Spatial and seasonal distribution of dissolved and particulate bioactive metals in Antarctic sea ice

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Iron (Fe) has been shown to limit growth of marine phytoplankton in the Southern Ocean, regulating phytoplankton productivity and species composition, yet does not seem to limit primary productivity in Antarctic sea ice. Little is known, however, about the potential impact of other metals in controlling sea-ice algae growth. Here, we report on the distribution of dissolved and particulate cadmium (Cd), cobalt (Co), copper (Cu), manganese (Mn), nickel (Ni), and zinc (Zn) concentrations in sea-ice cores collected during 3 Antarctic expeditions off East Antarctica spanning the winter, spring, and summer seasons. Bulk sea ice was generally enriched in particulate metals but dissolved concentrations were similar to the underlying seawater. These results point toward an environment controlled by a subtle balance between thermodynamic and biological processes, where metal availability does not appear to limit sea-ice algal growth. Yet the high concentrations of dissolved Cu and Zn found in our sea-ice samples raise concern about their potential toxicity if unchelated by organic ligands. Finally, the particulate metal-to-phosphorus (P) ratios of Cu, Mn, Ni, and Zn calculated from our pack ice samples are higher than values previously reported for pelagic marine particles. However, these values were all consistently lower than the sea-ice Fe:P ratios calculated from the available literature, indicating a large accumulation of Fe relative to other metals in sea ice. We report for the first time a P-normalized sea-ice particulate metal abundance ranking of Fe >> Zn/Cu >> Ni/Cd > Co.

1. Introduction

In the Southern Ocean (SO), the isolation from land masses and associated dust supply leads to low iron (Fe) availability in surface waters. As a consequence, marine phytoplankton cannot fully utilize the available macronutrients (Boyd et al., 2007) because Fe is required in many metabolic pathways in phytoplankton cells, including carbon fixation and respiration (Schulz et al., 2007). The widespread Fe limitation, combined with low light availability, leads to low chlorophyll concentrations, making the SO the largest high-nutrient low-chlorophyll area in the world (Martin, 1990; de Baar, 2005). In this context, seasonal sea ice can store 1–2 orders of magnitude greater concentrations of Fe and chlorophyll-a (Chla) relative to seawater (Lannuzel et al., 2016b, and references therein). In this highly biologically productive environment, Fe availability does not seem to limit algal growth. However, little is known about the role of other bioactive metals in controlling sea-ice algal productivity (Lannuzel et al., 2011). Metals such as cobalt (Co), copper (Cu), manganese (Mn), and zinc (Zn) can regulate productivity and species composition in pelagic systems because of large differences in metal requirements among species (Sunda, 2012).

Zinc is widely used in eukaryotic cells and plays an important role in carbon assimilation during photosynthesis (Lane and Morel, 2000). It is further involved in cell pH regulation, silicification, dephosphorylation of organic compounds, as well as DNA and RNA replication (Koch and Trimborn, 2019). Physiologically, Zn can be replaced by either Co or Cd in several species of centric marine diatoms and Phaeocystis antarctica (Price and Morel, 1990; Sunda and Huntsman, 1995a; Saito and Goepfert, 2008). Cobalt is also an essential element for vitamin B12 production by bacteria and archaea, which phytoplankton depend on (Banerjee and Ragsdale, 2003). Vitamin B12

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and Fe availabilities can simultaneously limit phytoplankton growth in coastal sea-ice edge communities during late austral summer (Bertrand et al., 2015). Manganese may be equally limiting in high-nutrient low-chlorophyll waters (Middag et al., 2013; Pausch et al., 2019). Manganese is required in photosystem II and to neutralize reactive oxygen species (ROS) as part of the antioxidant enzyme superoxide dismutase (SOD; Twining et al., 2004; Wolfe-Simon et al., 2005). Enhanced production of ROS by diatoms has been observed in Fe-limited environments, leading to increased oxidative stress and higher Mn-to-Fe ratios in particulate matter compared to Fe-replete waters (Peers and Price, 2004). Copper is used in both photosynthetic and respiratory electron transport chains (Twining and Baines, 2013). It is also present as SOD and plays a part in cellular Fe uptake (Maldonado et al., 2006). While beneficial when found in trace concentrations, high concentrations of free Cu and Zn ions can become toxic for some algae (Bruland, 1980; Sunda, 2012; Yang et al., 2019).

To date, the only established role of nickel (Ni) in eukaryotes is as a constituent of the metalloenzyme urease, which is responsible for the breakdown of urea (Twining and Baines, 2013). However, a Ni-containing form of superoxide dismutase (Ni-SOD), similar to those found in prokaryotes, has been observed in some oceanic diatoms (Cuvelier et al., 2010). Nickel was also found to be associated with diatom frustules, although the biological explanation for this association remains unknown (Twining et al., 2012). Metals are constituents of many other metalloproteins and are therefore likely to be involved in other biological functions yet to be discovered. Regardless of their specific roles, microalgal cellular uptake and metal quotas are determined by complex and sometimes competing mechanisms (Sunda, 2012). Physiological limitation by one metal can reduce the quotas of others, which can also be controlled by the substitution of one metal by another in some phytoplankton species, as observed for Zn, Cd, and Co (Koch and Trimborn, 2019). These intricate relationships are further complicated by the different affinities they have with organic ligands. Ligands can control the concentration of metal hydrate ions and hence their bioavailability (Sunda, 2012).

During the last decades, advances in trace-metal-clean water sampling and analytical techniques have increased the wealth of data available to investigate the biogeochemical cycling of metals in seawater. However, metal data from Antarctic sea-ice environments remain scarce, relative to the vast area that sea ice covers seasonally and the recognition that sea ice is an ocean fertilizer. Only a few studies have reported metals other than Fe in Antarctic pack ice (Lannuzel et al., 2011) and fast ice (Grottj et al., 2001; Grottj et al., 2005; Lannuzel et al., 2011; Noble et al., 2013), and these are limited to spring-time observations. Lannuzel et al. (2011) showed that sea ice was not enriched in dissolved metals compared to Antarctic seawater in late winter/early spring. However, particulate metals were one to two orders of magnitude higher relative to seawater collected below the ice (0–10 m; Lannuzel et al., 2011). In the Ross Sea, particulate Mn (PMn), Co (PCo), and Cu (PCu) concentrations and speciation patterns indicate that metal incorporation into sea ice is driven by resuspension of sediments, followed by release during melting, as the main processes affecting their distribution in coastal waters (Frache et al., 2001; Grottj et al., 2001; Grottj et al., 2005). On the other hand, Noble et al. (2013) found elevated particulate Mn and Co-to-Aluminim (Al) ratios in basal sea ice in comparison to the underlying sediments, suggesting that bioaccumulation is also an important source of PMn and PCo. In this work, we report and investigate the drivers of dissolved and particulate Cd, Co, Mn, Ni, Cu, and Zn distribution from 3 Antarctic sea-ice sampling campaigns conducted off East Antarctica between 2012 and 2017. Particulate Al (PAL) was measured as a tracer of lithogenic input (Taylor and McLennan, 1985). Data were used to identify key drivers of the spatial and temporal distribution of metals in sea ice and to probe our main question: Can metals other than Fe control algal productivity in the sea ice?

2. Materials and methods

2.1. Sampling sites

Sea-ice cores were collected off the East Antarctic coast during 3 field campaigns (Figure 1): the Sea Ice Physics and Ecosystem eXperiment-2 (SIPEX-2; a voyage conducted during the austral winter–spring 2012 transition; Meiners et al., 2016), the Davis time series (conducted in late spring 2015; Duprat et al., 2019; Duprat et al., 2019), and the Aurora Australis Voyage-2 (AAV2; carried out in summer 2016–2017; Duprat et al., 2020). Ice cores for SIPEX-2 were collected at 6 different locations within first-year pack ice (64–65.1°S, 116–121.1°E) between September 26 and November 10, 2012. Ice cores for Davis were collected on 6 different dates (between November 16 and December 2, 2015) at a single site located approximately 2 km north of Davis Station (68.5°S, 77.9°E) in an area of undeformed fast ice (maximum water depth of 20 m). Ice cores from AAV2 were collected at 9 different sites (3 fast ice and 6 pack ice stations) between Wilkes Land and King George V Land (63.2–67.2°S, 110.5–147.7°E) from December 19 to January 13. Sack-hole brines and under-ice seawater were also collected during the Davis and AAV2 sea-ice campaigns. Sampling sites were selected away and upwind from the study vessel (SIPEX-2 and AAV2) and research station (Davis). Additional information about the sampling sites can be found in Duprat et al. (2019), Lim et al. (2019), and Duprat et al. (2020).

