater (dominated by Thalassosira spp. and Proboscia spp.) suggest spring sea ice melt does not seed the ice free water in Marguerite Bay. Furthermore, our nutrient data presented here suggest that, in this case, dilution is sufficiently significant such that sea ice melt may not have an impact on the bulk content of bioactive metals in coastal waters. However, the release of micronutrients may depend on the timing and extent of sea ice melt. Brine expulsion during the early sea ice season may release important dissolved micronutrients into the water. Later in winter, sea ice porosity increases as ice temperatures fall below -5°C (air temperatures between -5 and -9°C; Golden et al. 1998, Perovich et al. 2004) allowing flushing of brine pockets and dilution through melting. Brine expulsion and biological uptake in persistent sea ice causes concentrations of metals in underlying seawater to exceed brine micronutrient concentrations, which may become limiting for some sea ice algae.

Observational records indicate that sea ice dynamics off the West Antarctic Peninsula are highly variable on a variety of timescales and may have retreated over recent decades (Cotte & Guinet 2007, Clarke et al. 2008). Our results show that fundamentally different processes control nutrient distribution in seawater and sea ice, and the timing and rate of melting may be important in determining the release of nutrients from sea ice. This implies future changes in sea ice dynamics, and the timing of advance and retreat of sea ice relative to seasonal light levels, may impact nutrient distribution and Antarctic marine ecosystems.

Summary

Here, we present a method for the sampling and measurement of cadmium in sea ice brine from coastal Antarctica. This method shows minimal contamination and could be applied to a wide range of dissolved micronutrients or trace metals.

We show brine Cd concentrations follow a simple dilution curve consistent with a closed ice-seawater system, suggesting that micronutrients are sourced only from the parental seawater. PO_4^{3-} exhibits a weaker relationship with salinity, which may be a result of biological uptake. In contrast, $Si(OH)_4$ correlates well with salinity, suggesting $Si(OH)_4$ variations are also controlled by physical processes rather than diatom productivity. The positive relationship between Cd and biomass indicates this dilution process is the primary control on the distribution of micronutrients in sea ice rather than biological uptake,

even in a highly productive setting. There appears to be a more complex relationship between Cd concentrations and biomass, consistent with changing Cd requirements, or other limiting factors, throughout the year. Differences in the biological community between sea ice and seawater, and the low micronutrient concentrations in brine later in the sea ice season, suggest that spring melting of sea ice does not contribute significantly to the biomass or nutrient status of seawater. The fundamentally different processes influencing nutrients in seawater and sea ice signify future changes in sea ice dynamics and seasonality may impact nutrient distribution in Antarctic seawater.

Acknowledgements

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