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Quantitative Analysis of Fe, Mn and Cd from Sea Ice and Seawater in the Chukchi Sea, Arctic Ocean

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Abstract

Sea ice is important for the health of the polar oceans yet its role in the biogeochemical cycling of trace metals is not so clear. To understand the geochemical behaviour of trace metals and their accumulation into sea ice, dissolved (D, < 0.2 μm), and labile particulate (LP, Total Dissolvable - Dissolved) Fe, Mn, and Cd were examined in sea ice and seawater collected from the Chukchi Sea in the Arctic Ocean. Samples were pre-concentrated utilizing the solid-phase extraction NOBIAS Chelate PA-1 resin (Hitachi High-Technologies Corporation) and analyzed on a Graphite Furnace Atomic Absorption Spectrometer. Chukchi seawater showed high percentage for DMn (71.5 %) and DCd (66.3 %) with a high percentage of LPFe (94.1 %). In seawater, DCd was the only metal to correlate with phosphate (R^2 = 0.78) indicating a biogeochemical cycling source. Chukchi seawater concentrations of Fe and Mn may have been controlled through external sources such as sediments (shelf or river) and/or sediment reductive processes. Trace metal concentrations in Chukchi sea ice were heterogeneous. Sea ice showed high percentages for the LP fraction (99.2% Fe, 63.6 % Mn and 71.2 % Cd). This data

indicated that, regardless of the trace metal behaviour in Chukchi seawater, Chukchi sea ice was observed to have a preference for the LP trace metal fraction.

Keywords: Sea Ice, Trace Metals, Dissolved, Labile Particulate

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1. Introduction

In the last 20 years, the Arctic Ocean has seen over a 50 % decline in summer sea ice (National Snow and Ice Data Center). It is possible that this decline may extend to an ice-free summer within this century (Massonnet et al., 2012). Sea ice is important for processes such as heat and gas exchange between the sea surface and atmosphere (Eicken et al., 1995), global climate circulation (Zwally et al., 1985) and the formation of bottom water (Comiso and Gordon, 1998). During the melting season sea ice can be a source of nutrients (Nomura et al., 2010) and trace metals (Aguilar-Islas et al., 2008) allowing it to initiate phytoplankton booms along the ice's edge. During sea ice formation brine drainage can release nutrients and, potentially, dissolved metals allowing for the formation of under-ice phytoplankton communities (Thomas et al., 2010; van der Merwe et al., 2011). Therefore, the decrease in sea ice coverage can have great impacts on the underlying water's physical and chemical structures and productivity (Eicken and Lange, 1989; Fritsen et al., 1994; Macdonald et al., 1999). In seawater, trace metals such as iron (Fe) and manganese (Mn) are well known for their essential role in phytoplankton growth (Martin et al., 1990; Sedwick and DiTullio, 1997). Cadmium (Cd), a rare element usually found in minute amounts in seawater, can either act as an essential element or as a toxin towards phytoplankton (Cullen et al., 1999; Singh and Yadava, 1983).

Currently, trace metal behaviour in sea ice has become an important point of discussion as the decline of Arctic sea ice becomes more prevalent. In the Antarctic region, sea ice has been observed to accumulate Fe up to two orders of magnitude higher than the underlying surface waters (Grotti et al., 2005). Within sea ice, the distribution and concentrations of trace metal size fractions have been observed for and compared to seawater (Lannuzel et al., 2010,

2011a, 2011b, 2014). In addition, observations of Antarctic sea ice brine has been shown to influence nutrient and trace metal interactions, along with possible retention or release from the ice interface (Hendry et al., 2009; Lannuzel et al., 2007, 2008; van der Merwe et al., 2011). Within the Arctic region, the study of trace metals in sea ice are not as extensive as for the Antarctic (Aguilar-Islas et al., 2007, 2008; Holemann et al., 1999; Kanna et al., 2014; Melnikov et al., 2002). Although studies from both the Arctic and Antarctic regions have shown that sea ice is able to accumulate trace metals, the mechanism behind trace metal accumulation into sea ice remains unclear. It is possible that trace metals accumulate during ice formation and sediment entrainment processes and are then transported as ice is exported from the area of formation into new areas (Eicken et al., 2005; Masqué et al., 2007; Nürnberg et al., 1994; Pfirman et al., 1995, 1997). This gives sea ice a geochemical role as a transporter of incorporated materials. Eicken et al. (2005) observed a westward export of sediment-laden sea ice in the Chukchi and Beaufort Seas. This suggests that sea ice can be a potential source of trace metals in the Arctic Ocean as they are released along with entrained sediments during ice melt.

Understanding the processes of how trace metals are able to accumulate into sea ice is very important to gain a clearer understanding of the role for trace metals geochemical cycling in the polar oceans. This study focused on dissolved (D, < 0.2 µm), and labile particulate (LP) concentrations of Fe, Mn and Cd in Chukchi sea ice and seawater. LP represents the dissolvable particulate metal size fraction and was determined by taking the difference between total dissolvable (TD, unfiltered) and the D size fractions (Lannuzel et al., 2007; Cid et al., 2011). Fe, Mn and Cd have different characteristics of source, sink, cycle and redox potential in seawater.

Thus, they were used to compare concentrations in Chukchi seawater to Chukchi sea ice (floe ice) to investigate the trace metal accumulation features of Arctic sea ice.

2. Materials and Methods

2.1 Sampling Location and Sample Collection

All materials used for the sampling and analysis of sea ice and seawater followed trace metal clean sample collection and preparation methods. Low density polyethylene (LDPE; Nalgene Company, Limited), Teflon bottles and devices were acid cleaned following documented procedures (Nishioka et al., 2001; Takeda and Obata, 1995).

Sea ice was collected during the Oshoro-Maru cruise in July 2013. Three individual free floating sea ice pieces were collected in the Chukchi Sea, about 8 - 16 km downwind from the sea ice edge. The ship approached the free floating sea ice from the downwind direction, to avoid the ship's exhaust, at three different locations: Ice 1) 70˚58'N, –165˚24'W; Ice 2) 71˚3'N, –164˚28'W; and Ice 3) 70˚48'N, –164˚9'W (Fig. 1). The three free floating sea ice pieces were within the size range of 0.5 m^3 to 2.25 m^3. Sea ice was collected using a 1.8 m x 1.8 m nylon sling mounted on a vinyl coated stainless frame. The sling was hung from the ship's crane from the bow. Once the ice was collected it was placed upon a clean tarp on the ship's deck. During collection care was taken to avoid touching any of the ice surface, with non-acid cleaned materials, to avoid contamination. Once on the tarp, each ice sample was individually separated into several block pieces using a titanium ice pick. The inside of the ice block was then immediately shaved with an acid cleaned ceramic knife and small chips (samples, Ice 1 n = 4, Ice 2 n = 4, Ice 3 n = 14) of ice were collected into separate acid cleaned polyethylene buckets,

92 double wrapped with clean plastic bags, then stored at −20˚C. In an on-shore clean area, each
93 sample bucket was placed in an incubator, with double plastic bags, and melted at 20˚C. This
94 decreased the chances of sample contamination. Once melted, the sample buckets were
95 transferred to a class 100 clean room. The outer bag was removed from each bucket in the
96 clean room; and half of the sample's meltwater was immediately filtered by acid cleaned 0.22
97 µm filters (Durapore, Millipore Ltd.) using acid cleaned Teflon filter holder and acid cleaned
98 Teflon micro-tubing connected to a peristaltic pump with Viton Tubing (Cole-Parmer Instrument
99 Company). The Viton Tubing was in contact with the waste solution only. During filtration, the
100 filtrate (D) was collected into acid clean 125ml LDPE bottes and acidified to pH 1.8 with 0.05M
101 hydrochloric acid (HCL, ultrapure, Tamapure-AA-10, Tama Chemical). The other half of the
102 sample meltwater (TD) was immediately placed into acid clean 125 ml LDPE bottes and acidified
103 to pH 1.8. Both the TD and D samples for each of the free floating sea ice pieces were stored for
104 three years, at room temperature, before analysis for this study.