2.2. Cleaning and sampling procedures

Cleaning and sampling procedures were carried out following the protocols described in detail in Miller et al. (2015), Lannuzel et al. (2016a), and Duprat et al. (2019, 2020). Plasticware was acid-cleaned according to GEOFACIES recommendations (Cutter et al., 2017). New low-density polyethylene (LDPE) sampling bottles were immersed in 2% (v/v) Decon90 baths for 1 week. Bottles were then thoroughly rinsed with ultra-high purity (UHP) water (Barnstead™, Waltham, MA), filled with 6M hydrochloric acid (HCl, 50% v/v reagent grade; Merck, Kenilworth, NJ) and left to soak in a 2M HCl (20% v/v
reagent grade, Merck) bath for a month. Next, bottles were rinsed with UHP water again and filled with 1M distilled HCl (10% v:v instrument quality; Seastar, Sidney, BC, Canada) for a week on a hot plate (60°C). Lastly, bottles were thoroughly rinsed (3–5 times) with UHP water in a class-100 laminar flow hood and stored triple-bagged in plastic press seal bags until use.

Sampling and processing for metal analysis followed protocols described by Lannuzel et al. (2006) and van der Merwe et al. (2009). Snow was collected using an acid-cleaned polyethylene (PE) hand shovel and stored in wide-mouth Nalgene® PE bottles. Ice cores were collected with an electric-powered, electropolished stainless steel corer (0.14-m internal diameter; Lichtert Industrie, Anderlecht, Belgium). Previous work has demonstrated that the coring strategy is fit for trace metal work (Lannuzel et al., 2006; Lannuzel et al., 2011; van der Merwe et al., 2009). After coring, ice cores were immediately sectioned using a medical-grade bone saw (Richards Analytical, Australia) into 6 or 7 discrete sections over the length of the core (10–15 cm from top, intermediate, and bottom layers), and placed into individual acid-cleaned PE containers. After melting, snow and sea-ice sections were filtered under gentle vacuum (<0.13 bar) through 0.2-m pore size polycarbonate membrane filters (47-mm diameter; Sterlitech, Auburn, WA) using a Teflon® perfluoroalkoxy filtration apparatus (Savillex, Eden Prairie, MN) to obtain the particulate (>0.2 μm) and dissolved (<0.2 μm) metal fractions. The dissolved fraction was collected in 125-ml LDPE bottles and acidified to pH 1.8 (approximately 1% v:v of 12M ultrapure HCl, Seastar Baseline, analytical grade) before triple-bagging and storage at room temperature until analysis. Polycarbonate filters retaining the particulate material were placed into acid-clean polystyrene Petri dishes, triple-bagged, and stored frozen (−20°C) in the dark until further processing and analysis.

2.3.1. Dissolved metal analysis
Samples collected for Davis and AAV2 were concentrated 10×, 20× or 40× (depending on the expected analyte concentrations) using an automated off-line sample pre-concentration system (seaFAST-pico™, Elemental Scientific; Nobias Chelate-PA1 resin) according to the method described by Wuttig et al. (2019). The system was proven effective and reliable for the determination of the range of trace elements and salinities encountered in the samples reported here (Wuttig et al., 2019). Dissolved metal concentrations were then determined using a Sector Field Inductively Coupled Plasma Mass Spectrometer (SF-ICP-MS, Element 2). SIPEX-2 samples were analyzed direct using SF-ICP-MS without any off-line preconcentration...
steps due to the higher concentration of dissolved metals expected in these early-season samples (Lannuzel et al., 2016a). Considering the SF-ICP-MS system, isotopes of interest were measured in both “low” and “medium” spectral resolution modes, as applicable. Cleaning procedures, calibrations, and quality control of the SF-ICP-MS results followed those described in Duprat et al. (2019) and Wuttig et al. (2019). Daily instrument drift and performance were monitored using standard quality control samples. The average blank concentrations and calculated detection limits (3σ of the acidified internal blank) for Cd, Co, Cu, Mn, Ni, and Zn are shown in Table 1. Final concentrations reported here are all blank-corrected.

As described in Section 2.3.1, solubilization of metal-associated colloidal matter and metal–organic complexes to the free inorganic form (before the determination of total dissolved metal using the cation exchange resin) was achieved through sample acidification. Nonetheless, systematic assessments (Vega and van den Berg, 1997; Saito and Moffett, 2002; Milne et al., 2010; Shelley et al., 2010; Wuttig et al., 2019) suggest that a partial amount of Co (and to a lesser extent Cu) remains very strongly bound to either dissolved or colloidal organic matter and can resist acid solubilization. Therefore, concentrations reported here for dissolved Cu (DCu) and particularly for dissolved Co (DCo) better reflect the labile fraction, rather than the total dissolved fraction. The absence of further sample processing to ensure a complete metal–organic complex dissociation (such as the use of an additional pretreatment ultraviolet irradiation step) could therefore result in underestimation of the total dissolved fraction concentration (15%–50% for Co; Milne et al., 2010; Rapp et al., 2017; Wuttig et al., 2019). However, this effect is expected to be minimized in our samples due to the commonly lower concentrations of this element in Antarctic surface waters (Milne et al., 2010).

Finally, metal data were normalized to sea-ice bulk salinity following Gradinger and Ikävalko (1998) and compared to seawater concentrations using an enrichment index (EI) calculated as:

$$\text{EI} = \left( \frac{[\text{Me}]_{\text{ice}}}{[\text{Sal}]_{\text{ice}}} \right) \times \left( \frac{[\text{Sal}]_{\text{sw}}}{[\text{Me}]_{\text{sw}}} \right),$$

where $[\text{Me}]_{\text{ice}}$ is the concentration of dissolved metal in the ice, $[\text{Me}]_{\text{sw}}$ is the concentration of dissolved metal in the underlying seawater, $[\text{Sal}]_{\text{ice}}$ is the bulk salinity of the ice, and $[\text{Sal}]_{\text{sw}}$ is the salinity of the underlying seawater. Values of 1, <1, or >1 correspond to being conservative, depleted, or enriched as compared to bulk salinity, respectively.

2.3.1.2. Particulate metals

A strong acid treatment was applied to the filters to ensure the complete digestion of the most refractory particles (Bowie et al., 2010). First, a mixture of acids (750 μL of 12M HCl, 250 μL of 16M HNO₃, and 250 μL of 29M HF, all ultrapure Seastar Baseline from Choice Analytical) was added to each sample and blank filter in a 15-mL
Table 2. Sector Field Inductively Coupled Plasma Mass Spectrometer results for metal concentrations in acid-digested filter blanks (0.25 ml HNO₃ + 0.25 ml HF + 0.75 ml HCl). DOI: https://doi.org/10.1525/elementa.2021.00032.12

| Blank                                      | Statistic | Al (nM) | Cd (nM) | Co (nM) | Cu (nM) | Mn (nM) | Ni (nM) | Zn (nM) |
|--------------------------------------------|-----------|---------|---------|---------|---------|---------|---------|---------|
| Digested filter blanks (SIPEX-2)          | Average (n = 7) | 1.382   | 0.001   | 0.003   | 0.03    | 0.013   | 0.058   | 1.097   |
|                                            | SD        | 0.606   | 0.001   | 0.001   | 0.01    | 0.002   | 0.020   | 0.476   |
|                                            | Detection limit<sup>a</sup> | 1.818   | <dl<sup>a</sup> | 0.002   | 0.003   | 0.03    | 0.006   | 0.059   | 1.427   |
| Digested filter blanks (Davis and Aurora Australis, Voyage [AAV2])<sup>b</sup> | Average (n = 3) | 0.963   | <dl<sup>b</sup> | 0.001   | 0.01    | 0.004   | 0.016   | 0.700   |
|                                            | SD        | 0.238   | <dl<sup>b</sup> | <dl<sup>b</sup> | 0.005   | 0.001   | 0.003   | 0.457   |
|                                            | Detection limit<sup>b</sup> | 0.713   | <dl<sup>b</sup> | 0.001   | 0.014   | 0.003   | 0.008   | 1.370   |

<sup>a</sup> The detection limit (dl) is 3 times the standard deviation (SD) of the procedural blank.

