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Impacts of metals and nutrients released from melting multiyear Arctic sea ice

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[1] Nutrients (C, N, and P) and metals (iron, molybdenum, nickel, zinc, vanadium, copper, and cobalt) were determined in water and multiyear ice sampled along the Greenland current and Fram Strait in July 2007. Total metal and nutrient concentrations in ice varied fivefold to tenfold, for most elements, across the area sampled. Data show that some nutrients (i.e., NH_4^+) and metals (i.e., Fe, Zn, V, Cu, Ni, Mo, and Co) are enriched in Arctic ice relative to surface seawaters, suggesting that ice melting is a significant source of metals to the receiving seawaters, particularly Fe and Zn whose concentrations were significantly (*t* test, $P < 0.05$) more than 2 orders of magnitude higher in ice than in surface seawater.

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1. Introduction

[2] Atmospheric deposition is a major source of biogenic elements to the ocean [*Duce et al.*, 1991; *Duce and Tindale*, 1991; *Jickells*, 1995]. In polar regions, the flux of atmospheric materials into the ocean is precluded by the presence of an ice cover, where materials may accumulate [*Maenhaut et al.*, 1996; *Granskog et al.*, 2003]. Other predominant inputs of materials to the sea ice in the Arctic are from suspended sediment incorporated into newly formed ice through the suspension freezing, river discharges, runoff from land and oceanic water mass exchange [*Yeats and Westerlund*, 1991; *Thomas and Dieckmann*, 2002], Melting of this ice cover may lead to the abrupt release of these materials into the ocean, where they may contribute to trace metals concentration of surface water [*Campbell and Yeats*, 1982] and affect biological activity [*Pfirman et al.*, 1995; *Ritterhoff and Zauke*, 1997].

[3] Recent evidence for accelerated rates of multiyear ice loss in the Arctic [*Rigor and Wallace*, 2004; *Nghiem et al.*, 2007] has prompted interest in the possible biological consequences of the shift from an ice-covered to an open water Arctic Ocean [*Aguilar-Islas et al.*, 2008; *Wassmann*, 2008; *Wassmann et al.*, 2008]. Most analyses have focused on the increased deep irradiance associated with ice loss and the ensuing increase in photosynthetic rates, as supported from evidence of increased primary production with reduced Arctic ice cover derived using remote sensing [e.g., *Arrigo et al.*, 2008; *Wassmann et al.*, 2008]. These reports argue that nutrient limitation may set a limit to the biological response on reduced ice cover [e.g., *Arrigo et al.*, 2008]. However, these studies have not yet considered the role of melting of multiyear Arctic ice as a potential vector of nutrient inputs into the Arctic Ocean, potentially amplifying biological responses to reduced ice cover. The reason for this gap in the discussion of possible impacts of ice melting on plankton communities may be the current paucity of data on the load of biogenic elements in multiyear Arctic ice.

[4] Here we report concentrations of biogenic elements in multiyear ice sampled along the Greenland current and Fram Strait. We examine concentrations of nitrogen, phosphorus and organic carbon, as well as those of trace metals incorporated by biological systems and used for a range of processes, from photosynthesis to nitrogen fixation (i.e., iron, molybdenum, nickel, zinc, vanadium, copper and cobalt).

2. Materials and Methods

[5] The ice samples were collected in the ATOS-Arctic cruise on board R/V *Hespérides* (a Spanish contribution to the GEOTRACES cluster of the International Polar Year). A total of 10 ice stations, corresponding to multiyear ice ranging in thickness from 2 to 3 m, were collected in July 2007 along the Greenland Current and Fram Strait (Figure 1).