105 Chukchi surface seawater (~ 3 m) was collected from off the coast of Barrow Canyon
106 (hereafter the Barrow Canyon samples; 70˚34'N, −160˚50'W to 70˚57'N, −161˚48'W) and off the
107 coast of Point Lay (hereafter the Point Lay samples; 70˚44'N, -164˚36'W to 71˚2'N, -164˚28'W,
108 and 69˚32'N, -166˚34'W to 70˚23'N, -165˚33'W Fig. 1). Seawater was collected near the sea ice
109 sampling sites (described above). Sampling was done following the methods outlined in
110 Tsumune et al. (2005). Briefly samples were collected via a towed-fish, metal free sampling
111 system with Teflon tubing (ID 12 mm) covered by polyvinyl chloride (PVC). The tubing opened
112 from the towed-fish's front and water was carried, by air driven Teflon pump, to a clean-air
113 space (clean booth, air filtered with a HEPA filter) built into the ship's laboratory. Sample tubing

was split into two and surface seawater samples were collected every 30 minutes to 2 hours with speeds up to 10 knots. One tube collected surface seawater into acid cleaned 125 ml LDPE bottles and the samples were immediately acidified (TD sample, 0.05 M ultrapure HCl, pH 1.8). The other tube collected surface water though a 0.22 µm filter (Millipak 100, Millipore Ltd.) into acid cleaned 125 ml LDPE bottles and were immediately acidified (D sample). Both the TD and D samples were also stored at room temperature after acidification for three years before analysis for this study.

Trace Metal Analytical Methods

2.2 DFe in Seawater Samples by Flow Injection Analysis

Comprehensive observation of surface seawater from the Bering Sea to the Chukchi Sea was conducted to measure DFe (Nishioka et al., Unpublished results). The seawater samples from Point Lay and Barrow Canyon used in this study are part of the comprehensive data set from the Bering Sea to the Chukchi Sea (Nishioka et al., Unpublished results); and were used to compare with one another. In an on-shore clean room DFe was initially analyzed, in all seawater samples 3 – 6 months after sampling, with the chemiluminescence and flow injection method (detailed in Obata et al. 1993). Once analyzed, the seawater samples were stored for three years at <pH 1.8. After this time period, seawater samples from Point Lay and Barrow Canyon were re-analyzed for the current study by pre-concentration via the NOBIAS chelating resin and analyzed for TD and D Fe, Mn, and Cd on a Graphite Furnace Atomic Adsorption Spectrometer (GFAAS; HITACHI).

2.3 Pre-concentration Procedure

All reagents used for the pre-concentration of trace metals were of reagent, pure or ultra-pure chemical grade. Milli-Q water (Millipore Ltd.) was used to prepare all solutions. The NOBIAS Chelate PA-1 M chelating resin (NOBIAS resin, 150 mg, Hitachi High-Technologies Corporation) was used for the pre-concentration of trace metals. The NOBIAS resin has an excellent affinity for metals, out competing natural ligands, as well as the ability to separate alkaline and alkali-earth metals from solution (Minami et al., 2015; Sohrin and Bruland, 2011; Ueda et al., 2010). The resin was initially cleaned with 25 ml of the following solutions passing through in succession at 5 ml/min via a hand syringe: acetone (Wako Pure), methanol (Wako Pure), Milli-Q water, 1 M HCl-0.01 M hydrogen peroxide (ultrapure, Tamapure-AA-10, H_2O_2, Wako Pure, respectively), Milli-Q water, 0.5 M ammonia (NH_4, Tamapure-AA-10), and Milli-Q water following methods outlined in Minami et al. (2015).

After the resin column was cleaned, it was mounted on a manual, acid cleaned in-line pre-concentration system modified from Sohrin et al. (2008) and Kondo et al. (2016; Fig. 2). Briefly, the system consisted of four Teflon micro-tubes connected to a 4-way valve with an in-line connected to the resin column. A waste line ran from the resin column, through a peristaltic pump connected with Viton Tubing, into a waste container.

The samples for sea ice and seawater followed the pre-concentration process methods outlined in Sohrin et al. (2008) as shown in Figure 2. Some of the TD samples were observed to have particles, so the NOBIAS manifold was slightly modified as described below. First an 3.36 M acetic acid-ammonium acetate (HAcO-NH_4AcO) buffer was made by mixing 30 g of glacial acetic acid (Optima, Fisher Chemical) with 50 g of 20 % NH_4OH (ultrapure, Tamapure-AA-10) and 70 g of Milli-Q water. A 0.05 M HAcO-NH_4AcO buffer was prepared by diluting 3.6 M HAcO-NH_4AcO

157 with Milli-Q water then double purifying it with the NOBIAS resin before storing the diluted buffer
158 in acid clean Teflon bottles. The 0.05 M HAcO-NH_4AcO buffer was used to condition the resin
159 column to pH 6 and removed alkali, alkaline earth metals and any remaining sea salts that
160 remained in the column (Minami et al., 2015; Sohrin et al., 2008).

161 Before each sample was pre-concentrated, the NOBIAS resin column was cleaned with 15
162 ml of 1 M acidic acid (HNO_3, ultrapure, Tamapure-AA-100, 1 ml/min.) then conditioned with 30
163 ml Milli-Q water (3 ml/min.) and 40 ml of 0.05 M HAcO-NH_4AcO (3 ml/min.). 30 − 50 ml samples
164 were simultaneously prepared by adding 1.8 ml of 3.6 M HAcO-NH_4AcO buffer and adjusting the
165 sample to pH 6 ± 0.1 with 20 % NH_4OH. The TD and D seawater and the D sea ice samples were
166 then loaded onto the pre-concentration system followed by 40 ml of 0.05 M HAcO-NH_4AcO both
167 at 3 ml/min. For the TD sea ice samples, a new line was made with acid cleaned filters so that the
168 sample was filtered (0.22 µm, Durapore, Millipore Ltd.) before loading onto the column followed
169 by 40 ml of the diluted buffer. To collect the eluent, the column was moved to an acid clean hand
170 syringe and back-eluted with 10 ml of 1 M HNO_3 (1 ml/min) into an acid clean polyethylene
171 collection tube. The initial and final weights of the elution and sample were used to calculate the
172 original concentration of the sample before pre-concentration. For subsequent samples, the
173 procedure was repeated from the beginning cleaning step (1 M HNO_3 at 1 ml/min) to ensure no
174 cross contamination between samples.

175 Samples were analyzed on a GFAAS for Fe, Mn, and Cd. Pre-concentrating samples before
176 analysis allowed for elements with low concentrations to be detected and removed chemical
177 interferences due to the presence of sea salts. Single element standards of Fe, Mn, and Cd were
178 made in 1 M HNO_3 from diluting 1000 ppm individual standards (Wako Chemical Ltd.).

Quantitative calibration curves were made by plotting the absorbance against the concentration of each element.

For each set of pre-concentrated samples, a procedural blank with 125 ml Milli-Q water was pre-concentrated first following the above outlined procedure. Recovery tests were made by spiking Mill-Q water with known concentrations of each element. NASS-6 seawater reference material (National Research Council of Canada) was used to validate the pre-concentration process.

