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Sources of elevated heavy metal concentrations in sediments and benthic marine invertebrates of the western Antarctic Peninsula

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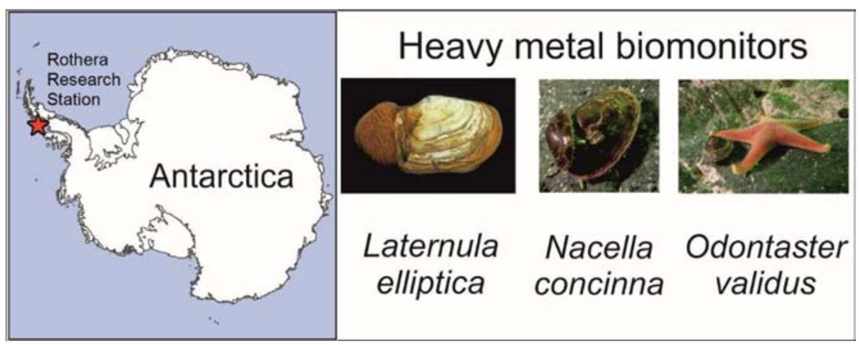
HIGHLIGHTS

- Antarctic research stations can be point sources for local marine pollution.
- Metals were analysed in sediments and tissues of three benthic biomonitor species.
- High metal concentrations were identified in the Antarctic marine benthos.
- Evidence of trace metal pollution from local anthropogenic sources was limited.
- Bedrock metals were released into the marine environment by glacial activity.

GRAPHICAL ABSTRACT



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ABSTRACT

Antarctica is one of the least anthropogenically-impacted areas of the world. Metal sources to the marine environment include localised activities of research stations and glacial meltwater containing metals of lithogenic origin. In this study, concentrations of nine metals (Cd, Co, Cr, Cu, Fe, Mn, Ni, Pb, Zn) were examined in three species of benthic invertebrates collected from four locations near Rothera Research Station on the western Antarctic Peninsula: *Laternula elliptica* (mudclam, filter feeder), *Nacella concinna* (limpet, grazer) and *Odontaster validus* (seastar, predator and scavenger). In addition, metals were evaluated in sediments at the same locations. Metal concentrations in different body tissues of invertebrates were equivalent to values recorded in industrialized non-polar sites and were attributed to natural sources including sediment input resulting from glacial erosion of local granodioritic rocks. Anthropogenic activities at Rothera Research Station appeared to have some impact on metal concentrations in the sampled invertebrates, with concentrations of several metals higher in *L. elliptica* near the runway and aircraft activities, but this was not a trend that was detected in the other species. Sediment analysis from two sites near the station showed lower metal concentrations than the control site 5 km distant and was attributed to differences in bedrock metal content. Differences in metal concentrations between organisms were attributed to feeding mechanisms and habitat, as well as depuration routes. *L. elliptica* kidneys showed significantly higher concentrations of eight metals, with some an order of magnitude greater than other organs, and the internal structure of *O. validus* had significantly higher Ni. This study supports previous assessments of *N. concinna* and *L. elliptica* as good biomonitors of metal concentrations and suggests *O. validus* as an additional biomonitor for use in future Antarctic metal monitoring programs.

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1. Introduction

By virtue of its geographic remoteness and short history of human occupation, Antarctica is one of the least anthropogenically polluted regions on Earth. In recent years however, evidence of pollutants such as microplastics (Reed et al., 2018), persistent organic pollutants (Kallenborn et al., 2016; Szopińska et al., 2019) and metals (Tuohy et al., 2015) occur from long-range transport as well as from local point sources. Heavy metals within the global environment have been increasing in concentration since the industrial revolution, and it is inevitable that metals are deposited in the Antarctic marine and terrestrial biospheres through atmospheric deposition and precipitation (Calace et al., 2017; Hur et al., 2007; Tuohy et al., 2015).

Increasing scientific and tourist activity around the continent have also enhanced any anthropogenic influences on the marine environment. Antarctica contains over 100 active scientific research stations and field camps (COMNAP, 2017) with human activities at some coastal stations having resulted in localised and occasionally severe contamination of terrestrial and marine environments (Aronson et al., 2011; Cabrita et al., 2017; Fryirs et al., 2015; Gröndahl et al., 2009; Kennicutt II et al., 1995). To determine the effects of these activities, an assessment of localised baseline metal concentrations must be established at sites of increased human activity, along with careful ongoing monitoring of metals in the surrounding environment to identify and assess anthropogenic perturbations (Ahn et al., 2002; Bargagli, 2000; Choi et al., 2003; Grotti et al., 2016; Lohan et al., 2001; Sanchez-Hernandez, 2000; Trevizani et al., 2018).

There are four possible sources of metals to the Antarctic marine environment: weathering, long range atmospheric transport and deposition, biological transportation (i.e. bird guano), and anthropogenic activities. Glacial movement and rock weathering release trace metals by eroding the underlying bedrock and transporting the released metals in both dissolved and particulate form in runoff streams (Badgeley et al., 2017; Green et al., 2005; Plouffe, 1998; Syvitski and Lewis, 1992). In contrast, metals originated from elsewhere on the globe are transported in the atmosphere, deposited in snowfall and incorporated into the glacial ice (Hur et al., 2007), where they are released upon melting and ice breakup. Seasonal variations in snow deposition and melt, as well as glacial sediment release and on-shelf transport of warmer upwelled water contributing to ice melt, may cause pulse events where high concentrations of metals are released into the marine environment (Annett et al., 2015; Hendry et al., 2010). Localised metal contamination can also be caused by seabird and penguin guanos (Chu et al., 2019). Anthropogenic activities with the potential to release metals have been identified in a wide range of spatial and temporal scales: long term small-scale impacts occur from scientific research stations, yet short-term but wide-ranging emissions occur from passing tourist vessels. Sewage outfalls, former waste disposal sites, aging station infrastructure, electric power generators, refueling operations and vehicular, aircraft and ship traffic generally constitute the dominant pollution pathways associated with human activities in Antarctica (Amaro et al., 2015; Bargagli, 2008; Hughes and Thompson, 2004; Stark et al., 2014; Tin et al., 2009). In 1991, the Protocol on Environmental Protection to the Antarctic Treaty (also known as the Madrid Protocol or Environmental Protocol; see: http://www.ats.aq/e/ep.htm) was ratified, which made monitoring of human impacts within the Treaty area a key principle (Hughes et al., 2011). In accordance with the Treaty, a number of research stations are now undertaking monitoring of metals within their research areas to establish a baseline against which the impact of long-term human habitation can be determined (Fryirs et al., 2015; Grotti et al., 2016; Majer et al., 2014; Palmer et al., 2006; Trevizani et al., 2016).