[6] At each station, ten to twelve 1 m deep ice cores, 7.25 cm in diameter, were collected using a Mark III motorized coring device (Kovacs Enterprise Inc), removing the unconsolidated surface snow and ice before sampling. The blades of the coring device were stainless steel and were cleaned prior to each sampling event. The individual ice cores were inserted into PVC tubes and transported to the research vessel, where they were kept at −12°C until sectioned, typically within 2 h after sampling. Two sections, each 20 cm in length, were manually sectioned from the top (0–20 cm depth) and the base (80–100 cm depth) of each

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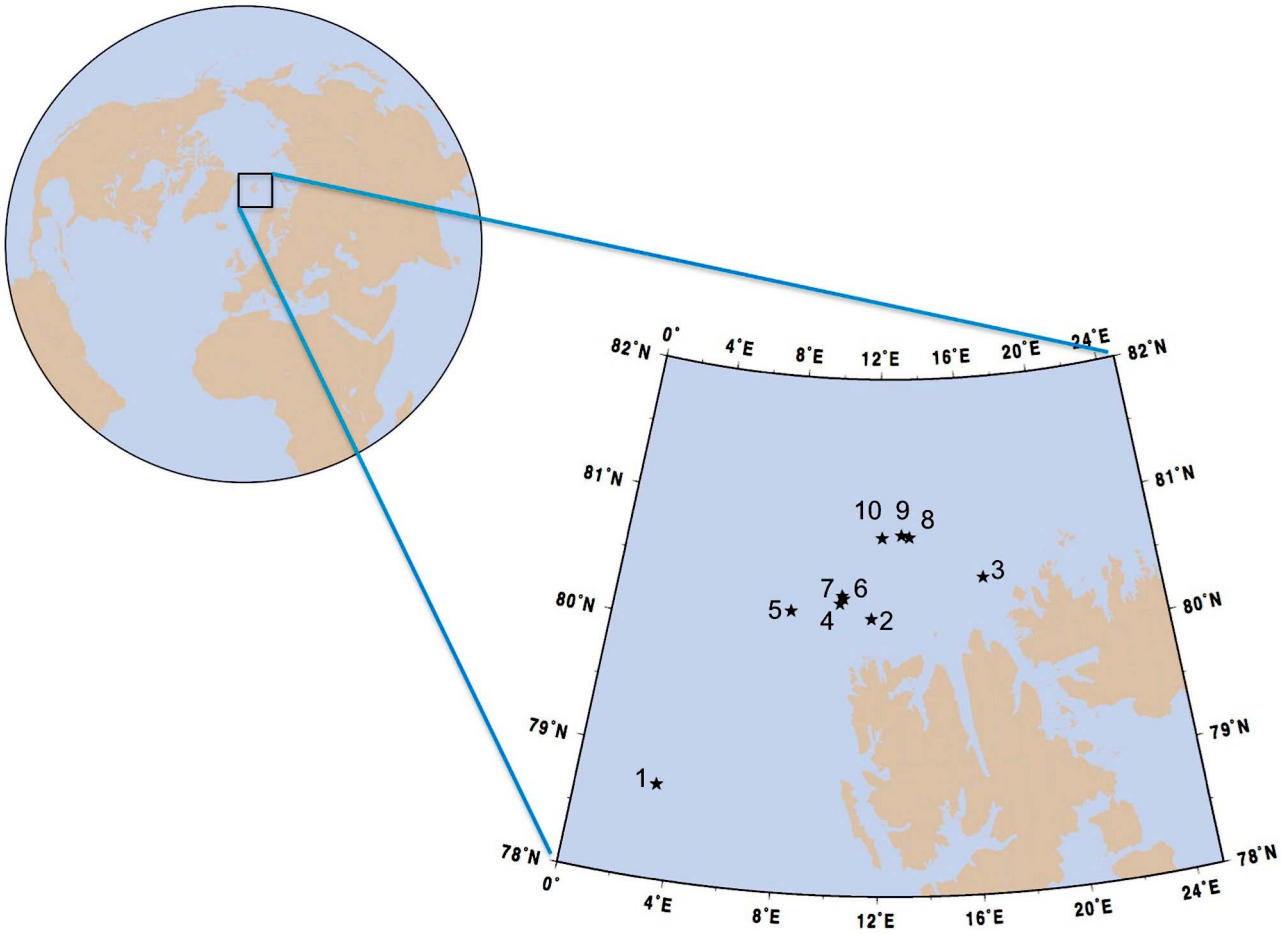

Figure 1. Position of multiyear ice sampling stations occupied during the ATOS-Arctic cruise.

core and transferred to acid-washed Teflon bags (Welch Fluorocarbon Inc.). The ice samples were then allowed to thaw at room temperature before analyses. Samples for nutrient analyses from station 4 were accidentally lost, so only metal concentrations are reported for this station.