3. Results

3.1 Procedural Blanks, Recovery Blanks and Reference Materials

Milli-Q water procedural blanks were pre-concentrated for Fe, Mn and Cd and analyzed on a GFAAS. The pre-concentration detection limit (DL), after the pre-concentration step and analysis on the GFAAS, was determined for each element by multiplying the standard deviation (SD) of the Milli-Q procedural blanks, by three (DL = 3.9 nM Fe, 0.7 nM Mn, and 0.002 nM Cd, Table 1). After the sea ice and seawater samples were pre-concentrated, their measured values were compared to the DL. If the samples were above the DL, then their measured values were calculated with the concentration factor (seawater range of 4.2 – 8.6 times, sea ice range of 2.7 – 3.2 times) and reported in this study. The final *in situ* DL of our method varied depending on the pre-concentration factor used for each sample type but resulted in the following averages: 0.3 nM for Fe, 0.06 nM for Mn and 0.0002 nM for Cd (Table 1). Recovery of Fe, Mn and Cd from spiked Milli-Q water blanks after pre-concentration was 102.1 % ± 5.6, 100.3 % ± 1.8, and 106.3 % ± 5.1 respectively (Table 2). Values of NASS-6 seawater reference materials (n = 8) measured in

this study utilizing the NOBIAS resin pre-concentration method showed: 9.5 ± 1.3 nM Fe, 11.2 ± 1.4 nM Mn and 0.3 ± 0.1 nM Cd. Measured seawater reference values were comparable to the certified values (National Council of Canada; Table 3).

3.2 Dissolved Metals from Chukchi Sea Ice and Seawater

DFe in sea ice samples ranged from 0.9 − 10.8 nM. Ice 1 held significantly higher concentrations (avg. 6.08 ± 3.3 nM, Fig. 3a, $p < 0.05$, n = 4) when compared to Ice 2 and 3. The trend of DFe concentration showed Ice 2 to have lower concentrations (avg. 1.2 ± 0.2 nM, n = 4) than observed in Ice 3 (avg. 2.4 ± 1.4 nM, n = 14). DFe in seawater ranged from 2.3 − 10.7 nM. Concentrations of the Point Lay samples (avg. 5.1 ± 2.4 nM, n = 16) were similar to the Barrow Canyon samples (avg. 4.5 ± 0.6 nM, n = 8).

DMn in sea ice samples ranged from 1.4 − 35.9 nM. As seen with DFe, Ice 1 held significantly higher concentrations of DMn (avg. 19.9 ± 10.1 nM, Fig. 3b, $p < 0.05$, n = 4) when compared with Ice 2 and 3 (5.5 ± 1.3 nM, n = 4 and 5.0 ± 2.2 nM, n = 14, respectively). DMn in seawater ranged from 13.9 − 109.7 nM and was observed to have significantly higher concentrations than found in sea ice ($p < 0.05$). DMn concentrations observed in the Point Lay samples had significantly higher concentrations (avg. 46.6 ± 30.0 nM, $p < 0.05$, n = 8) than the concentrations observed in Barrow Canyon samples (avg. 18.3 ± 2.9 nM, n = 16).

DCd concentrations were very low (Fig. 3c). In sea ice block samples they ranged from < DL − 0.2 nM. DCd did not have any discernible differences between the three sea ice samples. In seawater DCd concentrations ranged from < DL − 0.5 nM. The Barrow Canyon samples were

significantly higher (avg. 0.23 ± 0.1, $p < 0.05$, n = 8) when compared to the Point Lay samples (avg. 0.1 ± 0.05, n = 16).

3.3 Labile Particulate Metals from Chukchi Sea Ice and Seawater

The LP fraction was calculated as the difference between the TD and D metals as explained in Cid et al. (2011) and used to represent dissolvable particulate metals (Lannuzel et al., 2007). LPFe in sea ice ranged from 75.9 – 2278.9 nM (Fig. 4a). Ice 1 showed significantly higher concentrations (avg. 1447.8 ± 678.9 nM, $p < 0.05$, n = 4) when compared to Ice 2 and 3 (avg. 389.5 ± 132.4 nM and 372.4 ± 283.1 nM respectively). LPFe in seawater ranged from 12.7 – 702.9 nM. Barrow Canyon samples had significantly higher concentrations (avg. 421.8 ± 99.2 nM, $p < 0.05$, n = 8) when compared to the Point Lay samples (avg. 205.2 ± 200.0 nM, n = 16).

LPMn in sea ice blocks ranged from < DL – 1650.2 nM (Fig. 4b). Ice 1 had significantly higher concentrations (avg. 781.9 ± 712.0 nM, $p < 0.05$) when compared to Ice 2 and Ice 3 (avg. 6.8 ± 2.5 nM and 10.4 ± 7.1 nM respectively). In seawater, LPMn ranged from < DL − 25.8 nM. Significantly higher concentrations were observed for the Barrow Canyon samples (avg. 19.5 ± 7.9 nM, $p < 0.05$, n = 8) when compared to the Point Lay samples (avg. 8.7 ± 5.0 nM, n = 16).

LPCd in sea ice and seawater was low (Fig. 4c). Sea ice ranged from < DL – 1.0 nM, but no discernible differences were observed among the samples. LPCd in seawater ranged from < DL – 0.2 nM. Barrow Canyon samples were observed to have significantly higher concentrations (avg. 0.1 ± 0.06 nM, $p < 0.05$, n = 8) when compared to the Point Lay samples (avg. 0.04 ± 0.03 nM, n = 16).

240 *3.4 Percent Contribution of Dissolved vs Labile Particulate Metals in Chukchi Sea Ice and*
241 *Seawater*

242 The distribution of sized fractioned trace metals (D or LP) within a medium (sea ice or
243 seawater) can be determined by analysing the amount (%) of each size fraction within the
244 medium (Lannuzel et al., 2014). This percent contribution was calculated by dividing a size
245 fraction (i.e. D) by the sum of the size fractions (i.e. D + LP) and multiplying it by 100. In Chukchi
246 sea ice the percent contributions for each trace metal are as follows (Table 4; % ± SD): 0.8 ± 0.7 %
247 DFe and 99.2 ± 0.7 % LPFe, 36.4 ± 22.1 % DMn and 63.6 ± 22.1 % LPMn, 28.8 ± 28.3 % DCd and
248 71.2 ± 28.3 % LPCd. Sea ice yielded high concentrations of LP metals. For Chukchi seawater, the
249 percent contributions for each trace metal are as follows (Table 4; % ± SD): 5.9 ± 11.9 % DFe and
250 94.1 ± 11.9 % LPFe, 71.5 ± 20.8 % DMn and 28.5 ± 20.8 % LPMn, 66.3 ± 25.2 % DCd and 33.7 ±
251 25.2 % LPCd. Seawater was observed to have high percentages of LPFe with high DMn and DCd.

252

253 **4. Discussion**

254 *4.1 DFe Comparison of NOBIAS Resin Pre-Concentration Method vs Flow Injection Analysis*

255 Acidified (< pH 1.8) seawater samples (from the Bering Sea to Chukchi Sea) were initially
256 analysed in 2013 for DFe (Nishioka et al., Unpublished results) using flow injection after pre-
257 concentration with the 8-HQ chelating resin and luminol-hydrogen peroxide
258 chemiluminescence detection methods (Obata et al., 1997). Samples were re-acidified to < pH
259 1.8 and held at room temperature in a clean room for 3 years before a portion of the samples
260 (off the coast of Barrow Canyon and off the coast of Point Lay samples) were pre-concentrated

via the NOBIAS resin at pH 6 for the this study. Comparing the DFe data collected with the NOBIAS resin pre-concentration method to the flow injection method, the NOBIAS resin data were 1.3 ± 0.4 (n = 24) times higher than the flow injection data. Both methods for the determination of DFe were applied successfully and validated by certified reference materials (NASS-6 reference seawater). A previous study also compared DFe in the same Chukchi seawater samples analyzed through flow injection (Hioki et al., 2014) and the NOBIAS resin pre-concentration method (Kondo et al., 2016). The DFe concentrations observed in Kondo et al. (2016) were 1.6 ± 0.5 times higher than those observed in Hioki et al. (2014). One reasoning for this is the acidification level in the samples. Seawater acidification allows for the disassociation of metals that are bound to colloids or ligands, thus increasing the concentration of D metals that can be analyzed (Bruland and Rue, 2001). Over the course of a couple of years, DFe in the low pH seawater samples had a longer time to disassociate with and substrates they were still bound to after the initial analysis. It is possible that this allowed for the samples to have higher concentrations of DFe that was reflected when pre-concentrated with the NOBIAS resin. Regardless of the analytical method, data from both methods are oceanographically correct and represent the chemically-labile dissolvable fraction of Fe in seawater.