On release into the environment, metals dissolved within the water column are scavenged onto particles which can accumulate in marine sediments (Phillips and Rainbow, 1993), exposing benthic invertebrates to differing degrees based on their habitats and feeding strategies. Antarctic benthos are already subjected to extreme polar environmental conditions, often exhibit extremely slow growth rates during critical larval stages and have a narrow reproductive season relative to their lower latitude counterparts (Peck, 2016, 2018; Peck et al., 2006; Stark et al., 2003); as a result invertebrates may be highly sensitive to increasing metal concentrations within their surrounding environment, and populations may be extremely susceptible to high mortality during pollution events or near new point sources. Due to their ease of collection, relatively large size and representation of a number of benthic habitats, marine invertebrates have been used to monitor the magnitude and spatial extent of trace metal bioavailability in coastal waters and estuaries worldwide (Chiarelli and Roccheri, 2014; Phillips and Rainbow, 1993; Rainbow, 1985). In Antarctica, previous studies provided the first measurements of heavy metals within a number of benthic organisms, including algae, sponges, molluscs, echinoderms, nemerteans, annelids and marine vertebrates (De Moreno et al., 1997; Duquesne and Riddle, 2002; Negri et al., 2006). Molluscs, in particular, have been found to be excellent biomonitoring organisms, as they are capable of tolerating heavy metals at high concentrations and provide a time-integrated indication of metal bioavailability in the marine environment (Giusti et al., 1999; Hamed and Emara, 2006; Szefer et al., 2002). To this end, the filter-feeding bivalve *Laternula elliptica* has previously been recommended as an Antarctic biomonitoring organism by virtue of its wide distribution, large body size, high population density, strong metal accumulation tendency and sensitivity in reflecting varying ambient metal concentrations (Ahn et al., 1996; Duquesne and Riddle, 2002; Lohan et al., 2001; Negri et al., 2006). In recent years, the grazing limpet *Nacella concinna* has also been suggested as a potential candidate for trace metal biomonitoring, being relatively simple to collect due to its life-strategy of living on exposed surfaces and its wide-scale distribution around the Antarctic continent (Ahn et al., 2002, 2004; Suda et al., 2015; Weihe et al., 2010). A more complete picture of total trace metal bioavailability in a marine habitat may be gained if more than one bioindicating organism is studied, as these may reflect the bioavailability of metals to organisms from various habitats and with different feeding strategies and longevities (Langston et al., 1998; Phillips and Rainbow, 1993; Rainbow, 1995, 2002). Therefore, in addition to the two molluscs, the opportunistic seastar *Odontaster validus* is investigated for its potential as a biomonitor, given its ubiquitous Antarctic distribution and ease of collection.

The British Antarctic Survey's Rothera Research Station at Rothera Point, Ryder Bay, western Antarctic Peninsula (WAP), has been in operation since 1975, and is a logistics hub for regular ship and aircraft movements throughout the austral summer. Despite the long-term occupation of Rothera Station, limited information regarding concentrations of metals within Ryder Bay (from both natural and anthropogenic sources) is available. This study attempts to establish a baseline for sediment metal concentrations, and subsequently builds on the previous work of Lohan et al. (2001) to determine the suitability of three benthic invertebrates to act as bioindicator organisms in an ongoing metal monitoring study. The concentrations of Cd, Cr, Co, Cu, Fe, Mn, Ni, Pb, Zn were determined from sediment as well as different tissues of the seastar *Odontaster validus*, limpet *Nacella concinna* and clam *Laternula elliptica*. These organisms were selected to represent a variety of life and feeding strategies, living in nearshore and intertidal areas of four locations within Ryder Bay, in the vicinity of Rothera Research Station. We discuss the sources of metals within Ryder Bay, and the relative importance of feeding strategy and habitat in the three organisms, as well as assess the impact of Rothera Station on the surrounding environment. Finally, we assess each organism for its suitability in a future biomonitoring programme.

2. Materials and methods

2.1. Study area, sample collection and storage

Sample collection sites were in the vicinity of Rothera Research Station, Rothera Point, Adelaide Island, Antarctic Peninsula (67° 34′S, 68°

07′W; Fig. 1) in the austral summer of 2005–06 and 2011. Three locations for sample collection were selected in the immediate vicinity of Rothera Research Station and associated infrastructure (Hangar Cove, South Cove and Cheshire Island), while a control site (Lagoon Island) was selected 5 km away from the research station and upstream of the predominant water movement within Ryder Bay.

An initial surface sediment sample (top 2 cm) was collected from Hangar Cove in 2006 and stored in a ziplock bag (Grand, 2006). Following analysis of this initial sample, a more detailed assessment of sediment metal concentrations was undertaken in 2011; samples of 250 g sediment were isolated and collected in amber glass jars by divers using sediment cores. These samples were collected below 10 m depth from three stations around Rothera (Fig. 1): Hangar Cove ($n = 3$), Lagoon Island ($n = 1$) and South Cove (n = 1). The seabed around a fourth site, Cheshire Island, consisted predominantly of exposed rock and therefore divers were unable to collect sediment. All sediment samples were transported back to the UK frozen at −20 °C for subsequent analysis.

In the summer seasons of 2005 and 2006 individual specimens from the three selected species (details given in Table 1) were hand-collected by divers from between 10 m and 25 m depth. Individual organisms and the sediment sample were frozen immediately once returned to shore and were transported at −20 °C to the UK for further analysis.

2.2. Sample preparation and trace metal extraction

Prior to preparation of the samples for metal analysis, all equipment was acid-washed in 10% (v/v) HCl to prevent metal contamination, and all equipment and tools were metal-free wherever possible. The smaller sediment sample from 2006 (Grand, 2006) was sieved through a 2 mm nylon mesh before oven drying and crushing. Pseudo-total metal extraction was estimated using aqua-regia extraction using a modification of the procedure of Sastre et al. (2002): 0.5 g of dried sediment was mixed with 5 ml of a solution of 37% HCl: 70% HNO_3 (3:1). After 2 h at room temperature, this was digested at 95 °C for 2 h before filtering through a Whatmann 540 ashless filter and diluted to 50 ml with Milli-Q.

Sediments collected in 2011 were freeze-dried and crushed in the laboratory, and 1 g was weighed into 10 ml of aqua regia solution consisting of 37% HCl: 70% HNO_3 (3:1) in a 50 ml digitube. The tube was capped and agitated prior to processing in a DigiBlock digester at 110 °C for 90 min, followed by dilution to 50 ml with deionised water. Tubes were spun in a centrifuge at 1000 rpm for 10 min, and the supernatant was decanted into a Sarstedt tube prior to analysis.

Specimens of *O. validus*, *L. elliptica* and *N. concinna* were measured (length, width, height and arm length) and the wet weight determined prior to partial thawing at room temperature and dissection (*L. elliptica* and *O. validus*) to obtain sub-samples of several soft tissue types (Table 1) using trace metal clean techniques. Where organs were in close proximity, such as the digestive gland and gonad in *L. elliptica*, tissues on the boundary between the two organs were discarded. All organisms were within the normal size distributions for adults (McClintock et al., 1988), and thereby removed the necessity of analysing different size classes. After dissection, the isolated soft tissue types were re-frozen at −20 °C overnight before freeze-drying for 48 h, followed by grinding into a homogenous powder using an acid cleaned an agate pestle and mortar. Determination was made of the dry weight of each tissue sample (±1 mg) prior to metal extraction by microwave acid digestion. A known sample weight of approximately 0.2 g was weighed into a Teflon pressure vessel, where it was immediately treated with 4 ml of reagent grade concentrated nitric acid (37% w/w, Fisher Scientific) and 1 ml hydrogen peroxide (30% w/v, Fisher Scientific). Each pressure vessel was loosely capped in a fume hood for 24 h to allow cold digestion. Vessels were then tightly sealed and microwaved at 600 W for two 2-min periods, separated by a 10-min cooling window during which the vessels were unopened. Once digestion had completed, the vessels were allowed to cool for a minimum of 15 min, after which they were uncapped and the digested samples diluted to 25 ml total volume and stored in acid-washed low density polyethylene (LDPE) sample containers. Three procedural blanks were prepared for each 20 samples using the same microwave method as above but with no addition of ground tissue material.