[7] Subsamples for ammonium concentration were analyzed within 2 h from collection using a fluorometric method [*Kéroue l and Aminot*, 1997]. Subsamples for nutrient (total phosphorus, TP, total nitrogen, TN, nitrate and nitrite and silicate) analyses were collected for two to three replicate cores and kept frozen until analyzed in a Bran Luebe AA3 autoanalyzer using standard methods [*Hansen and Koroleff*, 1999]. Subsamples for total organic carbon (TOC) analyses were transferred into precombusted glass ampoules and acidified with phosphoric acid to pH 2.0 before the ampoules were sealed under heat. Total organic carbon in ice and surface waters was analyzed by High Temperature Catalytic Oxidation on a Shimadzu TOC-5000A. Standards of 44–45 μmol C L^{-1} and 2 μmol C L^{-1}, provided by D.A. Hansell and Wenhao Chen (University of Miami), were used to assess the accuracy of the estimates. Unfiltered subsamples for metal analyses were transferred to 500 mL acid-washed LDPE bottles in a class-100 HEPA laminar flow hood and preserved by acidifying the subsamples with 2 mL of HCl ultrapure grade (Merck) until analyzed in the laboratory. Samples were analyzed by ICP-MS (PerkinElmer ELAN DRC-e). The accuracy of the analysis was established using River Water Reference Material for Trace Metals (SLRS-4, NRC-CNRC) with recoveries of 102.5%, 117.8%, 103.5%, 96.8%, 94.4%, and 96.7% for Co, Cu, Fe, Ni, V, and Zn, respectively.

[8] Unfiltered surface seawater (1 m depth) was collected from a Zodiac deployed from the research vessel. Seawater was pumped through acid-cleaned Teflon tubing coupled to C flex tubing using a Cole-Parmer™ peristaltic pump, and collected into an acid-washed 500 mL LDPE bottles. Samples were acidified on board to pH <2 with ultrapure grade HCl (Merck) in a class-100 HEPA laminar flow hood, and stored for at least 1 month before extraction. Metals were preconcentrated by the APDC/DDDC organic extraction method of *Bruland et al.* [1979], and analyzed by ICP-AES (Perkin Elmer Optima 5300 DV).

3. Results

[9] All total (unfiltered) nutrient and metal elements, except silicate, were present in significant concentrations in Arctic ice (Table 1). Surface (0–20 cm) and deeper (80–100 cm) ice layers had roughly comparable concentrations of nutrient species, although there was a tendency for deeper

Table 1. Average ± Standard Error and Range of Nutrient, DOC and Metal Concentrations in Different Ice Layers and Surface Seawater Along the Arctic[a]