4.2 Trace Metal Trends for Chukchi Seawater

Previous studies have stated that the composition of trace metals in Chukchi seawater showed high concentrations of LPMn, LPFe, LPCo and LPPb; and high concentrations of DNi, DCu, DZn and DCd (Cid et al., 2012; Kondo et al., 2016). Comparisons of observed surface (3 m) values for D and LP Fe, Mn and Cd, with the exception of DMn, in the current study were within range of Cid et al. (2012; ≤ 20 m; Table 5). Comparisons of the current studies data with Kondo et al.

(2016; ≤ 20 m; Table 5) surface values yielded higher concentrations, indicating possible annual variations in trace metal availability. The trace metal composition of Chukchi seawater from this study yielded the percent contributions of DFe (5.9 %) DMn (71.5 %) and DCd (66.3 %; Table 4). It is possible that the actions of each individual trace metal (Fe, Mn and Cd) within seawater may influence their concentrations. To examine the behaviour of Fe, Mn and Cd in seawater, their relationship with surface phosphate data collected from the towed-fish observation (Bering Strait to Barrow Canyon; Nishioka et al. Unpublished results) was examined. A relationship would indicate that any biogeochemical cycling processes controlling the removal of nutrients would also influence the trace metal (Boyle et al., 1981; Matsunaga and Abe, 1985). Out of the three metals, Cd was the only metal that showed a relationship with phosphate (Fig. 5c). DCd and PO_4 showed moderately strong correlations (r = 0.88) with a regression of:

[DCd nM] = 0.24 [PO^4 µmol / kg] + 0.042

R^2 = 0.78, *n* = 24

Cid et al. (2012) was also able to observe a relationship between Cd and phosphate in the Chukchi and Beaufort Seas, further suggesting that Cd is controlled though biogeochemical cycling processes.

Fe and Mn did not show any relationships with phosphate (Fig. 5a,b). This indicates that Fe and Mn may be controlled through external sources within Chukchi seawater. One possible source maybe river inputs. In the Chukchi Sea shelf the Mackenzie River (249 - 333 km^3/year; Dittmar and Kattner, 2003) can introduce significant amounts of Fe, Mn and sediments to surface waters (Macdonald et al., 1998; Cid et al., 2012). Shelf sediment can supply trace metals as they

304 are released into the water column (Cid et al., 2012; Kondo et al., 2016). It is possible that the
305 high concentrations of LPFe (Fig. 4a) observed in Chukchi seawater in this study may indicate that
306 sediments maybe a major source to Chukchi seawater.

307 In Chukchi seawater DMn concentrations were higher than LPMn concentrations (Fig. 6).
308 High DMn was also observed in the shelf area of the Bering Sea and decreased towards the Green
309 Belt area (Hurst et al., 2010). The distributions of Fe and Mn in the ocean are dependent on the
310 chemical characteristics of their oxidation states and the ocean's chemistry, physics and biology
311 (Balistrieri et al., 1992). A possible reason for high DMn and high LPFe in the water column of the
312 Chukchi Sea may result from chemical reactions between the water column and shelf sediments.
313 Reduction in sediment pore water supplies the water column with Fe(II) and Mn(II) where they
314 are oxygenated to insoluble Fe(III), Mn(III) and Mn(IV) respectively (Balistrieri et al., 1992;
315 Mortimer, 1941; Sunda et al., 1983). Fe oxidation from Fe(II) to Fe(III) is faster than for Mn. After
316 oxidation Fe can yield colloidal forms that can pass through filters and be analyzed as DFe (Stumm
317 and Morgan, 1981), quickly bind with organic ligands (99 %; Sunda, 2001; Wu and Luther, 1995)
318 or precipitate as Fe(III) oxyhydroxides that can create particulate Fe (Hurst et al., 2010; Lohan
319 and Bruland, 2008). This in turn can decrease the detectable amount of DFe in samples.

320 Mn oxidation is slower than observed for Fe, resulting in DMn to remain in the water
321 column longer. Oxidation rates can increase in the presence of bacterial processes (Nealson,
322 1978; Stumm and Morgan, 1981) but are significantly reduced in the presence of light (Sunda et
323 al., 1983). Removal processes such as phytoplankton uptake, scavenging of suspended and
324 sinking particles (Landing and Bruland, 1987; Sedwick et al., 2000) can also control the size
325 fraction concentrations of Fe and Mn in the water column. Although these processes are

important for the concentration of D and LP Fe and Mn, sediment reductive processes and shelf sediments may play a stronger role in the behaviour of Fe and Mn within the Chukchi Sea (Cid et al., 2012; Kondo et al., 2016).

4.3 Trace Metal Trends for Chukchi Sea Ice

Fe, Mn and Cd concentrations observed in each of the sea ice samples were heterogeneous. It is possible that this is due to the accumulation and release processes in sea ice. It was observed that the behaviour of Fe, Mn and Cd differed in Chukchi seawater. Fe and Mn had an external source (i.e. river and sediments) and Cd an internal source (i.e. biogeochemical cycling processes). The contribution of trace metal in Chukchi sea ice showed high LPFe (99.2 %), LPMn (63.6 %) and LPCd (71.2 %; Fig. 4, Table 4). When comparing Chukchi seawater trace metal concentrations to Chukchi sea ice trace metal concentrations, sea ice was observed to have higher LP concentrations (Fig.6a, Table 5). This indicates that Chukchi sea ice has a preference to accumulate or retain the LP faction of Fe, Mn and Cd. A possible explanation for the high concentrations of LP metals (representative of dissolvable particulate metals) in Chukchi sea ice may be due to sediment sources (shelf or river; Cid et al., 2012; Kondo et al., 2016). In the Arctic Ocean, the Chukchi shelf provides sediments (fine particles such as silt and clays) and a shallow environment (~ 50 m) were scavenging can occur (Nürnberg et al., 1994) during frazil ice formation (Reimnitz et al., 1993; Smedsrud, 2001). River inputs may add additional particles into the shelf areas (Cid et al., 2012; Kondo et al., 2016). During winter storm events, the water is mixed downward, re-suspending shelf sediments upward within the shallow shelf waters or polynyas (Eicken et al., 2005; Reimnitz et al., 1992).

At the same time frazil crystals form, and rise to the seawater surface. With the combination of re-suspending sediments and frazil crystals rising, the frazil crystals combine into a solid matrix where it can trap, nucleate or adhere to particulate matter of terrigenous or biogenic origin (Eicken et al., 2005; Ito et al., 2017; Reimnitz et al., 1993). This scavenging or suspension freezing of particles can allow for particulate trace metals to accumulate into the ice (Campbell and Collin, 1958; Reimnitz et al., 1993). Sediment-laden sea ice from the Chukchi and Beaufort Seas were associated with frazil ice growth formed in a well-mixed nearshore environment (Eicken et al., 2005). In the Antarctic region, high concentrations of PFe (biogenic or lithogenic) observed in land-fast ice were determined to be due to coastal shelf sediment re-suspension (Grotti et al. 2005; Lannuzel et al. 2008, 2010). Within the shelf areas wind speeds, up to 25 m s^{-1}, and current speeds, up to 1.5 m s^{-1}, can allow for re-suspended, trace metal bound, sediments to entrain into forming frazil ice (Ito et al., 2017; Eicken et al., 2005). Sediment-laden sea ice has been observed to be heterogeneous (Eicken et al., 2005) which may translate to the heterogeneity observed in the trace metals concentrations from the Chukchi sea ice. Once ice is formed into floes, enrichment of particulate trace metals may occur through wave propagation on the consolidated ice (Ito et al., 2017; Spindler, 1994).