2.3. Analysis

Sediments and digest solutions from *L. elliptica*, *N. concinna* and *O. validus* were analysed for nine metals (Cd, Cr, Co, Cu, Fe, Mn, Ni, Pb, Zn). From the 2006 samples, Cu, Fe, Mn and Zn were determined by flame atomic absorption spectroscopy (FAAS; 5 cm flame; SpectrAA 50, Varian, Oxford, U.K.) while Cd, Co, Ni and Pb were determined by

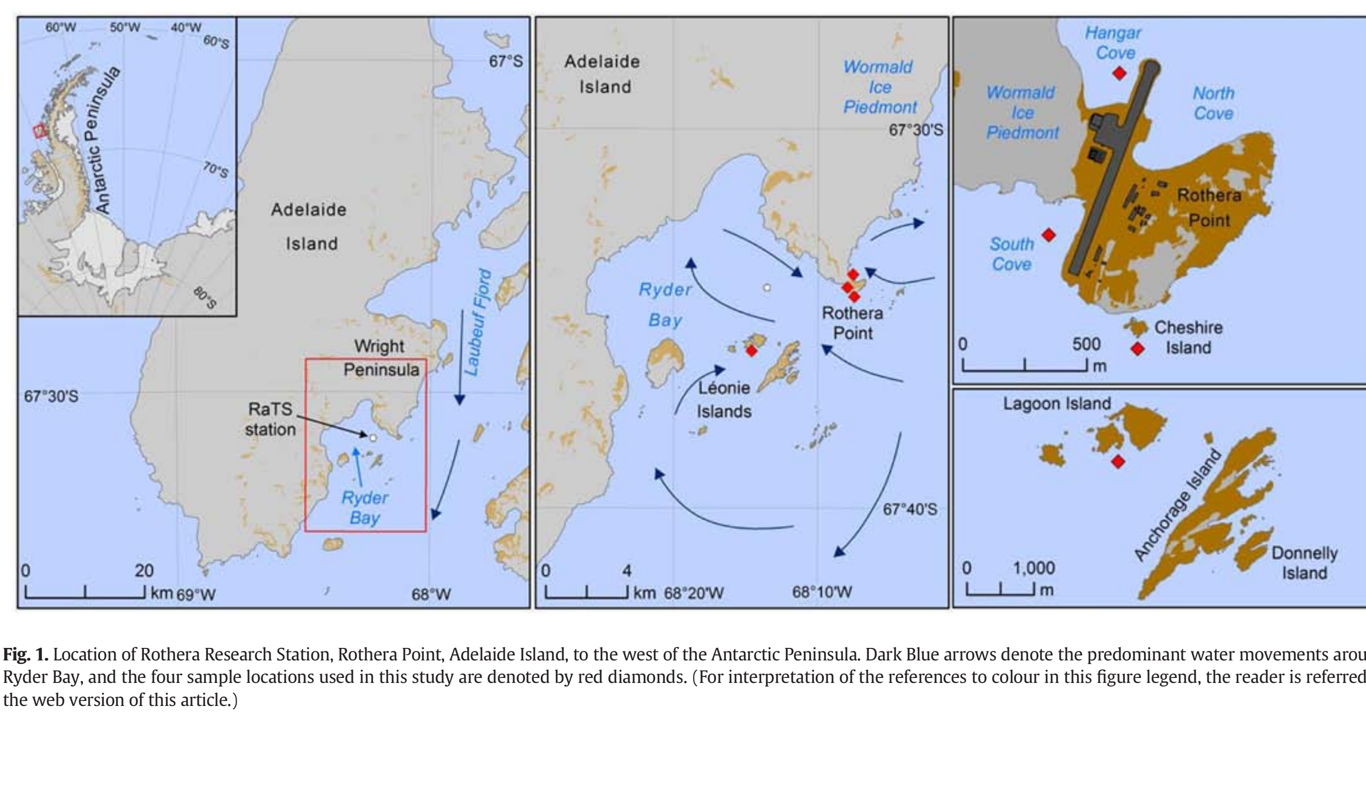


Fig. 1. Location of Rothera Research Station, Rothera Point, Adelaide Island, to the west of the Antarctic Peninsula. Dark Blue arrows denote the predominant water movements around Ryder Bay, and the four sample locations used in this study are denoted by red diamonds. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

Table 1
Life strategies, sample locations, number of samples analysed (n) and the body segmentation for the three benthic invertebrate species examined in this study.

Invertebrate	Location	Life strategy	Body size (mm) Range and mean ± standard deviation	Soft tissue type
Laternula elliptica	Lagoon Island ($n = 3$) South Cove ($n = 5$) Hangar Cove ($n = 5$)	Infaunal clam; filter feeder residing within soft sediments.	42–88 mm (mean = 62.5 ± 17.2 mm, $n = 13$)	Kidney Gill Digestive gland Mantle and siphon Gonad
Nacella concinna	Lagoon Island ($n = 10$) Cheshire Island ($n = 8$) South Cove ($n = 11$) Hangar Cove ($n = 11$)	Limpet; grazer on biofilms on solid substrates	18–33 mm (mean 23.7 ± 4.2 mm, $n = 38$)	Whole organism analysis
Odontaster validus	Lagoon Island ($n = 5$) Cheshire Island ($n = 5$) South Cove ($n = 5$) Hangar Cove ($n = 5$)	Seastar; omnivorous scavenger on mixed substrates	Disk diameter 25.1–43.6 (mean 35.7 ± 5.1 mm, $n = 20$)	Cardiac stomach Skeletal structure Gonad Digestive tract (pyloric stomach and pyloric caeca)

inductively coupled plasma mass spectrometry (ICP-MS; PlasmaQuad PQ 2 ± Turbo, Thermo Elemental, Cheshire, U.K.), finally Cr was measured by graphite furnace atomic absorption spectrometry (GFAAS; SIMAA 6000, Perkin Elmer). These analysis methods were determined as the most appropriate for each metal: Cu, Fe and Mn were too high for the more sensitive ICP-MS, whereas Cr on the ICP-MS suffered atomic interference. Prior to ICP-MS analyses, sample solutions were spiked with a 100 ppb Indium/Iridium internal standard. Mixed calibration standards were prepared in 2% HNO_3 by serial dilutions of 10,000 ppm commercial standards (AristaR Grade, BDH). Detection limits were calculated as three times the standard deviation of the blank samples analysed.

The sediment samples collected in 2011 (Hangar Cove $n = 3$, Lagoon Island $n = 1$ and South Cove n = 1) were analysed by ALcontrol Laboratories (Deeside, UK) using inductively coupled plasma optical emission spectrometry (Thermo Scientific iCap 6500 Duo ICP-OES). ICP-OES was determined as an appropriate instrument for analysis of all metals simultaneously, given the relatively high concentrations, but was not available in the analysis undertaken in 2006. The instrument was calibrated daily with a five-point calibration, using Analytical Quality Control (AQC) standards consisting of a mixture of 26 elements. Blanks were analysed every 20 samples. Samples were spiked with Indium as an internal standard.

The tissue samples were analysed by the same methods as the sediments collected in 2006: Cu, Fe, Mn (*N. concinna*) and Zn were determined by FAAS (5 cm flame; SpectrAA 50, Varian, Oxford, U.K.), Cd, Co, Ni and Pb by ICP-MS (PlasmaQuad PQ 2 ± Turbo, Thermo Elemental, Cheshire, U.K.), and Cr and Mn (*O. validus* and *L. elliptica*) by GFAAS (SIMAA 6000, Perkin Elmer).

2.4. Quality control

Certified Reference Material (CRM), an organic tissue (mussel tissue ERM-CE278; European Institute for Reference, Materials and Measurements) was analysed on two separate occasions ('batches') during the study, using the same microwave digestion techniques and processes as the tissue samples. Analysis of Cu, Fe and Mn was performed on FAAS, Cd, Co, Ni and Pb on ICP-MS and Cr on GFAAS. The analysis showed good agreement for the elements that were certified (Information on metal recoveries is given in Supplementary Table 2).

Sediment analysis was performed on ICP-OES at an ISO 17025 accredited laboratory using certified reference materials traceable to ISO Guide 34.

2.5. Statistics

Data were tested for normality and homogeneity using Kolmogorov-Smirnoff and Levene's tests respectively. Differences in the concentration of metals in different soft tissues and locations were tested using two-way Analysis of Variance (ANOVA) with associated Tukey's test. Since the number of specimens collected varied between locations, some samples were excluded at random to ensure a balanced statistical design. In cases where significant heteroscedasticity was detected ($p < 0.05$), non-parametric Mann-Whitney *U* tests were conducted instead of ANOVA.

To determine the influence of body size on metal concentrations, Pearson's Product Moment Correlation tests were performed on total dry weights and body size of individual organisms. Where significance was identified, differences were identified using Analysis of Covariance (ANCOVA). All statistical analysis was performed using SPSS 11.0 software and results were deemed significant at 95% confidence level.