<sup>b</sup> Samples for Davis and AAV2 were processed and analyzed together.

digested filter blanks (Davis and Aurora Australis detection limit for each metal was calculated as 3
run along SIPEX-2 samples (Lannuzel et al., 2016a). The Council of Canada and BCR-414; Joint Research Centre)
certified reference materials (MESS-3; National Research
efficiency of the digestion procedure was confirmed with
lowing procedures outlined in Section 2.3.1.1. The
pylene tubes for metal quantification using SF-ICP-MS fol-
(10 ppb), was added as an internal standard. Finally, an
tion, diluted to reach the final concentration of 87.1 nM
(Seastar Baseline
Teflon® perfluoroalkoxy vial (Savillex). Vials were capped
and heated at 120°C for 12 h over a Teflon® coated hot-
plate (SCP Science, Baie-D’Urfe, QC, Canada) under a class-
100 fume hood, followed by dry evaporation of the acids
in opened vials at 120°C overnight. The dry residues were
then resuspended in 9.9 mL ultrapure 10% (v/v) HNO₃
(Seastar Baseline®), and 100 µL Indium commercial solution,
diluted to reach the final concentration of 87.1 nM
(10 ppb), was added as an internal standard. Finally, an
aliquot of 5 mL was transferred to acid-cleaned polypropylene tubes for metal quantification using SF-ICP-MS fol-
lowing procedures outlined in Section 2.3.1.1. The
efficiency of the digestion procedure was confirmed with
certified reference materials (MESS-3; National Research Council of Canada and BCR-414; Joint Research Centre)
run along SIPEX-2 samples (Lannuzel et al., 2016a). The detection limit for each metal was calculated as 3 × the
standard deviation of the acid-digested filter blanks (Table
2). Particulate inventories (µmol m⁻²) were determined by
multiplying the metal concentration of each ice core sec-
section (assuming seawater density around 1 g cm⁻³) with the
section thickness and summing them. For this purpose,
linear interpolations were applied to core sections where
concentrations were not measured.

2.3.2. Physicochemical and biological parameters
The thickness of sea ice and snow was measured at each site. Other standard physicochemical and biological para-
eters, including in situ ice temperature; bulk salinity; the
concentrations of Chlₐ, the macronutrients nitrate (NO₃⁻),
nitrite (NO₂⁻), phosphate (PO₄³⁻), silicic acid (Si(OH)₄), and
ammonium (NH₄⁺); and particulate organic carbon (POC)
and nitrogen (PON), were also determined for each sample
following the methods described in Duprat et al. (2020).

2.4. Statistical analysis
Nonparametric Kruskal–Wallis and Mann–Whitney tests
were performed in 3 groups (SIPEX-2, Davis, and AAV2)
to test for temporal variability. For this purpose, ice-
section values within each group were treated as independ-
tent. The Mann-Whitney test was also used to verify
differences between particulate metal-to-Al (PMe:PaL)
ratios from pack and fast ice, and particulate metal-to-
phosphorus (PMe:P) ratios from late winter–spring and
summer ice. Finally, a one-sample t-test (assuming
unequal variance) was used to check whether our ratios
differed from reported literature means. A generalized
mixed model (gamma distribution) was used to test the
spatial (2 groups: fast ice and pack ice) variation consid-
ering the dependence between measurements at different
depths in the same core. This choice was based on the
different vertical distributions of metals observed in pack
ice and fast ice. The Spearman correlation coefficient test
was used to investigate potential correlations between all
physical and biogeochemical parameters due to the non-
normality observed in most variables.

3. Results
3.1. Dissolved metal distributions
Summary statistics for salinity, macronutrients, and Chlₐ
are shown in Figure 2. Median and range concentrations
dissolved metals in snow (n = 14), pack ice (n = 74), fast
ice (n = 38), brine (n = 10), and under-ice seawater (n =
14) are summarized in Table 3. The dissolved fraction
contributed 92% (Cd), 24% (Co), 75% (Cu), 77% (Mn),
85% (Ni), and 82% (Zn) to the total (dissolved + particu-
late) metal pools. The notable lower dissolved-to-total ratio observed for Co could have resulted from a potential
underestimation of the total DCo, as considered in Section
2.3.1.1. Dissolved metal concentrations were enriched in
sea ice relative to seawater below (Table 4). Dissolved
metal concentrations in the snow were low compared to
sea ice and seawater (Table 3). Significantly higher
dissolved Mn (DMn) and DCo (P < 0.01) and lower
dissolved Ni (DNi) and Zn (DDzN) (P < 0.05) were found in fast ice
compared to pack ice, albeit concentrations for both types
of ice were within the same order of magnitude. Vertical
profiles of dissolved metals resemble an L-shaped vertical
distribution for fast ice, with no clear pattern for pack ice
(Figure 3).

A significant decrease (P < 0.01) in the concentrations of
dissolved Cd (Dcd), DCu, DNi, and DDzN in summer
(AAV2) compared to winter–spring (SIPEX-2; Figure 4; Table 3) sea ice was observed. However, no clear temporal trends were observed in the overall dissolved fractions (dissolved/total; Figure 5). Finally, the absence of correlations between dissolved metal concentrations and salinity supports their nonconservative distribution relative to salts. In fast ice, DNi and DCu were moderately correlated with POC (0.66 and 0.65, respectively;
Table 3. Median and range of dissolved metal concentrations in East-Antarctic snow, sea ice by season (expedition), pack ice, fast ice, brine, and under-ice seawater, with published ranges for Antarctic seawater south of the Polar Front for comparison. DOI: https://doi.org/10.1525/elementa.2021.00032.t3

| Sample Type                      | Source                        | Statistic | Cd   | Co   | Cu   | Mn   | Ni   | Zn   |
|----------------------------------|-------------------------------|-----------|------|------|------|------|------|------|
| Snow                             | This study                    | Median    | 0.01 | 0.04 | 0.37 | 0.35 | 0.15 | 4.13 |
|                                  |                               | (n = 14)  |      |      |      |      |      |      |
|                                  |                               | Range     | <0.01–0.05 | 0.01–0.53 | 0.07–2.77 | 0.08–31.0 | 0.04–1.65 | 1.66–15.2 |
| Winter–spring sea ice (SIPEX-2)  | This study                    | Median    | 0.47 | <dl | 5.55 | 1.46 | 12.4 | 63.7 |
|                                  |                               | (n = 36)  |      |     |      |      |      |      |
|                                  |                               | Range     | 0.18–1.57 | <dl | 0.32–26.5 | 0.47–8.70 | 2.31–533 | 14.1–543 |
| Late spring sea ice (Davis)      | This study                    | Median    | 0.23 | 0.06 | 1.65 | 1.70 | 1.70 | 40.2 |
|                                  |                               | (n = 42)  |      |      |      |      |      |      |
|                                  |                               | Range     | 0.07–3.72 | 0.02–0.29 | 0.68–19.5 | 0.58–23.1 | 0.43–17.3 | 13.6–97.6 |
| Summer sea ice (Aurora Australis Voyage-2) | This study                    | Median    | 0.16 | 0.03 | 3.05 | 1.23 | 4.29 | 18.0 |
|                                  |                               | (n = 56)  |      |      |      |      |      |      |
|                                  |                               | Range     | 0.01–2.61 | 0.01–0.42 | 0.72–18.7 | 0.31–13.4 | 1.33–119 | 2.34–79.0 |
| Pack ice                         | This study                    | Median    | 0.37 | 0.03 | 3.49 | 1.40 | 6.24 | 34.4 |
|                                  |                               | (n = 74)  |      |      |      |      |      |      |
|                                  |                               | Range     | 0.04–2.61 | 0.01–0.16 | 0.32–19.7 | 0.47–13.4 | 0.46–533 | 2.34–543 |
| Fast ice                         | This study                    | Median    | 0.21 | 0.05 | 1.94 | 1.58 | 1.96 | 33.5 |
|                                  |                               | (n = 60)  |      |      |      |      |      |      |
|                                  |                               | Range     | 0.04–3.72 | 0.01–0.42 | 0.66–19.5 | 0.31–30.0 | 0.43–119 | 2.94–98.6 |
| Brine                            | This study                    | Median    | 0.73 | 0.11 | 3.26 | 1.42 | 14.9 | 7.92 |
|                                  |                               | (n = 10)  |      |      |      |      |      |      |
|                                  |                               | Range     | 0.05–1.91 | 0.01–2.89 | 1.07–18.8 | 0.64–4.49 | 11.1–17.9 | 1.56–65.7 |
| Under-ice seawater (0 m)         | This study                    | Median    | 0.28 | 0.06 | 2.01 | 2.22 | 6.25 | 12.0 |
|                                  |                               | (n = 14)  |      |      |      |      |      |      |
|                                  |                               | Range     | 0.23–2.06 | 0.02–0.20 | 1.34–4.95 | 0.74–13.0 | 3.13–7.12 | 3.78–40.0 |
| Seawater, Weddell/Scotia confluence (0–100 m) | Nolting et al., 1991       | Range     | 0.29–0.76 | na | 1.64–10.2 | na | na | na |
| Seawater, Weddell Sea (0–100 m)  | Westerlund and Ohman, 1991a; 1991b | Range     | 0.46–0.71 | 0.01–0.05 | 1.65–3.35 | 0.15–1.24 | 4.75–7.24 | 1.82–9.62 |
| Seawater, Atlantic sector (40–100 m) | Loscher et al., 1998       | Range     | 0.15–0.90 | na | na | na | na | na |
| Seawater, Atlantic sector (40–100 m) | Loscher, 1999              | Range     | na | na | 0.95–6.66 | na | 3.70–6.90 | 1.70–10.8 |
| Seawater, Atlantic sector (0–300 m) | Nolting and de Baar, 1994 | Range     | 0.17–0.95 | na | 1.53–6.44 | na | 3.07–10.4 | 1.38–14.0 |
| Seawater, Atlantic sector (0–100 m) | Ellwood et al., 2005       | Range     | na | <0.01–0.12 | na | na | na | na |