Fraction	TP (μmol P/L)	SE	Minimum	Maximum	n
0–20 cm Ice	0.07	0.01	0.04	0.14	9
80–100 cm Ice	0.09	0.01	0.04	0.17	9
Seawater	0.37	0.03	0.23	0.52	10
Fraction	PO_4^{3-} (μmol P/L)	SE	Minimum	Maximum	n
0–20 cm Ice	0.03	0.01	0.00	0.09	9
80–100 cm Ice	0.05	0.02	0.01	0.17	9
Seawater	0.08	0.02	0.01	0.19	10
Fraction	DOP (μmol P/L)	SE	Minimum	Maximum	n
0–20 cm Ice	0.04	0.01	0.01	0.07	10
80–100 cm Ice	0.04	0.01	0.00	0.10	10
Seawater	0.29	0.04	0.16	0.49	10
Fraction	TN (μmol N/L)	SE	Minimum	Maximum	n
0–20 cm Ice	3.14	0.64	0.42	6.46	9
80–100 cm Ice	5.20	0.85	1.03	9.37	9
Seawater	6.89	1.13	2.25	14.35	10
Fraction	$NO_3^- + NO_2^-$ (μmol N/L)	SE	Minimum	Maximum	n
0–20 cm Ice	0.49	0.26	0.14	2.57	9
80–100 cm Ice	0.40	0.11	0.15	1.05	9
Seawater	0.86	0.24	0.11	2.50	10
Fraction	NH_4^+ (μmol N/L)	SE	Minimum	Maximum	n
0–20 cm Ice	0.86	0.05	0.67	1.09	9
80–100 cm Ice	1.07	0.09	0.70	1.41	9
Seawater	0.39	0.15	0.09	1.73	10
Fraction	DON (μmol N/L)	SE	Minimum	Maximum	n
0–20 cm Ice	2.07	0.44	0.00	3.72	8
80–100 cm Ice	3.74	0.86	0.00	8.34	9
Seawater	5.65	1.13	0.79	14.04	10
Fraction	SiO_4^{2-} (μmol Si/L)	SE	Minimum	Maximum	n
0–20 cm Ice	0.05	0.01	0.01	0.13	9
80–100 cm Ice	0.07	0.03	0.01	0.26	9
Seawater	1.61	0.25	0.88	3.60	10
Fraction	TOC (μmol C/L)	SE	Minimum	Maximum	n
0–20 cm Ice	57.51	6.56	29.28	97.60	10
80–100 cm Ice	69.44	7.68	41.81	112.27	10
Seawater	93.85	4.50	79.26	123.66	9
Fraction	Co (nmol/L)	SE	Minimum	Maximum	n
0–20 cm Ice	0.72	0.17	0.13	1.60	10
80–100 cm Ice	1.48	0.28	0.30	2.44	9
Seawater	0.08	0.01	0.05	0.11	10
Fraction	Cu (nmol/L)	SE	Minimum	Maximum	n
0–20 cm Ice	30.4	4.4	10.9	55.3	10
80–100 cm Ice	67.0	13.2	18.4	148.1	9
Seawater	4.9	1.4	2.1	16.8	10
Fraction	Fe (nmol/L)	SE	Minimum	Maximum	n
0–20 cm Ice	863.9	323.2	238.9	3599.4	10
80–100 cm Ice	531.7	130.5	219.9	1509.5	9
Seawater	10.0	1.8	5.7	23.1	10
Fraction	Mo (nmol/L)	SE	Minimum	Maximum	n
0–20 cm Ice	0.80	0.35	0.09	3.40	10
80–100 cm Ice	2.67	0.59	0.52	5.78	9
Seawater	122.59	2.22	108.10	130.72	10
Fraction	Ni (nmol/L)	SE	Minimum	Maximum	n
0–20 cm Ice	12.0	4.0	1.1	42.6	10
80–100 cm Ice	27.8	4.3	8.8	41.8	9
Seawater	4.1	0.1	3.9	4.6	10
Fraction	V (nmol/L)	SE	Minimum	Maximum	n
0–20 cm Ice	181.5	13.1	135.3	267.1	10
80–100 cm Ice	152.6	4.5	134.1	170.4	9
Seawater	60.5	5.3	49.1	94.7	10
Fraction	Zn (nmol/L)	SE	Minimum	Maximum	n
0–20 cm Ice	456.6	160	126	1808	10
80–100 cm Ice	438.4	142	133	1537	9
Seawater	4.0	0.9	2.0	11.1	10

[a]SE is standard error.

ice layers to have total nitrogen concentrations significantly higher (t test, $P < 0.05$) than those in shallow layers.