3. Results

3.1. Sediment metal concentrations

Sediment samples from Hangar Cove, South Cove and Lagoon Island all had a grain size of 0.063–0.1 mm. Lagoon Island sediments showed the highest concentration of Cd, Co, Cr, Fe, Mn, Ni and Zn, whereas Cu was highest at South Cove and Pb highest at Hangar Cove (Table 2). Comparing sediments collected for this study in 2011 with those collected from Hangar Cove in 2006 (Grand, 2006) showed very similar concentrations of most metals except Cr, which increased from 2.9 ± 1.1 mg kg^{-1} to 11.6 ± 2.4 mg kg^{-1} and Pb, which increased from 2.4 ± 0.7 mg kg^{-1} to 5.0 ± 1.1 mg kg^{-1}.

3.2. Laternula elliptica

The mean shell length was 62.5 mm (± 4.8 mm standard error, $n = 13$), and mean total body wet weight was 26.8 g (+5.5 g standard error). *L. elliptica* kidneys showed significantly higher concentrations in seven out of nine analysed metals than in the other tissues examined (Fig. 2): Cd ($F = 28.4$, $p < 0.05$, df = 12), Co ($F = 14.3$, $p < 0.05$, df = 12), Fe ($F = 19.0$, $p < 0.05$, df = 12), Mn ($F = 21.5$, $p < 0.05$, df = 12), Ni ($F = 12.1$, $p < 0.05$, df = 12), Pb ($F = 74.0$, $p < 0.05$, df = 12) and Zn ($F = 10.6$, $p < 0.05$, df = 12). This was despite the kidney representing the smallest percentage of the total dry body weight of *L. elliptica* (2–5%). Variation between other tissue types was identified as insignificant, with the exception of Ni significantly higher in the gill ($F = 9.6$, $p < 0.05$, df = 12; 10.8 ± 8.0 mg kg^{-1}) compared to the gonad (5.13 ± 4.6 mg kg^{-1}), digestive gland (5.2 ± 1.7 mg kg^{-1}) and mantle (3.3 ± 1.4 mg kg^{-1}).

Shell length (as an indicator of organism age) was compared to the concentrations in each body tissue in turn, and while no positive correlations were identified, metal concentrations often decreased with increasing organism size (See Supplementary Table 3 for all correlation coefficients). Of particular interest, the gonad showed significant negative correlation ($p < 0.05$) with shell length with six out of nine metals

Table 2
Sediment heavy metal concentrations from three sites around Ryder Bay (mg kg^{-1}). Data from sediments at Northern hemisphere sites subjected to substantial human impact are also shown for comparison. Values are given in mg kg^{-1} dry weight (dw) and as either a range or mean and standard error.

	This Study			Grand (2006)	De Mora et al. (2004)	Langston et al. (1999)
	Sediment (< 0.1 mm) mg kg^{-1}			Sediment (<2 mm crushed) mg kg^{-1}	Sediment (<1 mm crushed) mg kg^{-1}	Sediment (<0.1 mm) mg kg^{-1}
	Hangar Cove ($n = 3$)	Lagoon Island ($n = 1$)	South Cove ($n = 1$)	Hangar Cove (n = 3)	Arabian Gulf Range (Mean)	Dogger Bank, North Sea Range (Mean)
Cd	0.3 ± 0.1	0.5	0.2	0.1 ± 0.02	0.02–0.21 (0.1)	0.15–0.28 (0.22)
Co	6.1 ± 1.3	10.1	7.1	4.7 ± 0.5	0.1–45.2 (4.1)	
Cr	11.6 ± 2.4	18.0	10.0	2.9 ± 0.1	3.4–303 (60.8)	27.3–42.6 (34.7)
Cu	19.6 ± 7.3	32.4	44.3	20.7 ± 2.3	0.60–48.3 (5.2)	7.1–11.4 (9.3)
Fe	16,300.0 ± 3567.9	26,300.0	14,900.0		305–29,600 (5284)	14,244–21,420 (17650)
Mn	211.7 ± 53.5	404.0	244.0	211.0 ± 5.0	13.2–360 (114)	259–495 (379)
Ni	5.8 ± 1.5	11.2	5.8	5.2 ± 0.8	0.74–1010 (71.5)	11.6–20.6 (16.5)
Pb	5.0 ± 1.1	4.8	4.8	2.4 ± 0.7	0.25–99.0 (7.0)	21.7–45.3 (32.3)
Zn	29.6 ± 8.6	54.3	31.1	33.8 ± 1.5	1.6–52.2 (12.0)	47.8–77.6 (63.6)

(Co, $r = -0.69$; Cr, $r = -0.60$; Cu, $r = -0.70$; Fe, $r = -0.64$; Ni, $r = -0.64$; Zn, $r = -0.73$), as did the mantle (Co, $r = -66$; Cr, $r = -0.57$; Cu, $r = -0.79$; Mn, $r = 0.67$; Ni, $r = -0.59$; Pb, $r = -0.48$). In contrast, the kidney showed no correlation with any metal except Fe, which decreased in concentration as shell length increased ($r = -0.64$).

Mean whole body concentrations of *L. elliptica* from Hangar Cove were identified as having higher concentrations of Co (F = 6.30, $p < 0.05$, df = 12), Cr (F = 9.05, $p < 0.05$, df = 12), Cu (F = 8.48, $p < 0.05$, df = 12), Fe (F = 4.86, $p < 0.05$, df = 12), and Ni (F = 6.17, $p < 0.05$, df = 12) compared to individuals from Lagoon Island and South Cove. No significant difference was identified between the latter two sites.

3.3. *Nacella concinna*

Mean whole body metal concentrations of *N. concinna* displayed considerable spatial variation (Table 3), and were generally higher at sites adjacent to Rothera Research Station. For example, significantly higher mean concentrations of Co (F = 21.3, $p < 0.05$, df = 34), Cu (F = 13.0, $p < 0.05$, df = 34), Fe (F = 20.6, $p < 0.05$, df = 34), Mn (F = 22.1, $p < 0.05$, df = 34) and Pb (F = 26.2, $p < 0.05$, df = 34) were observed at Hangar Cove (Table 3) compared to the other sites. Ni was the only metal which had the highest mean body concentrations significantly higher at Cheshire Island (F = 20.5, $p < 0.05$, df = 34). Lagoon island had significantly lower concentrations ($p < 0.05$) of all metals except Cr compared to the sites around Rothera Research Station.

The mean shell length of *N. concinna* was 23.7 mm (±0.7 mm standard error, $n = 40$). Although the limpets were larger at Lagoon island, no significant differences were identified in shell length between the four sample locations. No metals were positively correlated with increasing shell length, with Mn ($r = -0.36$), Ni ($r = -0.33$) and Zn ($r = -0.43$) showing significant negative correlation.

3.4. *Odontaster validus*

Of the range of metals investigated, no single body compartment of *O. validus* had consistently significantly higher concentrations in all metals (Fig. 3), suggesting that *O. validus* had no metal storage organ (compared with the kidney in *L. elliptica*). Instead, maximum concentrations of different metals were in different organs: the central digestive tract (CDT comprising the pyloric caeca and the pyloric stomach; Temara et al., 1997b) contained the highest concentrations of Fe (F = 40.5, $p < 0.05$, df = 17) and Zn (F = 19.2, $p < 0.05$, df = 17), the gonad the highest Cd (F = 4.24, $p < 0.05$, df = 17) and the cardiac stomach the highest Cr (F = 7.89, $p < 0.05$, df = 17) concentrations, averaged across all sites studied (Fig. 3). Significantly higher Ni (F = 150.8, $p < 0.05$, df = 39) concentrations were identified in the internal structure. No significant accumulation of Cu, Mn and Pb were identified in any tissue ($p > 0.05$). Significantly lower concentrations of Zn (F = 19.2, $p < 0.05$, df = 39) and Cr (F = 7.89, $p < 0.05$, df = 39) were identified in the calcified skeletal structure compared to the other tissues.