(continued)
Figure 6A), while DCd was weakly correlated with Chl a (0.47; P < 0.01). In pack ice, a tendency of an inverse correlation between DZn with both POC (–0.55; <0.01) and Chl a (–0.44; <0.05) was found (Figure 6B). Moderate correlations were observed between DMn and DCo (0.76; P < 0.01) in fast ice and between DCu and DNi in both fast (0.79; P < 0.01) and pack ice (0.78; P < 0.01). DCd, DCo, and DMn all correlated with macronutrient concentrations in fast ice to different degrees (0.41–0.88; P < 0.05; Figure 6A). Only DCd correlated with macronutrients for pack (Figure 6B) and both types of ice analyzed together: PO₄³⁻ (0.77; 0.88; P < 0.01), NO₃⁻ (0.58; 0.62; P < 0.01), and Si(OH)₄⁻ (0.54; 0.67; P < 0.01).

3.2. Particulate metal distributions
Median and range concentrations in snow (n = 14), pack ice (n = 68), fast ice (n = 38), brine (n = 10), and seawater (n = 14) are summarized in Table 5. Except for Cd, concentrations of particulate metals were all higher in sea ice compared to under-ice seawater (Table 5). Sack-hole brine concentrations of particulate metals were in general lower than bulk sea ice, whereas snow concentrations were

Table 3. (continued)

| Sample Type | Source | Statistic | Cd | Co | Cu | Mn | Ni | Zn |
| --- | --- | --- | --- | --- | --- | --- | --- | --- |
| Seawater, Atlantic sector (0–100 m) | Boye et al., 2012 | Range | ~0.60–0.80 | na | ~1.00–1.60 | ~0.30–0.60 | na | na |
| Seawater, Ross Sea (0–375 m) | Fitzwater et al., 2000 | Range | 0.04–0.73 | <0.01–0.04 | 1.23–2.16 | na | 4.78–6.88 | 0.24–5.17 |
| Seawater, Ross Sea (0–380 m) | Frache et al., 2001 | Range | 0.08–0.99 | na | 0.90–3.75 | na | na | na |
| Seawater, Ross Sea (0–380 m) | Grotti et al., 2001 | Range | na | na | 0.50–11.6 | 0.01–6.60 | na | na |
| Seawater, Ross Sea (0–100 m) | Corami et al., 2005 | Range | 0.34–0.86 | na | 0.43–3.30 | 0.33–1.20 | na | 2.20–8.20 |
| Seawater, Ross Sea (0–100 m) | Coale et al., 2005 | Range | na | na | na | na | na | 0.28–5.58 |
| Seawater, Australian sector (0–100 m) | Sedwick et al., 1997 | Range | na | na | na | ~0.1 | na | na |
| Seawater, Australian sector (0–100 m) | Lai et al., 2008 | Range | na | na | 1.04–2.96 | na | 2.20–7.90 | na |
| Seawater, Australian sector (40 m), Southern Ocean Iron RElease Experiment (SOIREE) | Frew et al., 2001 | Range | 0.25–0.27 | na | 1.20–1.40 | na | 6.20–6.30 | 2.30–2.4 |
| Seawater, Pacific sector (0–100 m) | Elwood, 2008 | Range | ~0.20–0.40 | ~0.02–0.04 | ~0.80–1.00 | na | ~4.00–5.00 | ~0.30–0.70 |
| Seawater, Pacific and Indian sector (0–100 m) | Janssen et al., 2020 | Range | ~0.20–0.70 | na | ~1.00–2.00 | na | ~5.50–6.50 | ~1.00–4.00 |

a Concentration of dissolved Co was below detection limit (dl) for SIPEX-2.
b Not available.
c Concentrations measured outside the SOIREE patch.

P < 0.01; Figure 6A), while DCd was weakly correlated with Chl a (0.47; P < 0.01). In pack ice, a tendency of an inverse correlation between DZn with both POC (~0.55; <0.01) and Chl a (~0.44; <0.05) was found (Figure 6B). Moderate correlations were observed between DMn and DCo (0.76; P < 0.01) in fast ice and between DCu and DNI in both fast (0.79; P < 0.01) and pack ice (0.78; P < 0.01). DCd, DCo, and DMn all correlated with macronutrient concentrations in fast ice to different degrees (0.41–0.88; P < 0.05; Figure 6A). Only DCd correlated with macronutrients for pack (Figure 6B) and both types of ice analyzed together: PO₄³⁻ (0.77; 0.88; P < 0.01), NO₃⁻ (0.58; 0.62; P < 0.01), and Si(OH)₄⁻ (0.54; 0.67; P < 0.01).

3.2. Particulate metal distributions
Median and range concentrations in snow (n = 14), pack ice (n = 68), fast ice (n = 38), brine (n = 10), and seawater (n = 14) are summarized in Table 5. Except for Cd, concentrations of particulate metals were all higher in sea ice compared to under-ice seawater (Table 5). Sack-hole brine concentrations of particulate metals were in general lower than bulk sea ice, whereas snow concentrations were
comparable to seawater (Table 5). In fast ice, particulate metals displayed an L-shaped distribution with basal ice concentrations generally greater than pack ice (Figure 3).

Table 4. Median enrichment index for dissolved metals in all sea-ice, by season (expedition), pack ice and fast ice. DOI: https://doi.org/10.1525/elementa.2021.00032.t4

| Sample Type                        | Dissolved Metal Enrichment Indexa | Cd  | Co  | Cu  | Mn  | Ni  | Zn  |
|-----------------------------------|-----------------------------------|-----|-----|-----|-----|-----|-----|
| All sea ice (n = 134)             | 3.3                               | 4.8 | 12  | 3.4 | 7.0 | 17  |
| Winter–spring sea ice (SIPEX-2; n = 36) | 3.1                               | —   | 15  | 3.2 | 6.8 | 11  |
| Summer sea ice (AAV2; n = 38)     | 3.9                               | 3.7 | 12  | 4.1 | 6.8 | 11  |
| Pack ice (n = 74)                 | 3.5                               | 3.7 | 13  | 3.4 | 9.1 | 18  |
| Fast ice (n = 60)                 | 6.1                               | 4.8 | 9.2 | 16  | 3.2 | 30  |

a Enrichment indices >1 indicate the degree to which the concentration of dissolved metal was higher in sea ice compared to underlying seawater relative to the salinity of each fraction (Equation 1).

b Concentration of dissolved Co was below detection limit for Sea Ice Physics and Ecosystem eXperiment-2.

Significantly higher concentrations of PAl, PCo, and PMn were found in fast ice \((P < 0.01)\) compared to pack ice, while PCu and particulate Ni (PNi) concentrations were higher in pack ice than fast ice \((P < 0.01)\). The PMe:PAl ratio was used to fingerprint the lithogenic contribution to the total particulate pool, with Al used here as the normalizing lithogenic element (Taylor and McLennan, 1985). Ratios of particulate Cd (PCd), PCu, PMn, and PNi relative to PAl were an order of magnitude higher in fast ice than in pack ice \((P < 0.01);\) Table 6.