[10] Nutrient and metal concentrations in Arctic ice varied about fourfold to tenfold across stations, except for ammonium and vanadium concentrations that were remarkably uniform (range is less than twofold, Table 1). Total phosphorus and nitrogen concentrations in ice ranged from 0.04 (station 7) to 0.14 μmol P/L (station 1) and from 0.73 (station 10) to 6.14 μmol N/L (station 7) (Figures 1 and 2).

[11] Concentrations of nitrogen and phosphorus species, silicate and organic carbon were generally lower in ice than in surface waters, particularly for silicate, which was present at concentrations near the detection limit in ice (Average: 0.05 and 0.07 μmol L^{-1} for surface and deep ice layers, respectively; Table 1). Concentrations of total phosphorus and nitrogen in sea ice were, on average, 24% and 70% of those in surface seawater, whereas silicate concentrations in ice were 5% of those in surface seawater (Table 2). Ammonium tended to be enriched in ice meltwaters (Average: 0.86 and 1.07 μmol L^{-1} for surface and deep ice layers, respectively) compared to surface seawater (Average 0.39 μmol L^{-1}; Table 1).

[12] In contrast, total metal concentrations in ice were quite high, particularly for iron (863.9 and 531.7 nmol L^{-1} for surface and deep ice layers, respectively) and zinc (456.6 and 438.4 nmol L^{-1} for surface and deep ice layers, respectively), whereas molybdenum (0.80 and 2.67 nmol L^{-1} for surface and deep ice layers, respectively) was present in relatively low concentrations in ice (Table 1). Indeed iron and zinc concentrations were more than 2 orders of magnitude higher in ice than in surface seawater, whereas ice was strongly depleted in molybdenum, with 1% of the concentration in ice compared to surface seawaters (t test, $P < 0.05$, Table 2).

[13] As a result of contrasting patterns of elemental concentrations in ice and seawater, the elemental ratios differed greatly in these compartments. The average elemental ratios in the integrated ice samples was 930 C (as TOC): 58 N: 1 P: 10 Fe, indicative of a high enrichment in iron and a depletion in P relative to nitrogen and carbon in ice. The corresponding elemental ratios in surface seawater averaged 235 C (as TOC): 19 N: 1 P: 0.03 Fe, comparable to