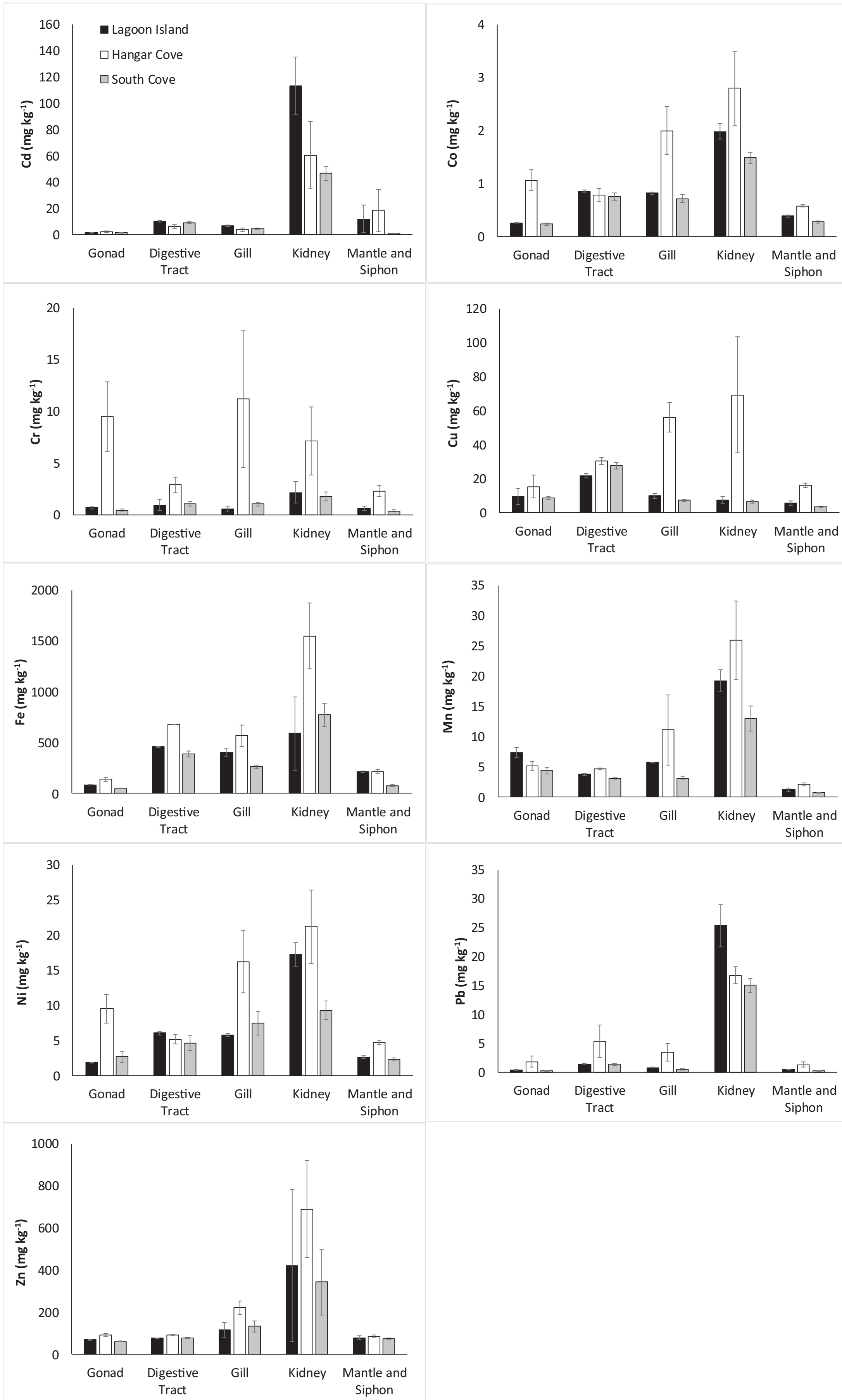
O. validus showed no positive correlation between body size (measured by disk diameter) and any metals; however negative correlation ($p < 0.05$) was identified between gonad size and Cd ($r = -0.61$), Co ($r = -0.57$), Cr ($r = -0.53$), Cu ($r = -0.50$), Fe ($r = -0.53$), Ni ($r = -0.57$) and Zn ($r = -0.62$). The wet weight of *O. validus* gonads, digestive gland and internal skeleton all increased in relation with disk diameter; however, the cardiac stomach showed little variation with body size (0.45 ± 0.18 g, $n = 20$). Of the four tissues studied, the gonad may be the only one that changes size significantly throughout the life history of the organism through spawning.

In general, little difference in metal concentrations was identified in *O. validus* tissues between the locations at Rothera Research Station (South Cove and Hangar Cove) and the control site at Lagoon Island. However, *O. validus* from Cheshire Island had significantly higher concentrations of Cd (F = 5.5, $p < 0.05$, df = 17), Co (F = 2.8, $p < 0.05$, df = 17) and Cu (F = 3.0, $p < 0.05$, df = 17) than the other three sites, in particular in the cardiac stomach and the gonad..

4. Discussion

4.1. Metal concentrations in Ryder Bay Benthos and comparison with other Antarctic sites

Variability in metal concentrations between the four locations showed different trends in *L. elliptica*, *N. concinna and O. validus*, but in general within each species higher metal concentrations were found towards the research station. Differences in metal bioaccumulation in comparing the three organisms for different metals resulted in additional variation between locations. *L. elliptica* showed significantly higher metal concentrations (Co, Cr, Cu, Fe, Ni) at Hangar Cove compared to both South Cove and at Lagoon island, very similar to *N. concinna* that had significantly higher concentrations of different metal combination (Co, Cu, Fe, Mn, Pb) at Hangar Cove compared to all other sites. In contrast, *O. validus*, showed much fewer differences between metals at the four sample sites, except for higher concentrations of Cd, Co, and Cu at Cheshire Island. Despite these differences between species, an overall a trend can be identified. The sites closest to the Research Station in general have higher metal concentrations in organisms than at Lagoon Island. These trends coincide with previous work of Lohan et al. (2001) in samples collected from Rothera seven years previously that identified higher concentrations of Cu, Fe, Mn, and Pb at the end of Rothera runway close to our sample location in Hangar Cove. However, on examination of Ryder Bay topography, the station


Lagoon Island
Hangar Cove
South Cove
Cd (mg kg-1)
Co (mg kg-1)
Cr (mg kg-1)
Cu (mg kg-1)
Fe (mg kg-1)
Mn (mg kg-1)
Ni (mg kg-1)
Pb (mg kg-1)
Zn (mg kg-1)
Gonad
Digestive Tract
Gill
Kidney
Mantle and Siphon

sites are also much closer to glacial sources of metal inputs (through the Wormald Ice Piedmont) compared to Lagoon Island that is further out within the bay (Fig. 1). It is therefore difficult to give a direct assessment of whether metal sources are anthropogenic or natural, and this will be discussed in later sections. Concentrations of metals within all three organisms are comparable with concentrations reported at King George Island (Ahn et al., 1996, 2002; De Moreno et al., 1997; Vodopivez et al., 2015; Weihe et al., 2010) and in *L. elliptica* and *O. validus* from Terra Nova Bay (Bargagli et al., 1996; Dalla Riva et al., 2004; Grotti et al., 2008; Nigro et al., 1997).

Differences in metal concentrations between species likely reflect differences in metal uptake, exposure, detoxification and depuration pathways, feeding habits, and habitat (Sanchez-Hernandez, 2000); differences in metal concentrations between individuals within a species can be affected by biotic parameters such as body size, sex, reproductive state, and age (Ahn et al., 2002; Phillips and Rainbow, 1993; Ramelow, 1985). This similar variation between species was also identified by De Moreno et al. (1997) in a much wider variety of invertebrate types. Indeed, it can be anticipated that these biotic processes have a greater influence on determining the metal concentrations in invertebrates in Ryder Bay: despite sediment analysis showing higher concentrations of Cd, Co, Cr, Fe, Mn, Ni, and Zn at Lagoon Island compared to the sites close to Rothera, overall metal concentrations in invertebrates at Lagoon Island were lower. Lagoon Island consists of a different underlying bedrock than Rothera Point and the areas underlying the glacial activity (Riley et al., 2011), but this localised high sediment metal burden is not reflected within the organisms living in that habitat. This implies bioaccumulation of metals originates from a source other than passive exposure in the habitat.