Below the ice floe, brine channels are a possible avenue for the release or introduction of trace metals. Chukchi sea ice showed low concentrations of the D fraction for Fe, Mn and Cd (Fig. 3). It may be that sea ice released the D metals during brine drainage. As ice forms, seawater salts precipitate out into the brine system. Brine that are trapped in the sea ice are released into the underlying water due to density differentials when the permeability of sea ice increases (Untersteiner 1968; Maykut, 1985). Through this process, sea ice can release 60 –

70 % of incorporated dissolved matter (i.e. salts, metals. etc) into the underlying seawater (Giannelli et al., 2001). A temporal decoupling showed that particulate Fe (PFe, metals on 0.2 µm filters and digested; Lannuzel et al., 2011a) was enriched in Antarctic sea ice. Whereas, DFe was observed to be enriched in the brine (Lannuzel et al., 2014; van der Merwe et al., 2011) indicating DFe release from sea ice. Particulate metals may be locked into the ice from frazil entrainment or attached to brine channels, as observed in Antarctic sea ice, allowing this fraction to be released during advanced ice melt (Lannuzel et al., 2007, 2008). It is possible that, due to the late season when Chukchi sea ice was collected and its subsequent high permeability, the observed low concentrations of the D metals (Fe, Mn and Cd) maybe due to brine release. This would allow for the LP (dissolvable particulate fraction) to be preferentially retained in the Chukchi sea ice. This indicates that this temporal partitioning of trace metals observed in the Antarctic may occur in Arctic sea ice. It is possible that atmospheric deposition (wet or dry) may add trace metals to sea ice (Fischer et al., 2007; Maenhaut et al., 1996; Wagenbach et al., 1998). Yet the current study did not measure snow or identify different ice types before analysis. To clarify the source of trace metals and the processes utilized by sea ice to accumulate trace metal, it is necessary to compare the concentrations of trace metals to sea ice structure. Therefore, more studies are needed to understand the mechanisms for trace metal accumulation into Arctic sea ice.

5. Conclusions:

Sea ice plays an important role in the biogeochemical cycling of trace metals in the Arctic Ocean. Therefore, it is important to understand the mechanisms of trace metal accumulation into sea ice. D and LP Fe, Mn and Cd was observed in Chukchi seawater and sea ice to understand the form and concentrations of trace metal in Arctic sea ice. In Chukchi seawater, Fe, Mn and Cd behaved differently. Fe and Mn were controlled by external sources: sedimentary inputs (shelf or river), where Cd was controlled though internal sources: biogeochemical cycling processes. The metal composition of Chukchi seawater showed high percentages for LPFe, DMn and DCd. Comparing the concentrations of Chukchi seawater to sea ice, Chukchi sea ice had high concentrations for LPFe, LPMn and LPCd. The low concentrations of D metals observed in Chukchi sea ice could be due to a temporal partitioning of trace metals from the sea ice (D fraction released with the brine; van der Merwe et al., 2011; and the particulate fraction retained until advanced melting; Lannuzel et al., 2008) as observed with Antarctic sea ice. Entrainment of sediments during frazil formation, in underwater polynyas or leads, can add LP metals to the ice (Ackley et al., 1987; Reimnitz et al., 1993; Weissenberger and Grossmann, 1998) as well as atmospheric deposition onto sea ice (Maenhaut et al., 1996). Based on the results of this study, Chukchi sea ice was observed to have preference to accumulate or retain the LP metals.

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Figure captions

Figure 1. Sampling locations for sea ice (black triangles) and seawater off the coast of Barrow Canyon (BC, white circles) and off the coast of Point Lay (PL, black circles) in the Chukchi Sea. Each sampling site can be located by the sampling ID.

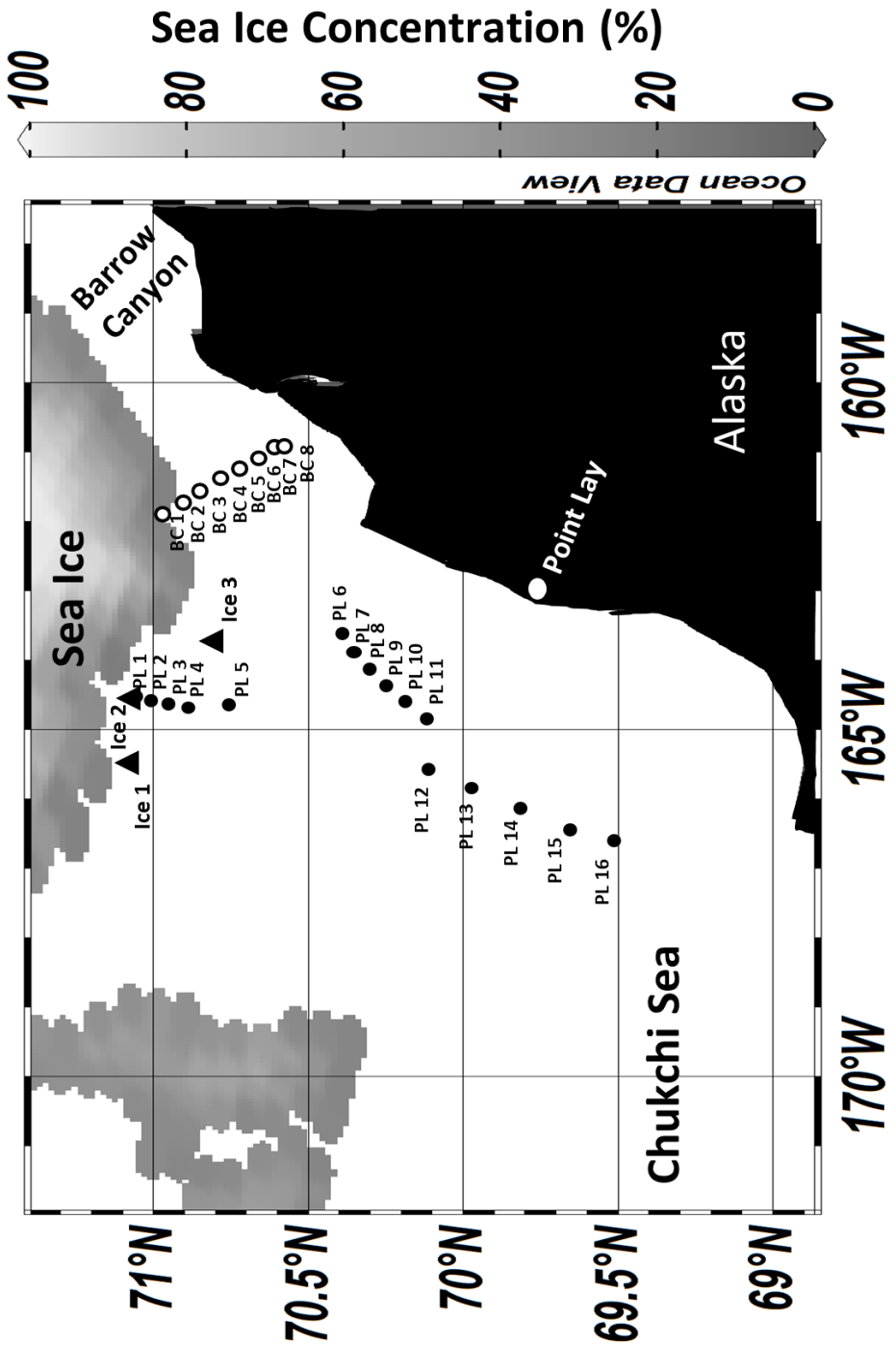
Figure 2. Diagram of manual pre-concentration system modified from Sohrin et al. (2008) and Kondo et al. (2016). Arrows represent the flow direction for solutions and samples.