Finally, evidence was obtained for a decrease of PCu, PNi, and particulate Zn (PZn) in summer sea ice (AAV2) compared to winter–spring sea ice (SIPEX-2; \(P < 0.01);\) Figure 4. Positive correlations between PAl and all particulate metals were observed in fast ice \((0.46–0.85; P < 0.01);\) Figure 6A. Positive correlations among particulate metals were more pronounced in pack ice \((P < 0.01);\) Figure 6A and B. Positive correlations between particulate metals and macronutrients also prevailed in pack ice. PCd correlated with Chl \(_a\) \((0.65; 0.66; P < 0.01);\) and POC \((0.47; 0.70; P < 0.01)\) for both fast and pack ice, respectively. In fast ice, moderate correlations between PZn and Chl \(_a\) \((0.68; P < 0.01)\) and between PCu, PMn, PNi, and POC \((0.69; 0.74; 0.78; P < 0.01)\) were also observed.

Figure 3. Vertical profiles of dissolved and particulate metals. Profiles of dissolved (D, dark blue) and particulate (P, gray) metals are composed from the median concentration throughout sections of all pack ice and fast ice stations sampled during Sea Ice Physics and Ecosystem eXperiment-2 (SIPEX-2), Davis, and Aurora Australis Voyage-2 (AAV2). Solid and dashed lines represent pack ice and fast ice, respectively. Depth (%) in the y-axis refers to the percentage depth of a specific ice layer (relative to the total core length). DOI: https://doi.org/10.1525/elementa.2021.00032.f3
3.3. Particulate Me:P ratios in Antarctic pack ice

PMe:P ratios (phosphorus-normalized following the Redfield C:P ratio of 106:1; Redfield et al., 1963) were obtained from analyses of bulk particles in sea ice (Figure 7). Past studies on Fe distribution in sea ice showed an overwhelming lithogenic contribution originating from...
nearby continental sources in fast ice compared to pack ice (Lannuzel et al., 2014; Duprat et al., 2020). Our results on other particulate metals also suggest a high lithogenic contribution in fast ice particles. Therefore, for this analysis, fast ice stations were excluded. PMe:P ratios were higher for Cu, Mn, Ni, and Zn ($P < 0.01$; Table 7) in winter–spring (SIPEX-2) compared to summer (AAV2). Sea-ice values were also higher than previously reported for natural assemblages of marine diatoms under Fe-rich conditions. We also show the particulate Fe:P ratios obtained from published Fe data of the respective voyages studied here (Lannuzel et al., 2016a; Duprat et al., 2019; 2020) in an attempt to understand how the incorporation of Fe compares to other metals. Sea-ice particulate Fe:P ratios are at least an order of magnitude higher than values obtained from bulk particle studies of coastal and open ocean areas (4.6–31 mmol:mol; Twining and Baines, 2013) and about 2 orders of magnitude higher than the maximum Fe:P of 1.9 mmol:mol obtained for marine phytoplankton using synchrotron-based X-ray fluorescence (SXRF) in a Southern Ocean Fe-enrichment experiment (Twining et al., 2004). Our results point toward a generalized sea-ice metal abundance ranking of Fe >> Zn ≈ Ni ≈ Cu > Mn > Co ≈ Cd.

4. Discussion

4.1. Drivers of dissolved metal distributions

In this study, median dissolved metals concentrations in bulk sea-ice samples were of the same order of magnitude as the seawater just below. Values were generally in the upper range of concentrations measured in ice-free Antarctic surface (0–100 m) waters using trace metal rosette sampling methods (Table 3). The only exception was DZn, for which concentrations in our study were 3 times greater than the highest concentration reported for SO surface waters (approximately 12 nM; Nolting and de Baar, 1994). Based on these results and in agreement with previous findings (Lannuzel et al., 2011), sea-ice melt should not represent a major source of the dissolved fraction of these elements to surface waters, except for a DZn signal (Neff, 2002). Other mechanisms such as the advection of seawater masses which have interacted with the continental shelf are likely to have a greater impact than sea ice on the distribution of dissolved metals in East Antarctic surface waters.

The 3 campaigns generally showed comparable concentration ranges of dissolved metals (Table 3). This observation suggests low spatiotemporal variability in dissolved metals concentrations in sea ice. However, subtle differences emerge when fast ice and pack ice are compared. For example, DMn and DCo concentrations were significantly higher in fast ice than pack ice ($P < 0.01$). Considering the shallow bathymetry along the Antarctic coast, especially at the fast ice stations visited in our study (e.g., 20 m at Davis), sediments can represent a major source of metals to fast ice. Benthic inputs of dissolved Fe, Co, and Mn have been observed in highly productive coastal waters (Tappin et al., 1995), and water column profiles of DMn were also found to be closely correlated with those of DCo in sediment pore waters (Zhang et al, 2002). Results also show lower concentrations of DCd, DCu, DNi, and DZn in summer (AAV2) compared to winter–spring sea ice (SIPEX-2; Figure 4), which could suggest an overall faster removal than replenishment over time. It is plausible that when in equilibrium with the seawater, part of the dissolved metal fraction within brine channels is continually converted to particulate metal by the binding to exopolymeric substances (EPS) and uptake into cells. However, the absence of any substantial changes in the dissolved-to-total ratio between SIPEX-2 and AAV2 data (Figure 5) points toward a subtle balance between biological (e.g., autotrophic and heterotrophic uptake and remineralization), physical (e.g., brine drainage, precipitation), and chemical processes (e.g., adsorption to organic material, ligand-binding) in the sea-ice–brine matrix.

Finally, all metals analyzed here were enriched in sea ice relative to seawater when normalized to salinity (Table 4). We suggest that organic ligands, most likely EPS, are responsible for this enrichment in sea ice, as they can bind a wide range of metal cations due to their negatively charged surfaces (van der Merwe et al., 2009; Janssens et al., 2018). The high uronic acid content of EPS (Decho and Gutierrez, 2017) provides EPS with the ability to chemically complex and adsorb metals, leading us to suggest EPS as a prime pathway for organic matter and metal incorporation into newly forming sea ice. Several studies have assessed the binding potential of EPS for a range of metals in seawater (Gutierrez et al., 2008; Gutierrez et al., 2012; Hassler et al., 2011; Hassler et al., 2017). These studies shared similar levels of uronic acids (approximately 25%) in the EPS and predominantly DCu, DFe, and DZn as major associated metals (Nichols et al., 2005; Gutierrez et al., 2008; Gutierrez et al., 2012; Hassler et al., 2011). In the present study, DCu and DZn showed the highest EI (15 and 23, respectively, in winter sea ice; Table 4), which is close to the EI of 24 observed for Fe in newly formed Antarctic sea ice (Janssens et al., 2016). On the
Figure 6. Spearman’s Rank correlations between sea-ice salinity, dissolved and particulate metals, macronutrients, chlorophyll-α, and POC concentrations. Correlograms A and B show values for fast ice and pack ice samples, respectively. Positive and negative correlations are represented by the colors blue and red, respectively. The size of the circle is proportional to the correlation coefficient \( r \), and blank cells represent statistically insignificant values. Chla indicates chlorophyll-α; POC, particulate organic carbon; D, dissolved; and P, particulate. DOI: https://doi.org/10.1525/elementa.2021.00032.f6
Based on our EI results, metal enrichment in sea ice may be a function not only of their concentration in seawater but also their affinity to bind to organic ligands present in seawater or produced in situ in sea ice (Aslam et al., 2012; Genovese et al., 2018).

### 4.2. Drivers of particulate metal distributions

Positive correlations between particulate metals and PAl (Figure 6) suggest an input from continental sources such as ice-free land masses, sediments, and icebergs into sea ice (Grotti et al., 2001; Smith et al., 2007; Noble et al., 2013; Hawking et al., 2018). This lithogenic signal is most pronounced near the coast as evidenced by the lower PMe:PAl ratio (Table 6) and stronger correlations between metals and PAl (Figure 6) in fast ice compared to the predominantly biogenic pack ice particles. The proximity to coastal sources is suggested as the likely driver of the significantly higher concentrations of PMn and PCo in fast ice compared to pack ice, as previously suggested for Fe.