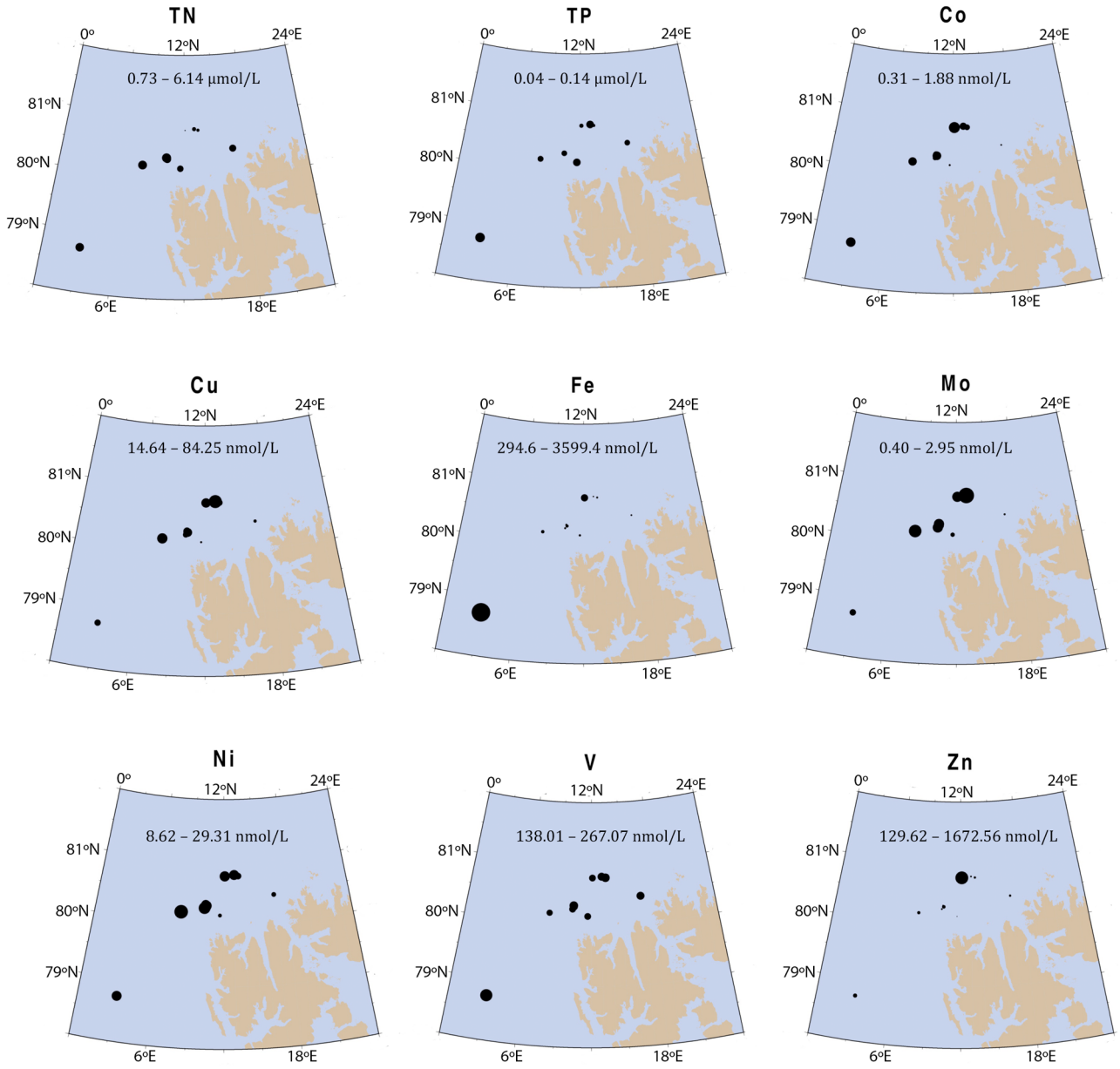

Figure 2. Maps of the ice sampling stations showing the range and concentration of elements, proportional to the diameter of the circles.

elemental ratios reported elsewhere in the ocean [*Sañudo-Wilhelmy et al.*, 2001, 2004; *Price*, 2005].

4. Discussion

[14] The results presented here demonstrate that multiyear Arctic ice in the Greenland Current and Fram Strait holds substantial loads of nutrients and metals, although it is depleted in molybdenum, silicate and phosphorus. Data on nutrient and metal concentration in Arctic ice is remarkably sparse, with only a handful of studies reporting concentrations of metals [e.g., *Campbell and Yeats*, 1982; *Measures*, 1999; *Krachler et al.*, 2005a; *Aguilar-Islas et al.*, 2008] and nutrients [e.g., *Thomas et al.*, 1995; *Granskog et al.*, 2003]. Total metal and nutrient concentrations in ice varied fivefold to tenfold for most elements across the area sampled, with total nitrogen and phosphorus concentrations declining from the Greenland Current to the Fram Strait. Differences in ice chemistry may reflect differences in metal and nutrient inputs at the location where the ice was formed (e.g., river mouths versus central areas). This hypothesis could not be explored here, since the ice leaving the Arctic Ocean through the Fram Strait, the region sampled here, may have been produced in a variety of remote locations.