Figure 3. Concentration of dissolved metals from the three sea ice samples (concentration factor range of 4.2 – 8.6 times), and seawater from below Barrow Canyon and off the coast of Point Lay (concentration factor range of 2.7 – 3.2 times). Different symbols next to each data bar indicate the statistical difference between samples. a) DFe, b) DMn, c) DCd

Figure 4. Concentration of liable particulate metals from the three sea ice samples (concentration factor range of 4.2 – 8.6 times), and seawater from below Barrow Canyon and off the coast of Point Lay (concentration factor range of 2.7 – 3.2 times). Different symbols next to each data bar indicate the statistical difference between samples. a) LPFe, b) LPMn, c) LPCd

Figure 5. Seawater regression analysis of dissolved metals with phosphate. a) DFe, b) DMn, c) DCd.

Figure 6. Concentrations of dissolved and labile particulate a) Fe, b) Mn and c) Cd in sea ice and seawater. Concentration factors varied between sea ice (4.2 – 8.6 times) and seawater (4.2 – 8.6 times) due to sample volume variability. Seawater was collected below Barrow Canyon and off the shore of Point Lay. Dissolved concentrations are represented in white and labile particulate concentrations are in gray.



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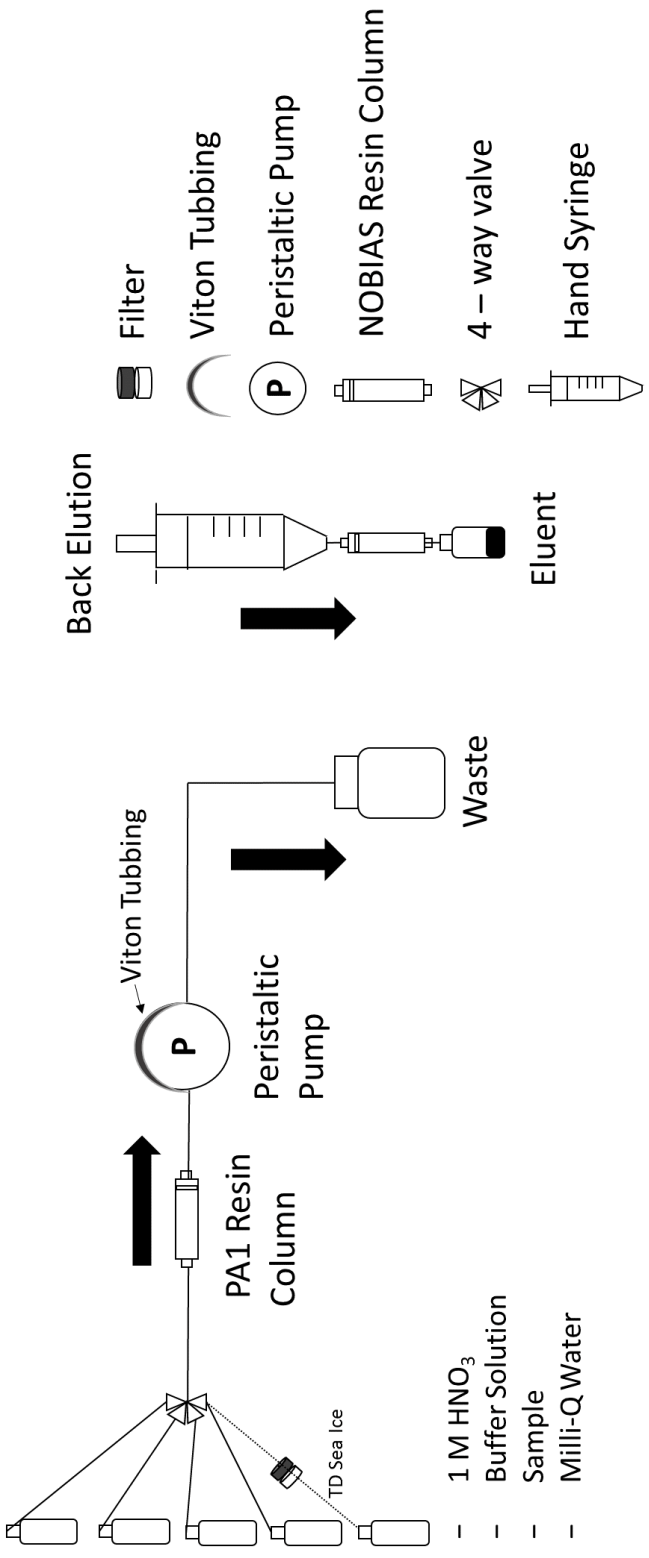

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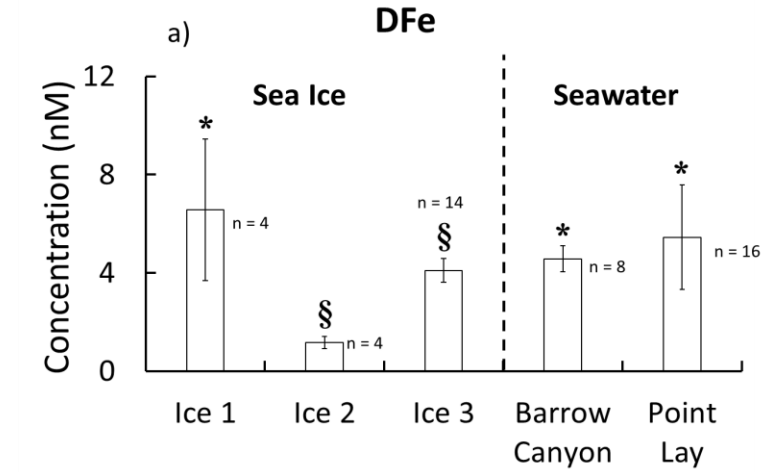
663 Figure 2.



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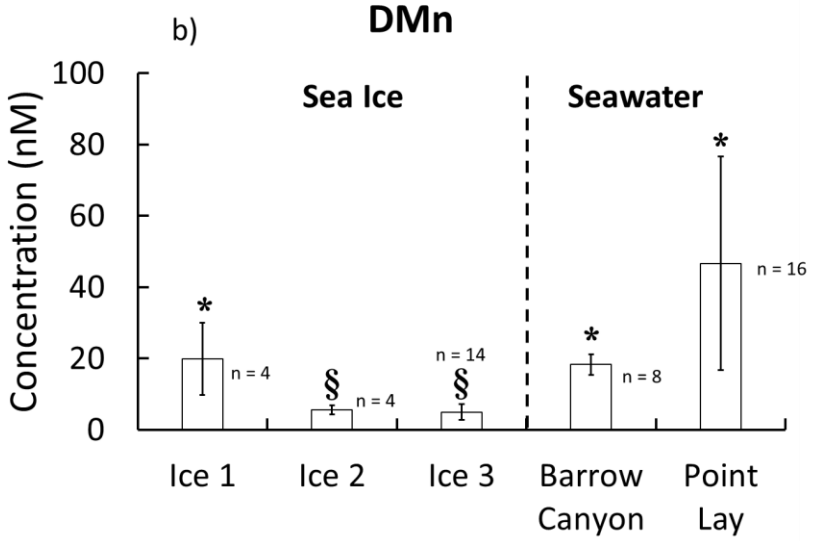