### Table 5. Median and range of particulate (>0.2 μm) metal concentrations in East-Antarctic snow, sea ice by season (expedition), pack ice, fast ice, brine, and under-ice seawater. DOI: https://doi.org/10.1525/elementa.2021.00032.15

| Sample Type                                      | Statistic | Cd     | Co     | Cu     | Mn     | Ni     | Zn    |
|-------------------------------------------------|-----------|--------|--------|--------|--------|--------|-------|
| Snow                                            | Median    | <0.01  | 0.02   | 0.09   | 0.73   | 0.07   | 1.40  |
| Range                                           |           | <0.01–0.01 | <0.01–1.27 | 0.03–11.5 | 0.09–66.6 | 0.01–11.2 | 0.17–16.0 |
| Winter–spring sea ice (SIPEX-2)                 | Median    | 0.01   | 0.04   | 2.60   | 0.65   | 4.22   | 12.4  |
| Range                                           |           | <0.01–0.25 | <0.12–0.23 | 0.01–70.4 | <0.01–5.11 | 0.01–195 | 0.01–158 |
| Late spring sea ice (Davis)                     | Median    | 0.02   | 0.75   | 0.29   | 0.16   | 0.18   | 7.54  |
| Range                                           |           | <0.01–2.53 | 0.02–6.62 | 0.03–14.2 | 0.01–15.6 | 0.02–7.46 | 2.37–168 |
| Summer sea ice (Aurora Australis Voyage-2)      | Median    | 0.03   | 0.03   | 1.01   | 0.82   | 1.12   | 1.85  |
| Range                                           |           | <0.01–2.77 | <0.01–2.36 | 0.11–4.48 | 0.08–113 | 0.17–8.48 | 1.28–73.4 |
| Pack ice                                        | Median    | 0.02   | 0.03   | 1.34   | 0.60   | 1.90   | 8.69  |
| Range                                           |           | <0.01–1.78 | <0.01–2.35 | 0.01–70.4 | <0.01–10.4 | <0.01–195 | 0.01–158 |
| Fast ice                                        | Median    | 0.02   | 0.46   | 0.83   | 0.39   | 0.33   | 7.21  |
| Range                                           |           | <0.01–2.77 | <0.01–2.35 | 0.01–70.4 | <0.01–10.4 | <0.01–195 | 0.01–158 |
| Brine                                           | Median    | 0.02   | 0.01   | 0.47   | 0.21   | 0.22   | 2.69  |
| Range                                           |           | 0.02–0.20 | <0.01–0.01 | 0.07–1.50 | 0.05–4.49 | 0.04–5.17 | 0.50–7.72 |
| Under-ice seawater (0 m)                        | Median    | 0.05   | 0.01   | 0.09   | 0.25   | 0.22   | 0.79  |
| Range                                           |           | 0.01–0.18 | <0.01–6.91 | 0.03–1.63 | 0.06–2.07 | 0.03–1.88 | 0.47–33.6 |

### Table 6. Median ratios of particulate (>0.2 μm) metal to particulate Al (PMe:PAl ratio; nM:nM) for pack ice, fast ice, and Earth’s upper crust. DOI: https://doi.org/10.1525/elementa.2021.00032.16

| Sample Type                                      | Median PMe:PAl Ratio (nM:nM) |
|-------------------------------------------------|------------------------------|
|                                                 | Cd     | Co     | Cu     | Mn     | Ni     | Zn     |
| Pack ice                                        | 0.0012 | 0.001  | 0.071  | 0.014  | 0.064  | 0.409  |
| Fast ice                                        | 0.0003 | 0.009  | 0.007  | 0.004  | 0.006  | 0.026  |
| Earth upper crusta                               | 0.0003 | 0.0002 | 0.0001 | 0.004  | 0.0003 | 0.0004 |

*a Composition of the upper continental crust revised from Taylor and McLennan (1985).*
This coastal signature is less clear, however, for other metals. For example, concentrations of Pcd and PZn were similar in fast ice and pack ice, while significantly lower PCu and PNi were observed in fast ice. A lower PCu in fast ice than pack ice was also observed by Lannuzel et al. (2011), suggesting that the physically mediated coastal supply may be masked by biological processes. This behavior could potentially apply to other metals that display nutrient-type profiles in the ocean (Cd, Ni, Zn), and for which the vertical profiles are driven by biological uptake at the surface and remineralization at depth (Bruland and Lohan, 2003).

Our data also reveal an interesting contrast between our fast ice particulate samples and those previously reported in the Ross Sea, where sedimentary supply of predominantly biogenic nature seems to dominate the sea-ice pool (Grotti et al., 2005; de Jong et al., 2013; Noble et al., 2013). In modern marine sediments, Mn is enriched relative to its crustal abundance (Calvert and Pedersen, 1996), and areas of shallow bathymetries, such as those dominating the Ross Sea, would contribute to the supply of authigenic Mn to sea ice (Section 4.4). On the other hand, PMe:PAL values close to crustal ratios indicate a highly lithogenic content in our fast ice samples. This observation could be explained by the proximity to sources of dust (Davis; Duprat et al., 2019) and glacial melt (AAV2; Duprat et al., 2020). In areas of higher dust and glacial influence, as exemplified by Davis and AAV2 fast ice, the expected lower bioavailability of lithogenic particles as well as lower abundance of Mn relative to other metals could potentially impact the biological productivity and microbial composition of such areas.

The concentration of particulate metals in sea ice results from the co-occurrence of physical and biological processes. Initial loading (frazil ice scavenging of suspended particles during sea-ice formation), replenishment (seawater percolation and/or meteoric deposition), and biological uptake can all contribute to the particulate pool. Temperature-driven brine drainage, ice ablation, and sloughing-off processes of ice algae and EPS drive the loss term (Meiners and Michel, 2017). Concentrations of particulate metals in brines were generally lower than bulk sea ice likely due to the retention of this fraction to ice-attached components in the brine channel network during sampling, as previously observed for Fe and macronutrients (Fripiat et al., 2017; Duprat et al., 2019). The fact that significantly lower bulk concentrations of PCu, PNi,

Figure 7. Bulk particulate metal to phosphorus ratios in pack ice. Range of particulate metal: phosphorus ratios obtained from the median value of winter (Sea Ice Physics and Ecosystem eXperiment-2 [SIPEX-2]) and summer (Aurora Australis Voyage-2) pack ice samples. Ratio values are log-transformed. DOI: https://doi.org/10.1525/elementa.2021.00032.f7

Table 7. Median ratios of particulate (>0.2 μm) metal to particulate phosphorus (Me:P ratio; mmol:mol) for pack ice stations, with published ratios of bulk particulate Me:P in Southern Ocean diatoms from Fe-limited and replete conditions for comparison. DOI: https://doi.org/10.1525/elementa.2021.00032.t7

| Sample Type                          | Cd   | Co   | Cu   | Fe*  | Mn   | Ni   | Zn   |
|--------------------------------------|------|------|------|------|------|------|------|
| All pack ice (n = 67)                | 0.06 | 0.19 | 3.6  | 140  | 2.2  | 6.1  | 61   |
| Winter–early spring pack ice (SIPEX-2, n = 36) | 0.05 | 0.26 | 17   | 540  | 4.6  | 17   | 91   |
| Summer pack ice (Aurora Australis Voyage-2, n = 31) | 0.07 | 0.10 | 1.2  | 73   | 1.5  | 1.7  | 28   |

Southern Ocean diatoms

Fe limited (<0.1 nM)* | 1.29 | 0.15 | 1.44 | –    | 1.7  | –    | 11.1 |
Fe replete (>0.5 nM)b | 0.36–0.41 | 0.02–0.10 | 0.45–0.60 | – | 0.53–0.70 | – | 2.14–2.91 |
Antarctic upwelling watersc | 0.07 | –    | 2.0  | –    | –    | 0.68 | 13.3 |

*Fe:P was calculated from published Fe results obtained during the respective voyages (Lannuzel et al., 2016; Duprat et al., 2019; Duprat et al., 2020).

b Bulk particulate values from a shipboard Fe-enrichment incubation experiment in the Antarctic Zone of the Pacific sector of the Southern Ocean (Cullen et al., 2003).

c Bulk particulate values from Antarctic upwelling waters with high dissolved metal concentrations (Collier and Edmond, 1984).
and PZn were found in summer (AAV2) compared to winter–spring (SIPEX-2; \( P < 0.01 \)) sea ice suggests that loss generally exceeds accumulation during the seasonal progression of melting for the suite of metals analyzed here (Figure 4). The lack of seasonal increase contrasts with previous findings for Fe, where PFe continuously accumulates in sea ice between winter and summer, despite sea-ice decay and brine drainage, to reach the highest concentrations in summer (approximately 110 nM; Duprat et al., 2020). This difference highlights the decoupling between the processes driving Fe and other metal distributions.