The three organisms studied include a sessile suspension feeder, a grazer, and an opportunistic scavenger/predator, and therefore metal concentrations within each organism can potentially be used to indicate the distribution of metals within the food web. While residing within the high concentrations of sediment-bound metals, individual *L. elliptica* showed significantly higher concentrations of Co, Cr, Cu, Fe, and Ni at Hangar Cove than at Lagoon Island or South Cove, despite Hangar Cove showing the lowest sediment concentrations of these metals. This observation suggests that *L. elliptica* accumulates metals from its diet rather than through passive exposure from both dissolved and particulate origin (faecal pellets, phyto and zoo-plankton, dead organisms; Dalla Riva et al., 2004; Duquesne and Riddle, 2002). Metal concentrations in the gill were not notably higher than the other organs, but while the gill may subsequently respond rapidly to pulses of marine metal input or contamination (Langston et al., 1998), metals will be rapidly passed on to the digestive gland. Indeed, the digestive gland has been shown to have higher metal concentrations than the gills and muscle in previous studies (Bargagli et al., 1996; Dalla Riva et al., 2004; Grotti et al., 2008). Similarly for *N. concinna*, the primary metal sources are likely to be the main food sources of biofilms and microphytobenthos (Brêthes et al., 1994; Pongratz and Heumann, 1999; Qiu et al., 2001), and indeed previous studies have found the highest concentrations of metals in the digestive glands and viscera of *N. concinna* (Ahn et al., 2004, 2002), rather than the foot that is directly exposed to the rock substratum. As an opportunistic scavenger with a long life-span (McClintock et al., 1988), *O. validus* is potentially the most suitable indicator of the wider food web metal distribution as it is exposed to metals through a range of food types. Given the digestive tract and cardiac stomach showed the highest concentrations of Fe, Zn, and Cr, these metals at least are likely to have been absorbed through feeding and not passive exposure. The seastar will feed on exposed *L. elliptica* (Philipp et al., 2011; Zamorano et al., 1986) and *N. concinna* (Mahon et al., 2003), as well as individuals damaged by ice scour in near-shore environments. As *O. validus* metal concentrations were rarely higher than those of the two molluscs, biomagnification was not indicated within the Ryder Bay food web for *O. validus*. Strong accumulation of Cd within the seastar was attributed to wide range of utilised food items and feeding behaviours and low predation pressure (Dalla Riva et al., 2004; De Moreno et al., 1997; Grotti et al., 2008).

Antarctic benthos are identified as being long-lived (decades) compared to similar species of temperate origin and have low growth and development rates (Brêthes et al., 1994; McClintock et al., 1988; Peck, 2016, 2018; Philipp et al., 2008). Therefore, Antarctic species that are subject to high concentrations of heavy metals over long periods and may accumulate them to a toxic level, unless mechanisms for long term metal storage or depuration exist. Evidence for metal detoxification pathways in all three species is shown in the metal to size relationships: increasing body size (shell length or disk diameter) is generally negatively correlated with metal concentration. In *L. elliptica*, the highest concentrations of Cd, Co, Cu, Fe, Mn, Ni, Pb and Zn were found in the kidney, which accounts for <5% of the dry body weight. This is very similar to previous metal studies in *L. elliptica*, both in Ryder Bay (Lohan et al., 2001) and King George Island (Ahn et al., 1996; Vodopivez et al., 2015). Metals are stored bound to metallothioneins in the kidney (Choi et al., 2001, 2003; Langston et al., 1998; Park et al., 2007), a process induced in particular by exposure to elevated Cd (Amiard et al., 2006; Park et al., 2007); however no significant correlation was found in this study between Cd and the other metals in the kidney of *L. elliptica*. A positive correlation was identified by Lohan et al. (2001) in *L. elliptica* from Ryder Bay, and it is suggested that the sample size of 13 *L. elliptica* individuals used in this study (maximum of 5 from each site) was insufficient to identify significant relationships and that a larger sample size is required in future biomonitoring studies. In addition, differences in tissue partitioning between metals needs further study.

Given the viscera (including the kidney) of *N. concinna* has been previously identified as having the highest metal concentrations (Ahn et al., 2002; De Moreno et al., 1997), it is likely that metal storage occurs in limpet kidneys, although individuals were too small in this study to accurately separate the kidney from other visceral organs. Although *O. validus*, unlike the molluscs, has no kidney, it is suggested that metallothionein-like proteins are used to bind heavy metals and prevent toxicity, similar to that seen in the temperate seastar *Asterias rubens* exposed to high Cd levels over long timescales (den Besten et al., 1989). All three organisms will also lose metals through the spawning process. A previous study by Ahn et al. (2002) showed that female *N. concinna* gonads contained higher levels of Zn, Cu, and Mn relative to male specimens. In the black mussel *Choromytilus meridionalis*, females had higher concentrations of Cu, Mn, Fe, and Zn than males prior to spawning, but no significant difference afterwards (Orren et al., 1980). This indicates that differences in metal concentrations between sexes would vary with the reproductive cycle, and might suggest a loss route for metal accumulation. Concentrations of Cd, Cr, Cu, Fe, and Zn were significantly higher in *A. rubens* pre-spawning compared to post-spawning (Temara et al., 1997b). It is known that *O. validus* gonad weight can more than double prior to winter spawning (Grange et al., 2007; Pearse, 1965; Stanwell-Smith and Clarke, 1998); gonads from this study comprised 7–42% of body weight. Loss of this volume could result in a significant proportion of total adult body metal burden being released annually; however, it is unlikely that eggs are released with a high, potentially damaging, metal burden. On this basis, it is clear that the metal loss pathway during spawning requires further study that was impossible within the boundaries of this investigation, but also that timing of reproductive cycles will be an important consideration in the planning of a biomonitoring programme.

In *O. validus* it was notable that Ni concentrations were over five times higher in the internal structure than the other organs, and 3–5

Fig. 2. Mean concentrations (mg kg^{-1} ± standard error) of a) Cd, b) Co, c) Cr, d) Cu, e) Fe, f) Mn, g) Ni, h) Pb and i) Zn in five soft tissues (gonad, digestive tract, gill, kidney, and mantle and siphon) from *L. elliptica*. Samples were collected from three sites in Ryder Bay, Antarctica: the control site Lagoon Island (black bars), Hangar Cove (white bars) and South Cove (grey bars).

Table 3
Comparison of heavy metal concentrations in *N. concinna* from Ryder Bay and those measured both in *N. concinna* from different areas of Antarctica, and in other limpets from around the world. Values are given in mg kg^{-1} dry weight (dw) and as either a range or mean and standard error.