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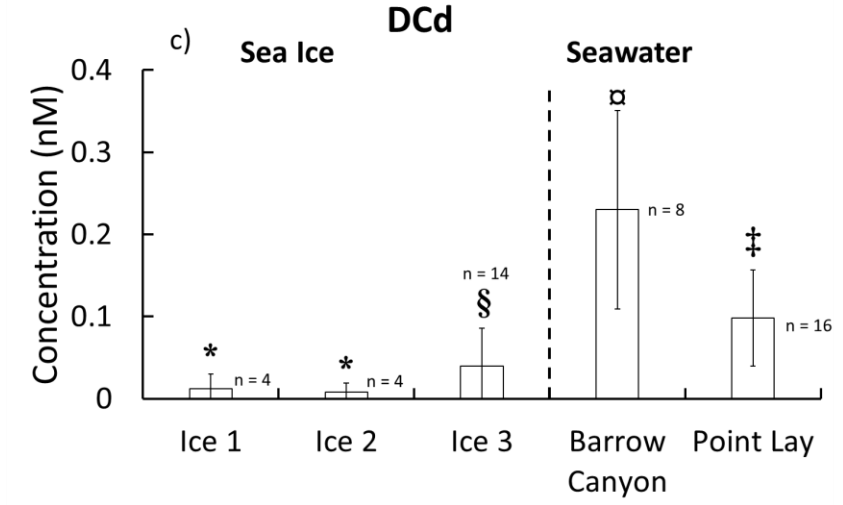

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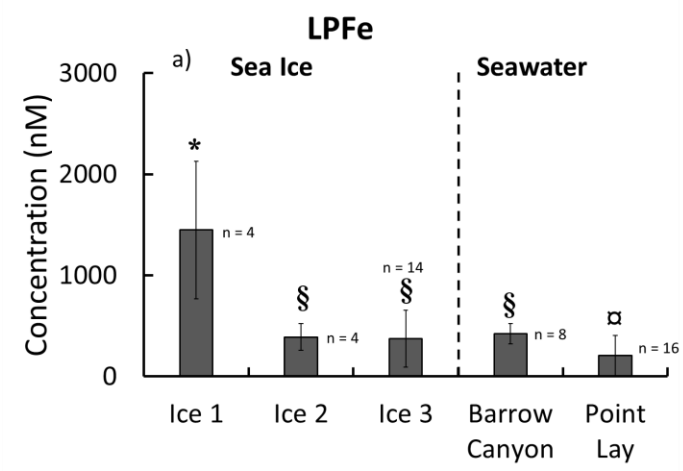
667 Figure 3.



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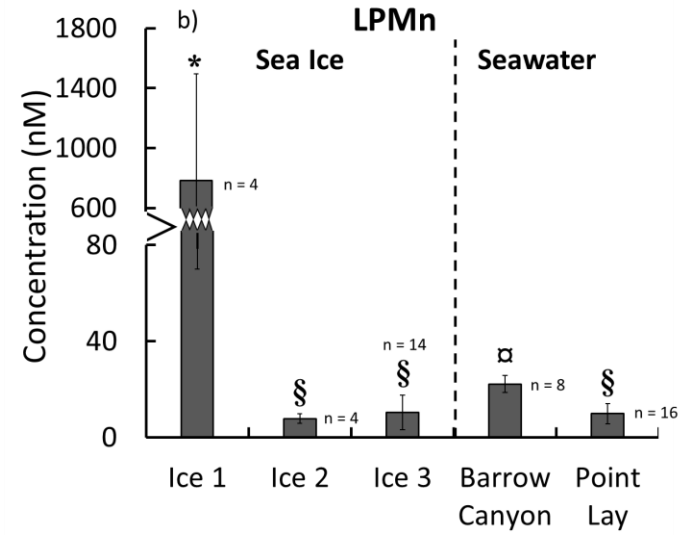

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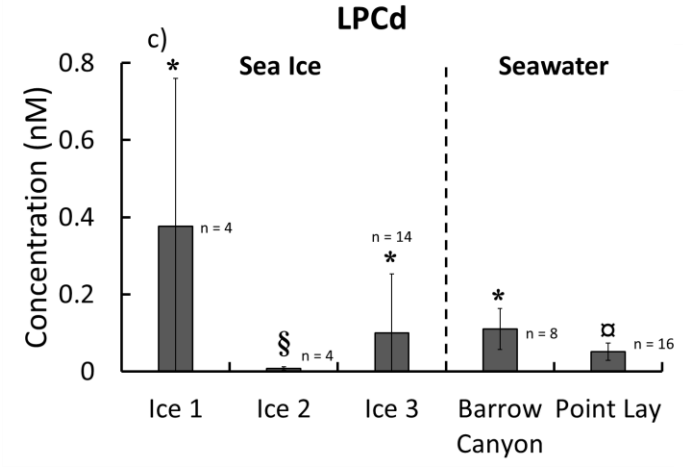

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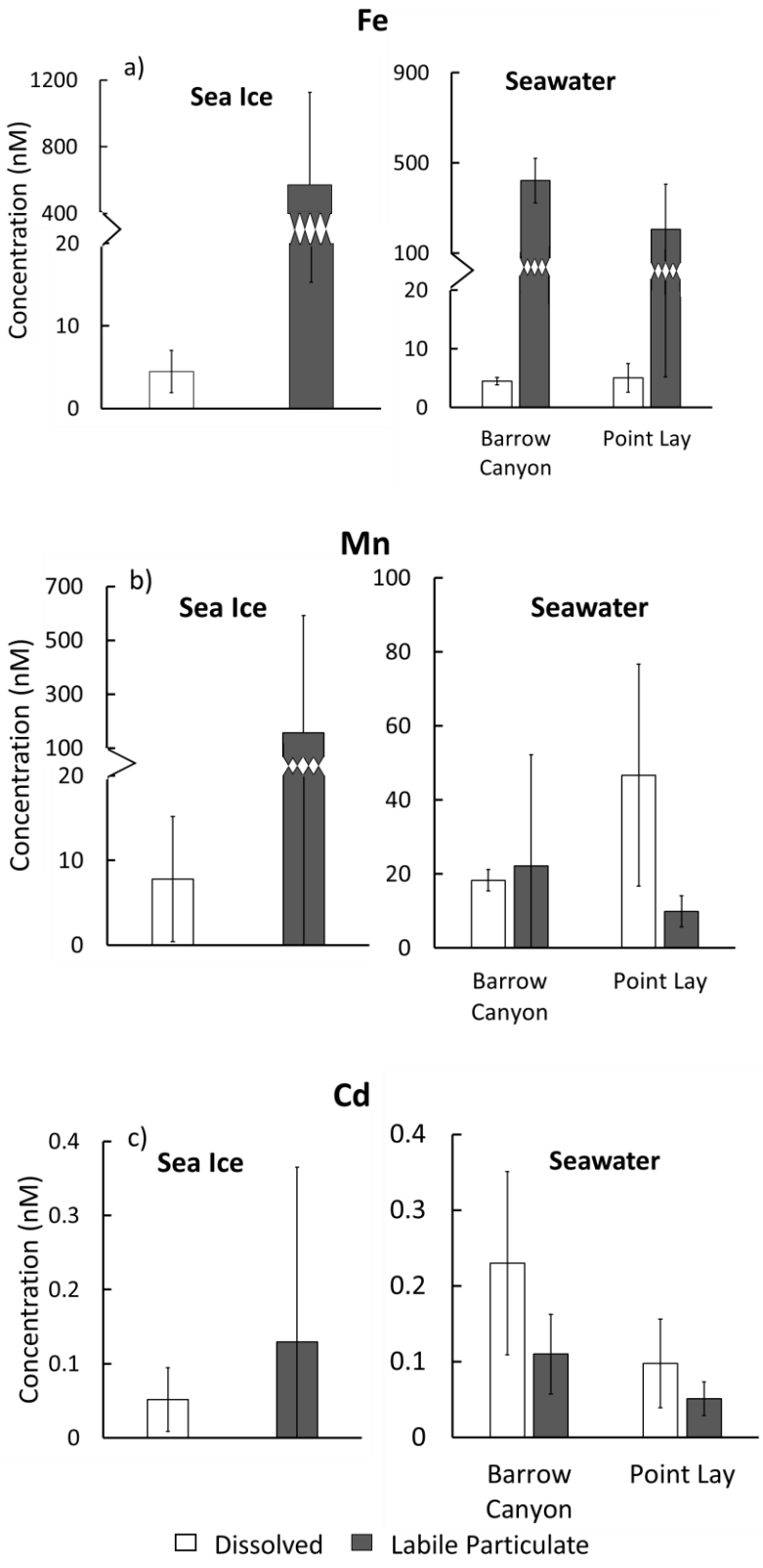
671 Figure 4.