Finally, one common trend among particulate Co, Cu, Mn, Ni, and Zn is that they were up to an order of magnitude higher in bulk sea ice compared to the seawater below. Based on median depth-integrated values for both winter–spring and summer pack ice, an estimated 0.07 \( \mu \text{mol m}^{-2} \) Co, 1.8 \( \mu \text{mol m}^{-2} \) PCu, 1.4 \( \mu \text{mol m}^{-2} \) PMn, 3.1 \( \mu \text{mol m}^{-2} \) PNi, and 12.4 \( \mu \text{mol m}^{-2} \) PZn could be released from sea ice if all of the ice melted by the end of austral summer. Like Fe, both Mn and Co concentrations in the SO can be extremely low due to limited atmospheric input (Middag et al., 2011). If bioavailable within surface waters, this seasonal addition from sea ice could alleviate phytoplankton limitation, representing a coupled Fe-Mn-Co fertilization source (Noble et al., 2013; Duprat et al., 2020). In the surface mixed layer of the ocean, PMn can be photo-reduced to DMn(II) at a daily rate of 70% (Sunda and Huntsman, 1988; 1994). High rates of DCo regeneration from biogenic PCo have also been reported in the upper water column (Dulaquais et al., 2017). Light also reduces the rate of Mn oxidation and Co coprecipitation by inhibiting Mn-oxidizing bacteria, thereby favoring the partitioning of these metals into the dissolved phase (Sunda and Huntsman, 1988; Tagliabue et al., 2018). An increase in the DMn:PMn and DCo:PCo ratios from our summer pack ice samples (from 2.5 and 0.8) to their underlying seawater ratios (14.0 and 4.0, respectively) aligns with high rates of biogenic PMn and PCo dissolution in Antarctic surface waters and potential enhancement of their bioavailability.

4.3. Particulate metal stoichiometry in Antarctic sea ice

The analyses of individual cells, bulk particle assemblages and ratios of dissolved metals and macronutrients in the water column show that pelagic phytoplankton generally require metals as follows: Fe \( \approx \) Zn \( > \) Mn \( \approx \) Ni \( \approx \) Cu \( > \) Co \( \approx \) Cd, from most to least needed (Twining and Baines, 2013). Phosphorus-normalized Mn, Fe, Ni, and Zn ratios from bulk particulate material have also been shown to be significantly higher in diatoms (which dominate ice algal biomass) compared to other phytoplankton species (Twining et al., 2011). Sea ice imposes a unique regime, with steep gradients in light, salinity, temperature, and nutrient concentrations compared to seawater. One could therefore expect nutritional requirements between sea-ice algae and pelagic phytoplankton to differ, as suggested in the case of SiOH4 for diatoms (Lim et al., 2019). Based on calculated P-normalized particulate metals, we present a generalized metal stoichiometry for pack ice particulate matter: Fe \( > \) Zn \( > \) Ni \( \approx \) Cu \( \approx \) Mn \( > \) Co \( \approx \) Cd. Except for Cd, our results from pack ice suggest an overall higher sea-ice metal stoichiometry compared to seawater (Table 7).

However, this trend was only significant (\( P < 0.01 \); one-sample t-test) for the winter–spring dataset. It is possible that sea-ice algae could accumulate metals during early spring in preparation for more favorable conditions later in the season or in response to stimulation of the cell metabolism as environmental conditions improve (Twining et al., 2004; Miao et al., 2005; Baines et al., 2011; Marchetti et al., 2012). Another plausible explanation for the observed difference between our winter and summer data sets is that not the entire particulate fraction is expected to be associated with living sea-ice algae and their intracellular pool. A considerable amount of the particulate pool could be composed of detritus, normally enriched in winter sea ice, as well as authigenic oxides formed in situ.

The relative metal abundances in sea-ice particles reflect, to a certain degree, the sequence in the dissolved concentrations (Zn \( > \) Fe \( > \) Ni \( \approx \) Cu \( \approx \) Mn \( > \) Cd \( > \) Co). Procedural artifacts associated with the dissolution of the particulate phase during ice-core melting potentially could have skewed these relationships. That said, a disproportionate enrichment of PFe relative to other elements is observed. The concentration of PFe (approximately 110 nM; Duprat et al., 2020) is 5-fold higher than PZn (approximately 23 nM; this study). The sea-ice median particulate Fe:P of 140 mmol:mmol is almost 2 orders of magnitude higher than values reported for temperate marine diatoms (Twining and Barnes, 2013). Luxury uptake and storage amid excessive availability of Fe has been reported previously for diatoms in pelagic systems (Sunda and Huntsman, 1995b; Marchetti et al., 2006; Marchetti et al., 2009), and could also happen in sea ice. The high Fe:P found in our samples contrasts with the uniquely low Fe quota observed for marine phytoplankton isolated from the SO (Kustka et al., 2007; Strzepek et al., 2011). However, a high fraction of detrital Fe and extracellular Fe oxide formation contributing to such a large difference in our Fe:P results cannot be ruled out. Intracellular Fe uptake experiments by ice algae must be carried out to quantify if these Fe requirements are valid.

Elevated Ni:P and Cu:P relative to Mn:P were observed in winter–spring sea ice (Figure 7). Cu and Ni are quite soluble in seawater and their concentrations are likely dominated by biogenic particles (Twining et al., 2011). In eukaryotes, urease is the only characterized Ni-dependent function (Price and Morel, 1991; Mulrooney and Hausinger, 2003). The overall 6-fold higher Ni:P found in sea ice compared to oceanic particles could reflect the extremely high fraction of (pennate) diatoms found in sea ice (van Leeuwe et al., 2018). SXRF analyses showed Ni association with diatom opal frustules, bringing new evidence of its contribution to cellular quota (Twining et al., 2012). Sea-ice algae could also have developed alternative metabolic pathways allocating Cu, such as in the antioxidant enzyme SOD, to cope with the potentially toxic levels of dissolved inorganic species (Cu\(^{+} \)) (Wolfe-Simon et al., 2005; Peers and Price, 2006).
Finally, the particulate Cd:P ratios obtained for both the winter–spring and summer data sets were relatively low (Figure 7) and comparable to marine particles. Such low ratios could be due to the high concentration of DZn observed in sea ice, which potentially could inhibit DCd uptake (Sunda and Huntsman, 2000). Past studies in coastal waters showed that DZn strongly suppresses DCd uptake by diatoms (Sunda and Huntsman, 1998) and that the addition of Zn to incubations above background concentrations can suppress Cd uptake in productive waters, also decreasing phytoplankton Cd:P ratios compared to controls (Cullen and Sherrell, 2005). Therefore, our low particulate Cd:P ratio could result from the strong control exerted by dissolved inorganic Zn (Zn’) on the uptake of DCd by sea-ice algae.

4.4. Can metals regulate sea-ice productivity?
Metal availability has been shown to limit marine phytoplankton growth, therefore shaping the abundance and diversity of algal communities in a way that can influence both carbon and nitrogen cycles (Sunda, 2012). Because Co, Cu, Mn, Zn, and in the absence of Zn, Cd are cofactors of metalloenzymes that are essential for phytoplankton metabolism, these elements, along with Fe, have been hypothesized to control phytoplankton productivity in the SO (Hassler et al., 2012). In the sea-ice realm, however, approximately an order of magnitude higher levels of metals were found when bulk ice concentrations were normalized to the brine volume fraction (approximately 12%; inferred from the bulk ice salinity and temperature; Cox and Weeks, 1983). This finding suggests that the metal concentrations experienced by microorganisms within the brine channels, if the metals bioavailable, are unlikely to impose a direct limitation to sea-ice algae growth. On another hand, high concentrations could be toxic.