Metal	This study				Ahn et al. (2002)	Li et al. (2009)	Dutton et al. (1973)	Bu-Olayan and Subrahmanyam (1997)
	Hangar Cove, Ryder Bay	South Cove, Ryder Bay	Cheshire Island, Ryder Bay	Lagoon Island, Ryder Bay	*N. concinna* King George Island	*Onchidium struma* Yangtze Estuary, China	*Patella vulgata*, North Sea	*Lunella coronatus*, Arabian Gulf
	Mean (mg kg^{-1} dw)	Mean (mg kg^{-1} dw)	Mean (mg kg^{-1} dw)	Mean (mg kg^{-1} dw)	Mean (mg kg^{-1} dw)	Mean (mg kg^{-1} dw)	Range (mg kg^{-1} dw)	Mean (mg kg^{-1} dw)
Cd	25.2 ± 2.1	17.9 ± 1.8	23.5 ± 2.9	14.9 ± 1.5	5.0 ± 1.6	2.2 ± 0.3	2.9–7.1	
Co	2.9 ± 0.2	1.8 ± 0.1	1.6 ± 0.1	1.0 ± 0.1				
Cr	1.6 ± 0.2	2.1 ± 0.4	6.1 ± 1.1	6.1 ± 2.4	2.2 ± 0.6	7.2 ± 1.1		
Cu	15.6 ± 0.7	7.6 ± 1.2	6.5 ± 1.8	4.7 ± 1.3	27.6 ± 5.4	155.5 ± 22.3	6.9–13	55.0 ± 11.2
Fe	2866 ± 235	2015 ± 99	1048 ± 161	1129 ± 156	3133 ± 665	9.5 ± 1.1	1600–2700	
Mn	41.9 ± 2.6	29.0 ± 2.5	23.3 ± 4.7	8.8 ± 0.8	58.5 ± 15.4	1.9 ± 0.4	15–62	
Ni	5.9 ± 0.3	4.4 ± 0.4	8.4 ± 0.9	2.8 ± 0.2			4.5–14	17.0 ± 15.3
Pb	2.2 ± 0.2	1.3 ± 0.1	1.0 ± 0.2	0.5 ± 0.0	1.4 ± 0.4	1.0 ± 0.1	1.5–9.3	0.57 ± 0.37
Zn	82.6 ± 2.8	78.9 ± 3.3	81.1 ± 5.3	61.2 ± 2.3	69.9 ± 7.7	26.1 ± 3.6	94–140	486.6 ± 28.9

times higher than the mean concentrations in *L. elliptica* and *N. concinna*. This calcified structure is the rigid basis of the water vascular system, and is the support for the arms. Nickel has a known affinity for calcite (Hoffmann and Stipp, 2001), allowing the internal skeleton to act as a Ni sink; Ni concentrations were equally high across all locations, and therefore this is unlikely to be evidence of point-source contamination. Although at smaller scales than Ni, Pb also showed accumulation in the internal structure of *O. validus* from Cheshire Island, as also seen in *A. rubens* from the North Sea (Temara et al., 1997a, 1998). Mean body concentrations of Pb in *N. concinna* were also elevated at Cheshire Island. All calcified shell material in *L. elliptica* and *N. concinna* was removed during dissection, so it remains to be seen if the shells also accumulate Ni and Pb.

4.2. Sources of metals in Ryder Bay

4.2.1. Natural inputs

Nearshore seawater salinity and temperature vary greatly in the Antarctic due to freshwater inputs from melting sea ice and increased glacial runoff in the spring and summer (Ahn et al., 2004; Annett et al., 2015; Grotti et al., 2001). This glacial runoff is rich in dissolved minerals and metals originating from the scouring of underlying bedrock (Badgeley et al., 2017; Green et al., 2005) as well as released from glacial ice after snow deposition (Hur et al., 2007). The bedrock of Rothera Point, including Cheshire Island, and much of the rest of Ryder Bay, is predominately granodiorite, a highly metalliferous rock type (Brimhall et al., 1988), and therefore likely to comprise the dominant component in rock flour deposited into the marine environment by glacial action, while Lagoon Island is comprised of basaltic breccias and lava (Riley et al., 2011), and is unaffected by glacial action. Sediments from all three locations were within the same size fraction, and therefore could be directly compared, and showed very similar concentrations to samples collected 6 years previously at the same time as the invertebrates were collected (Grand, 2006). The average metal concentrations in the sediment analysis lie within the range that is considered typical of areas unaffected by anthropogenic activities in Antarctica (Alam and Sadiq, 1993; Ciaralli et al., 1998).

Water movement in Ryder Bay shows open exchange with the larger Marguerite Bay, and upwelling of nutrients, including dissolved metals, occurs at times from the Antarctic Circumpolar Current (ACC) flooding onto the continental shelf along the length of the Antarctic Peninsula. The principle water movement enters the south side of Ryder Bay flowing west past Lagoon Island and the Sheldon Glacier before turning north at the head of the bay and then passing out of the bay flowing east to the south of Rothera Point (Fig. 1; Clarke et al., 2008; Wallace et al., 2008). Ryder Bay glacial runoff is therefore, dominated by the Sheldon Glacier, and in addition, both Hangar Cove and South Cove are influenced directly by the Wormald Ice Piedmont (Davenport, 2001), with water residence times likely to be long due to the runway at Rothera Research Station limiting water movement (Fig. 1). As a result of this water circulation, the glacial runoff may have a greater impact at those station locations compared to the Lagoon Island control site. Indeed, both *L. elliptica* and *N. concinna* were elevated in several metals at Hangar Cove. Different bedrock composition at Lagoon Island may also contribute to the generally higher metal concentrations identified at Lagoon Island compared with the other locations. Annett et al. (2015) showed that within Ryder Bay, Fe inputs from glacial sources dominated the summer dissolved Fe input (3.5–9.4 nM), providing Fe for development of the spring and summer phytoplankton production, and subsequently significant food sources for *L. elliptica* and *N. concinna*. To investigate the relationship with glacial Fe a little further, metal concentrations within the three organisms were correlated with Fe. In *L. elliptica*, all other metals showed significant positive correlations with Fe; in *N. concinna* it was correlated with six other metals (Cd, Co, Cu, Mn, Pb, and Zn); and in *O. validus* with three metals (Cr, Ni, and Zn; see supplementary Table 6 for all correlation coefficients). Fig. 4 gives examples of the most interesting of these correlations, and shows the varying responses of *L. elliptica* and *N. concinna* likely due to their different depuration pathways and metal storage methods. *O. validus* shows significant negative correlation between Fe and Ni as a result of the accumulation of Ni in the internal structure, but shows only positive correlation between Fe, Zn and Cr. This response of fewer metals in *O. validus* to Fe concentrations is another result of its varied diet and higher trophic level, compared with the phytoplanktivorous *L. elliptica* and the surface biofilm consuming *N. concinna* which will respond rapidly to changes in algal metal uptake. On King George Island, the influence of glacial meltwater inputs of heavy metals on *N. concinna* was demonstrated by Ahn et al. (2004) that suggests the increasing metal concentrations in limpets collected near the Rothera Research Station is likely associated with glacial runoff. Husmann et al. (2012) did not associate higher tissue metal concentrations directly with increased particulate material expected of glacial runoff, and this could explain why *L. elliptica* individuals collected at Lagoon Island did not show universally lower metal concentrations compared to sites near Rothera Research Station.

4.2.2. Anthropogenic input

Metal concentrations in surface sediments suggest minimal anthropogenic signal at sampling sites close to Rothera Research Station, as Lagoon Island showed the highest sediment concentrations for all metals except Cu at South Cove and Pb at Hangar Cove. Of all the locations around Rothera Point, Hangar Cove was proposed as the site most likely to exhibit metal contamination, if present, due to the close proximity of current aircraft activities and fuel storage. In marine and aquatic environments, metals are known to associate preferentially with suspended particulate material rather than remaining in solution (Phillips and Rainbow, 1993), and settlement of particulates into sediments can provide a long term integrated metal concentration which would highlight long term low-level contamination.

L. elliptica concentrations followed closely with the previous study of Lohan et al. (2001) in Ryder Bay, except that this study found no evidence of elevated Cu concentrations (>800 mg kg^{-1} dw) identified in *L. elliptica* digestive glands collected from the end of Rothera Runway in that study. These high concentrations were suggested to be caused by a contamination event from Rothera Station, given the proximity to aircraft activities. Hangar Cove is located close to the end of the runway, and spatial differences may be apparently between the *L. elliptica* included in this study and those from Lohan et al. (2001). In the present work, Cu was elevated in the gill and kidney of Hangar cove, but at lower concentrations than that of Lohan et al. (2001) (up to 202 mg kg^{-1} dw), and the digestive gland concentration was not higher than the other sites. It is suggested that given the seven years elapsed between the sample collections, *L. elliptica* that survived the contamination event processed excess Cu in the kidney; however, the significantly higher concentration of Co and Ni in *L. elliptica* in Hangar Cove combined with the Cu suggest low-level anthropogenic impact. This finding is reinforced by the trend of *N. concinna* being higher in some metals at Hangar Cove compared to South Cove and Cheshire Island. Hangar Cove has limited in water movement, and any potential contamination might not be flushed from the area as rapidly as at an exposed site such as Cheshire Island.