[15] Whereas annual sea ice should be largely free of nutrients and metals, released into the water along with salts as the seawater freezes, multiyear Arctic ice can collect and accumulate materials delivered with either dry or wet atmospheric deposition [*Isaksson et al.*, 2003; *Krachler et al.*, 2005b]. Although Arctic ice was relatively enriched in ammonium relative to surface seawater, Arctic ice tended to support lower concentrations of phosphorus, nitrogen,

Table 2. Mean ± Standard Error Nutrient and Metal Ratios in Deeper Relative to Shallow Ice Layers and the Mean ± Standard Error Ratio in Ice Relative to Seawater of Nutrient, DOC, and Metal Concentrations[a]

Ratio	TP	SE	n
(80–100)/(0–20) cm Ice	1.52	0.33	9
Ice/Seawater	0.24	0.04	9
Ratio	PO_4^{3-}	SE	n
(80–100)/(0–20) cm Ice	2.46	0.75	8
Ice/Seawater	1.14	0.56	9
Ratio	DOP	SE	n
(80–100)/(0–20) cm Ice	0.85	0.19	9
Ice/Seawater	0.17	0.04	10
Ratio	TN	SE	n
(80–100)/(0–20) cm Ice	2.08	0.38	9
Ice/Seawater	0.70	0.13	9
Ratio	$NO_3^- + NO_2^-$	SE	n
(80–100)/(0–20) cm Ice	1.17	0.16	9
Ice/Seawater	0.88	0.25	9
Ratio	NH_4^+	SE	n
(80–100)/(0–20) cm Ice	1.27	0.13	9
Ice/Seawater	3.96	0.60	9
Ratio	DON	SE	n
(80–100)/(0–20) cm Ice	2.12	0.53	7
Ice/Seawater	0.85	0.34	9
Ratio	SiO_4^{2-}	SE	n
(80–100)/(0–20) cm Ice	3.99	2.81	9
Ice/Seawater	0.05	0.01	9
Ratio	TOC	SE	n
(80–100)/(0–20) cm Ice	1.30	0.15	10
Ice/Seawater	0.66	0.07	9
Ratio	Co	SE	n
(80–100)/(0–20) cm Ice	3.46	1.06	10
Ice/Seawater	15.30	3.08	10
Ratio	Cu	SE	n
(80–100)/(0–20) cm Ice	2.37	0.65	10
Ice/Seawater	12.61	2.16	10
Ratio	Fe	SE	n
(80–100)/(0–20) cm Ice	1.01	0.21	10
Ice/Seawater	127.77	59.66	10
Ratio	Mo	SE	n
(80–100)/(0–20) cm Ice	13.01	5.87	9
Ice/Seawater	0.01	0.00	10
Ratio	Ni	SE	n
(80–100)/(0–20) cm Ice	7.88	3.59	10
Ice/Seawater	4.75	0.51	10
Ratio	V	SE	n
(80–100)/(0–20) cm Ice	0.82	0.10	10
Ice/Seawater	3.01	0.29	10
Ratio	Zn	SE	n
(80–100)/(0–20) cm Ice	1.13	0.20	10
Ice/Seawater	158.00	63.73	10

silicon and organic carbon than the surface seawater did. As a result, ice melting should lead to a dilution of these nutrient elements in the receiving seawater, thereby enhancing any possible limitation of biological activity by these elements in the receiving waters. Enrichment of ice in ammonia is likely to be a consequence of biological activity within the ice [*Thomas and Dieckmann*, 2002], but may also derive from diffusive inputs from the atmosphere during ice formation, as emissions of ammonia in the Northern Hemisphere have greatly increased over the past decades [*Clarisse et al.*, 2009] supporting high inputs to the ocean [*Doney et al.*, 2007].

[16] In contrast, however, metal concentrations were highly enriched in Arctic ice relative to surface seawaters. The concentration of metals in Arctic ice we report here is consistent with published values from other regions of the Arctic [*Hölemann et al.*, 1999; *Aguilar-Islas et al.*, 2008]. For instance, *Hölemann et al.* [1999] report 10,585 nmol Fe L^{-1} and 479 nmol Zn L^{-1} in ice of off the Russian coast and *Aguilar-Islas et al.* [2008] found concentrations of total Fe at the Bering Sea ranging from 111 to 71,500 nmol Fe L^{-1}. The elevated concentration of metals in Arctic ice has been linked to high atmospheric inputs, associated with aerosol deposition in the Arctic [*Krachler et al.*, 2005b; *Planchon et al.*, 2004; *Barbante et al.*, 2001], resulting from continuous emissions in the highly industrialized countries in the Northern Hemisphere [*McConnell and Edwards*, 2008]. On the other hand, high concentrations of reactive trace metals like Fe or Al have been also associated with rafted sediment present in the ice [*Measures*, 1999]. Since melted ice samples were not filtered the analysis may include metals derived from both sediments and aerosols. Although in this study we cannot differentiate the sources, further research are necessary in order to understand the different release mechanisms, dissolution and availability associated to each source.