672

673 Figure 5.



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677 Figure 6.

678 Table 1. Detection limit for Fe, Mn and Cd determined from multiplying the standard deviation
679 of the 125 ml Milli-Q water procedural blank by three. The detection limit was calculated after
680 the pre-concentration step and analysis with the GFAAS. The final *in situ* detection limits were
681 lower as they were calculated with the pre-concentration factor.

Element	*n*	avg ± SD (nM)	Detection Limit[a] (nM)	*in situ* Detection Limit[b] (nM)
Fe	6	3.3 ± 1.3	3.9	0.3
Mn	6	0.57 ± 0.24	0.7	0.06
Cd	6	0.007 ± 0.0006	0.002	0.0002

682

683 [a] 3*SD of Procedural Blank

684 [b] 3*SD of the procedural blank after calculation with the pre-concentration factor

685

686 Table 2. Recovery of Fe, Mn, and Cd from spiked Milli-Q water. Samples were pre-concentrated
687 with the NOBIAS resin.

		Added	Recovery (%)
Element	*n*	(nM)	avg ± SD
Fe	3	10.03	102.1 ± 5.6
Mn	3	1.73	100.3 ± 1.8
Cd	3	1.33	106.3 ± 5.1

688

689

690 Table 3. Recovery data for seawater reference materials (NASS-6) utilizing the NOBIAS resin
691 pre-concentration method in this study verses certified values from The National Research
692 Council of Canada.

		This Study	NASS-6 Certified Value
		avg ± SD	avg ± SD
Element	*n*	(nM)	(nM)
Fe	8	9.5 ± 1.3	8.9 ± 0.8
Mn	8	11.2 ± 1.4	9.7 ± 0.9
Cd	8	0.3 ± 0.1	0.3 ± 0.02

693

694 Table 4. Mean percent contribution of dissolved and liable particulate trace metals in Chukchi
695 sea ice and Chukchi seawater. a) Fe, b) Mn and c) Cd

a)	DFe	LPFe
	(% ± SD)	(% ± SD)
Sea Ice	0.8 ± 0.7	99.2 ± 0.7
Seawater	5.9 ± 11.9	94.1 ± 11.9

696

b)	DMn	LPMn
	(% ± SD)	(% ± SD)
Sea Ice	36.4 ± 22.1	63.6 ± 22.1
Seawater	71.5 ± 20.8	28.5 ± 20.8

697

c)	DCd	LPCd
	(% ± SD)	(% ± SD)
Sea Ice	28.8 ± 28.3	71.2 ± 28.3
Seawater	66.3 ± 25.2	33.7 ± 25.2

698

699

Table 5. Comparison of minimum and maximum surface seawater (≤ 20 m). Dissolved and labile particulate Fe, Mn and Cd concentrations from the Chukchi Sea Shelf to the Canada Basin were compared to published studies with the current study.

		This Study	Cid et al. (2012)	Kondo et al. (2016)
Element		**(nM)**	**(nmol/kg)**	**(nM)**
Fe	D	2.3 – 10.7	1.4 – 10.4	1.1 – 2.7
	LP	12.7 – 702.9	24.1 – 9300.4	2.7 – 33.4
Mn	D	13.9 – 109.7	0.3 – 26.3	8.2 – 15.0
	LP	<DL – 25.8	3.8 – 193.9	1.2 – 22.8
Cd	D	<DL – 0.5	0.2 – 0.5	0.1 – 0.4
	LP	<DL – 0.2	<DL – 0.09	<DL – 0.2

Table 6. Raw data from a) sea ice and b) seawater samples. D- dissolved and LP- labile particulate. Sea ice pre-concentration factor ranged from 4.2 – 8.6 times and the seawater pre-concentration factor ranged from 2.7 – 3.2 times.

a)	**Sea Ice**					
Sample	DFe (nM)	LPFe (nM)	DMn (nM)	LPMn (nM)	DCd (nM)	LPCd (nM)
1	2.7	1947.6	12.3	33.5	0.04	0.1
1	3.2	2278.9	10.2	1316.1	<DL	0.1
1	10.8	875.3	21.3	127.6	<DL	1.0
1	7.6	689.4	35.9	1650.2	<DL	0.3
2	0.9	297.2	3.5	5.8	<DL	0.01
2	1.4	611.0	6.9	10.4	<DL	0.01
2	1.0	370.5	5.9	7.3	<DL	0.01
2	1.5	279.2	5.8	3.6	0.03	<DL
3	1.3	518.5	5.0	17.1	0.02	0.05
3	2.1	344.2	6.5	10.0	<DL	0.1
3	2.4	714.0	8.5	15.1	0.02	0.04
3	2.7	75.9	5.0	<DL	0.2	<DL
3	1.4	81.5	5.1	2.7	<DL	0.02
3	5.5	647.8	1.4	21.2	0.05	0.1
3	1.6	223.2	2.9	12.6	<DL	0.04
3	4.0	560.2	7.9	15.4	0.1	0.6
3	1.1	101.3	3.6	2.9	0.02	0.04
3	0.9	88.6	3.7	3.4	<DL	0.03
3	5.0	888.9	9.3	17.5	0.03	0.1
3	3.3	729.3	4.5	19.2	0.08	0.06
3	1.2	150.8	2.6	5.9	0.03	0.03
3	1.5	89.4	3.9	1.6	0.03	0.01

707

b)	Seawater					
Sample	DFe (nM)	LPFe (nM)	DMn (nM)	LPMn (nM)	DCd (nM)	LPCd (nM)
Barrow Canyon 1	4.9	459.5	21.9	18.5	0.1	0.09
Barrow Canyon 2	4.5	451.4	21.8	15.7	0.09	0.2
Barrow Canyon 3	4.2	426.7	21.9	<DL	0.09	0.05
Barrow Canyon 4	3.7	272.4	14.4	25.8	0.2	0.2
Barrow Canyon 5	3.5	245.7	16.6	20.9	0.3	0.04
Barrow Canyon 6	5.1	506.1	17.9	25.1	0.3	0.1
Barrow Canyon 7	5.4	477.2	15.7	25.1	0.3	0.1
Barrow Canyon 8	4.6	535.5	16.0	24.3	0.5	<DL
Point Lay 1	3.4	148.8	13.9	12.0	0.07	<DL
Point Lay 2	3.3	121.0	25.4	5.6	<DL	0.04
Point Lay 3	4.3	330.1	31.1	10.2	<DL	0.08
Point Lay 4	5.2	668.4	32.8	16.7	0.06	0.03
Point Lay 5	5.8	702.9	36.2	17.7	0.07	0.05
Point Lay 6	5.3	298.4	41.2	<DL	0.2	0.04
Point Lay 7	3.7	132.1	37.4	9.9	0.2	<DL
Point Lay 8	2.3	116.2	29.7	9.4	0.08	0.03
Point Lay 9	2.4	152.2	31.0	12.0	0.06	0.08
Point Lay 10	2.7	155.8	33.9	10.5	0.09	0.05
Point Lay 11	5.2	119.5	35.7	4.4	0.09	0.02
Point Lay 12	5.4	197.1	36.6	0.9	0.1	<DL
Point Lay 13	3.4	68.2	38.2	<DL	0.07	0.04
Point Lay 14	10.0	13.5	107.9	10.9	0.2	0.04
Point Lay 15	10.7	12.7	109.7	8.6	0.2	0.08
Point Lay 16	8.0	46.9	105.6	9.2	0.2	0.09

708