4.4.1. Zinc
In marine phytoplankton, quantitative requirements for Zn are similar to those for Mn (Sunda, 2012). An enrichment of \( P_{Zn} \) relative to \( P_{Mn} \) (ratio of 6.5) was previously observed for SO diatoms (Cullen et al., 2003) and is in alignment with our results in sea ice (\( P_{Zn}:P_{Mn} \) ratio = 4.7) where diatoms are expected to be the dominant taxonomic group (van Leeuwe et al., 2018). Continued production of biogenic silica during spring (Fripiat et al., 2017) could help to explain the seasonal decrease in DZn concentrations found in this study via a physiological mechanism connecting SiOH4 and DZn uptake (Ellwood, 2008). However, concentrations of DZn in sea ice remained consistently high (approximately 35 nM), well above the concentrations found to limit cultured diatom growth (0.44–1.51 nM; Koch et al., 2019). The abundance of DZn in sea ice potentially reflects the high levels of this element in the SO (>1 nM; Baars and Croot, 2011; Croot et al., 2011) as well as its high affinity for EPS (Gutierrez et al., 2012). Instead of being limiting, sea-ice Zn concentrations raise the question of toxicity if the Zn is not appreciably chelated (Miao et al., 2005). The inverse correlation found between DZn and both Chla and POC in pack ice supports this hypothesis (Figure 6B). Zinc toxicity can manifest in several ways, usually by affecting the assimilation of other bio-metals such as Cd, Co, and Mn (Sunda and Huntsman, 1996).

4.4.2. Cadmium and cobalt
Cadmium and Co uptake systems are downregulated at high Zn’ levels (Sunda, 2012). The high DZn concentrations found in sea ice could therefore repress intracellular transport of both elements and explain the low particulate Cd:P and Co:P ratios observed in our study (Sunda and Huntsman, 2000; Lane et al., 2008). Mounting evidence suggests that Co and Zn can replace one another metabolically in the enzyme carbonic anhydrase in eukaryotic species (Price and Morel, 1990; Sunda and Huntsman, 1995a; Lane and Morel, 2000; Saito and Goepfert, 2008), potentially minimizing the effect of Co limitation. Nevertheless, Co could still influence growth and species composition in the ice indirectly by limiting bacterial vitamin B12 production (Panzea et al., 2008). When experimentally combined with Fe, the Co-containing vitamin B12 enhanced phytoplankton growth and changed community composition relative to Fe additions alone (Bertrand et al., 2007; Bertrand et al., 2015). Hence, Co control on B12-auxotrophic algal growth in sea ice cannot be ruled out and could be particularly important in polar areas where the distribution of vitamin B12-producing cyanobacteria is drastically reduced (Saito and Moffett, 2002).

4.4.3. Manganese and copper
A recent study showed that Mn and Fe colimit the growth of the Antarctic diatom Chaetoceros debilis (Pausch et al., 2019). Using natural Antarctic seawater, Mn limitation was observed at concentrations of approximately 0.6 nM despite the addition of Fe (Pausch et al., 2019). Based on this observation, Mn does not seem to impose limitations on diatom physiology within the sea-ice environment, where concentrations of both median bulk ice and brine were generally above this threshold, even during summer. However, sea-ice algae may have higher Mn requirements than phytoplankton, as suggested for SiOH4 (Lim et al., 2019). On the other hand, in the absence of organic complexation, Cu can be toxic and preclude the growth of diatoms via competition between Cu and Mn for the cellular sites involved in Mn transport (Sunda et al., 1981; 1983). Copper can therefore antagonize Mn uptake.

In oceanic surface waters, most DMn is thought to be dominated by its photochemically reduced state Mn (II) (Sunda, 2012). This form of Mn is highly soluble and not appreciably bound to organic ligands (Sunda and Huntsman, 1994), which could facilitate algal uptake and assimilation. Recently, the observation of significant concentrations of soluble and potentially bioavailable Mn(III)-ligand complexes in oxygenated waters in the western North Atlantic has also prompted a reevaluation of Mn speciation (Oldham et al., 2017). On the contrary, Cu has a high affinity for organic ligands. Organically bound Cu is less bioavailable, and thus less toxic, than free Cu(II) (Sunda and Ferguson, 1983; Piotrowicz et al., 1984; Leal and Van den Berg, 1998; Buck and Bruland,
2005; Buck et al., 2007). The abundance of natural ligands in sea ice, as observed in the case of Fe (Genovese et al., 2018), could therefore potentially reduce Cu' availability and toxicity while not affecting Mn uptake (Sunda and Ferguson, 1983; Piotrowicz et al., 1984). Ultimately, a more conclusive answer on Mn limitation will largely depend on future work assessing concentrations of Cu' and Zn' and their potential toxicity to sea-ice algae.

4.5. Conceptual model of colimitation of macro- and micronutrients

Although light, Fe and Si are often considered to be the primary drivers of SO productivity (Hoffmann et al., 2007), other elements can also play an important role. Within the sea-ice environment, Fe availability can stimulate phytoplankton growth. Enhanced algal biomass could further stimulate bacterial growth, increasing vitamin B12 production, which can also boost algal growth (Bertrand et al., 2015). At the same time, Fe availability can increase the consumption of nitrogen and the maximum specific uptake rate of SiOH4 via an increase in the number of active Si transporters in the diatom cell membrane (De La Rocha et al., 2000; Franck et al., 2003; Brzezinski et al., 2005; Lim et al., 2019). Higher growth also demands a greater capability to photosynthesize and detoxify reactive oxygen species, thereby increasing the intracellular demand for Mn. Ultimately, at some point in this enhanchive cycle played by sea-ice algae and bacteria, the supply of inorganic sources of SiOH4 (e.g., in late spring; Lim cive cycle played by sea-ice algae and bacteria, the supply of Mn availability for Mn. Ultimately, at some point in this enhancive oxygen species, thereby increasing the intracellular demand for Mn. Ultimately, at some point in this enhanchive cycle played by sea-ice algae and bacteria, the supply of inorganic sources of SiOH4 (e.g., in late spring; Lim et al., 2019), NO\textsubscript{3} (e.g., during summer; Duprat et al., 2020), and Co (e.g., late summer; Bertrand et al., 2015) might become limiting. While this hypothesis still needs to be tested, if Mn uptake is antagonized by Cu' or Zn' activity, Mn limitation could occur before other nutrients.

5. Conclusion

The role, availability, and potential toxicity of metals, other than Fe, within sea ice, are still largely unexplored. Our results show a high enrichment of metals relative to seawater and a relatively low spatiotemporal variability of metal content in the sampled sea ice. These observations suggest that sea-ice metal availability is unlikely to limit algal growth. If present in the free ion forms, the high concentrations of DCu and DZn may be toxic to sea-ice algae. Ligands may alleviate this toxicity by complexation, but Cu'- and Zn-binding ligands have not yet been quantified in sea ice. Results for Fe suggest that EPS contributes largely to the organic ligand pool of sea ice. Further quantitative and qualitative assessments of kinetic processes between different metals and EPS would improve our understanding of their nutritional and potential toxicological effects on sea-ice algae. Finally, the late release of sea-ice particulate metals after complete melting could alleviate possible limitations (particularly of Mn and Co) for phytoplankton in the summer season.

Data accessibility statement

Full dataset supporting the analysis and conclusions presented can be accessed through the University of Tasmania Open Access Repository website [http://rdp.utas.edu.au/metadata/e580a176-10d7-4bf3-97f7-36978d50a2d]. DOI: https://dx.doi.org/10.25959/0122-cm10. Any other details of interest are available from the authors.

Supplemental files

The supplemental files for this article can be found as follows:

Table S1. Sea-ice physical and biogeochemical parameters. Temperature (°C), salinity, concentration of chlorophyll-a (Chla [μg L\textsuperscript{-1}]), particulate organic carbon (POC [μM]), nitrate + nitrite (NO\textsubscript{x} [μM]), phosphate (PO\textsubscript{4} \textsuperscript{3-} [μM]) and silicic acid (Si(OH) [μM]) in bulk sea ice for each section of all stations (Sample ID) encountered along the three field campaigns (Voyage) are listed.

Table S2. Bulk sea-ice concentrations of dissolved Me\textsubscript{x} (nM). Concentrations for each section of all stations (Sample ID) encountered along the three field campaigns (Voyage) are listed.

Table S3. Bulk sea-ice concentrations of particulate Me\textsubscript{x}. Concentrations for each section of all stations (Sample ID) encountered along the three field campaigns (Voyage) are listed.

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Competing interests

The authors have no competing interests to declare.

Author contributions

Led the conception and design of the study: DL.
Conducted the field work: DL, KMM.
Contributed to the sample analysis: LD, DL, PVdM, ATT.
Contributed to analysis and interpretation of data: LD, DL, PVdM, KMM.
Wrote this article with input from all authors: LD.
Approved the submitted version for publication: DL, KMM, PVdM, ATT.
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