[17] Whereas Arctic ice is a negligible source of nitrogen, phosphorus, silicate and organic carbon to the waters receiving its melt products, melting of Arctic ice may significantly enhance metal concentrations in the receiving waters, particularly for Fe and Zn. For instance, considering that iron concentrations are, on average, 138-fold higher in Arctic ice than in surface waters (Table 2) and assuming an average multiyear ice thickness of 2 m, ice melting can increase the iron content in the top 20 m of the water column by over tenfold. Indeed, total iron concentrations in the Arctic surface seawater sampled averaged 10 nmol Fe L^{-1}, relatively high compared to surface waters elsewhere in the ocean [*Millero*, 1996]. We submit that the elevated iron concentrations in the Arctic waters adjacent to melting multiyear ice platforms sampled here must be supported by inputs from meltwaters.

[18] The contrast between the chemical composition of multiyear Arctic ice and seawater is best portrayed by the contrasting average elemental ratios of 930 C (as TOC): 58 N: 1 P: 10 Fe for ice and 235 C (as TOC): 19 N: 1 P: 0.03 Fe for surface seawater. In particular, the Arctic ice sampled here is 300-fold enriched in iron relative to phosphorus

Notes to Table 2:

[a]SE is standard error. Deeper and shallow ice layers are 80–100 cm and 0–20 cm, respectively.

compared to the surface seawater. Melting of multiyear ice should, therefore, drive the receiving communities toward P limitation, as nitrogen and iron are delivered in excess relative to phosphorus with ice meltwaters. The hypothesis of an Arctic Ocean limited by P awaits experimental test and is particularly relevant in the context of discussions as to the possible biogeochemical consequences of changes in sea ice [*Arrigo et al.*, 2008].

[19] The calculations above are not academic exercises, as melting of multiyear ice accelerated greatly in the summer of 2007, when this study was conducted. *Arrigo et al.* [2008] reported, on the basis of remote sensing products, an increased primary production in associated to this melting event, and argued that limitation of nitrogen fixation by insufficient iron inputs could reduce this response. The results presented here suggest that melting of multiyear ice delivers substantial iron inputs into the receiving Arctic waters, which should allow for nitrogen fixation to increase. The potential biological consequences of the iron inputs associated with sea ice melting depends on the availability of the iron delivered, which was not assessed here. Instead, we suggest that it will be the supply of phosphorus, which is present in low concentrations relative to other biogenic elements, which may limit the response of phytoplankton to Arctic ice melting. As multiyear ice is lost with accelerated rates of summer ice melting in the Arctic [*Rigor and Wallace*, 2004; *Nghiem et al.*, 2007], the load of metals and nutrients on ice is expected to be reduced, as the ice melting will be progressively dominated by seasonal ice that cannot accumulate significant amounts of these elements. Hence, the delivery of nutrients and metals contained in ice reported here is likely to be a transient process encompassing the transition from the past period of stable ice cover to the likely future of an Arctic Ocean free of ice in the summer.

[20] In summary, the results presented show that Arctic ice is a significant reservoir of biogenic metals, particularly Fe and Zn. The effects of Arctic ice melting, which is predicted to continue in the near future [*Zhang et al.*, 2008] are not limited to altering the light regime, expanding the productive season of Arctic phytoplankton as suggested by *Wassmann* [2008] and *Arrigo et al.* [2008], but may significantly impact the biogeochemical balance of the Arctic waters, potentially affecting the nature of nutrient limitation of primary production therein.

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