As a result, little evidence was found to suggest that current or past activities at Rothera Research Station are substantially increasing metal concentrations above background levels. Trace metal contamination has been detected in the vicinity of Antarctic research stations in the past (e.g. Kennicutt II et al., 1995; Santos et al., 2005; Snape et al., 2001) and it is possible that any low-level contamination from Rothera Research Station may be masked by high natural background levels.

4.3. Comparison with non-polar locations

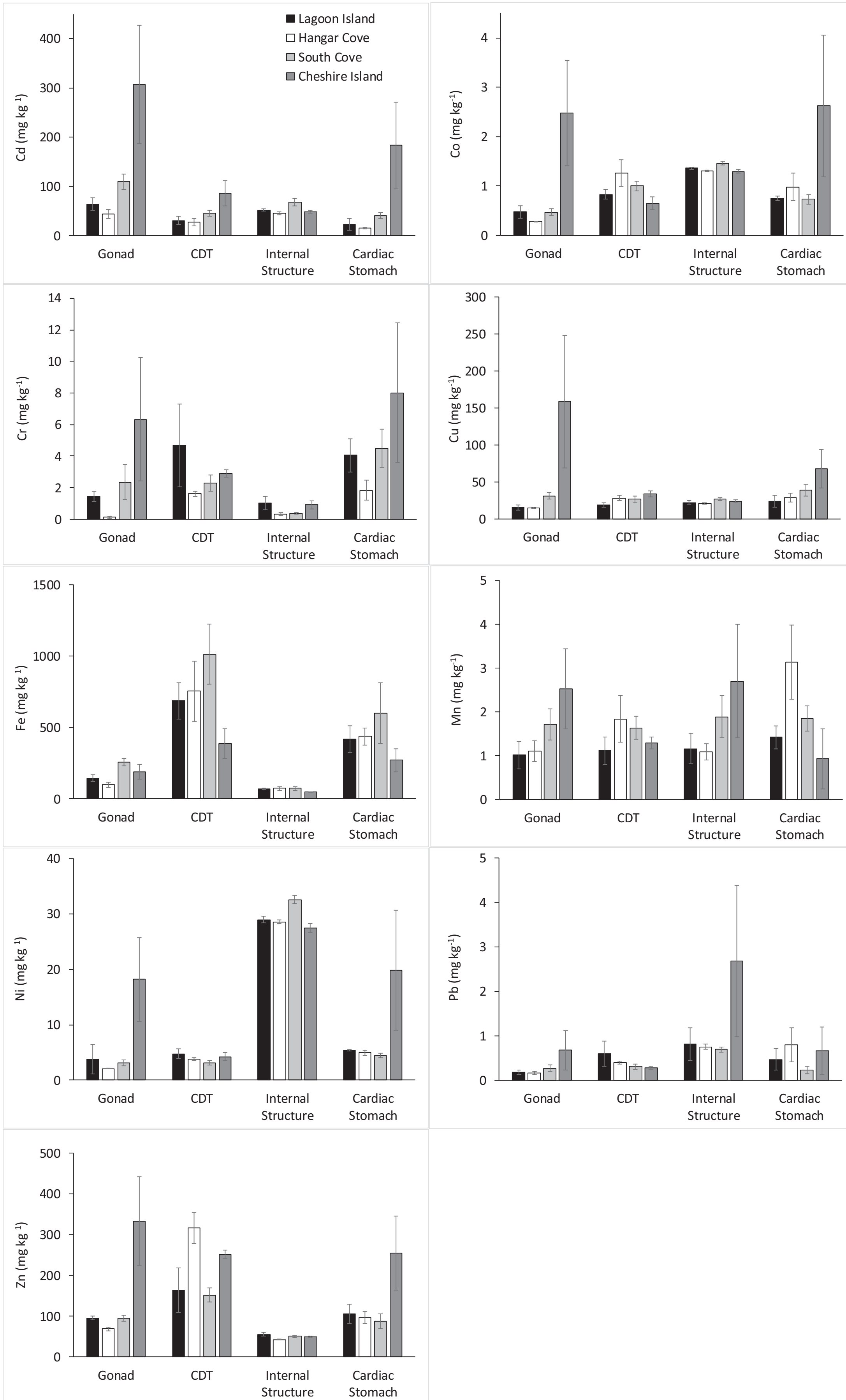
Despite the low level of human activity in Ryder Bay relative to other more industrialized areas of the world, sediment metal concentrations were within the same order of magnitude as non-polar sites impacted by a range of industrial activities, e.g., the Yangtze River Estuary (Li et al., 2009), the Gulf of Persia (De Mora et al., 2004) and the North Sea (Langston et al., 1999) (Table 2). Cadmium levels in *N. concinna*, *L. elliptica* and *O. validus* were elevated compared to temperate sites (Dutton et al., 1973; Fung et al., 2004; Li et al., 2009; Temara et al., 1997b), and were also higher than measured in other Antarctic sites (Ahn et al., 1996, 2002; De Moreno et al., 1997; Grotti et al., 2008). Cadmium elevation in marine biota has been previously reported around the Antarctic continent (Honda et al., 1987), and indeed both De Moreno et al. (1997) and Grotti et al. (2008) identified *O. validus* as bioaccumulating Cd. In this study, we found no evidence that *O. validus* was storing Cd to a greater extent than *L. elliptica* or *N. concinna*, but concentrations were 2–3 orders of magnitude higher than observed in *Asterias rubens* in the North Sea (Danis et al., 2004; Temara et al., 1997b). High Cd concentrations in the Antarctic are generally attributed to the transport of upper circumpolar deep water (CDW) onto the WAP shelf (Ahn et al., 1996, 2004; Bargagli et al., 1996; Martinson and McKee, 2012; Sanchez-Hernandez, 2000). Indeed, Annett et al. (2015) identified modified CDW as a significant source of dissolved Fe and other dissolved metals into Ryder Bay on a consistent basis through winter mixing (Annett et al., 2017). Surface water Cd concentrations in Ryder Bay (up to 0.1 μg l^{-1}; Bown et al., 2017) were equivalent to those in the Weddell Sea that is located on the eastern side of the Antarctic Peninsula (0.06–0.1 μg l^{-1}), and significantly higher than those in the North Sea (0.02 μg l^{-1}; Kahle and Zauke, 2003; Nolting and De Baar, 1994). Given the lack of global pollution affecting Antarctic Cd distribution (Sanchez-Hernandez, 2000), the observed levels in invertebrates in Ryder Bay are likely to originate from biomagnification from high algal background levels. It is likely, therefore, that the Cd elevation seen in this study is characteristic of the Antarctic environment rather than resulting from anthropogenic influence.

For the remaining metals, whole body concentrations of Cr, Cu, Fe, Mn, Pb, and Zn within three different bivalve bioindicators (*Meretrix meretrix*, Alyahya et al., 2011; *Ruditapes philippinarum*, Fung et al., 2004; *Mytilus edulis*, Herut et al., 1999) fell within the range of *L. elliptica* gill, mantle, gonad and digestive gland tissues, but were notably lower than the kidney concentrations. Metal concentrations from *L. elliptica* in Ryder Bay are therefore comparable to those found in shorter-lived bivalves from more polluted temperate sites. Similarly, Cr, Cu, Mn, Ni, Pb, and Zn in *N. concinna* were considered equivalent to levels found in limpets from more polluted Northern Hemisphere locations, i.e. in the Yangtze river (Li et al., 2009), the Arabian Gulf (Bu-Olayan and Subrahmanyam, 1997) and the North Sea (Dutton et al., 1973; Herut et al., 1999) (Table 3). The greater longevity of Antarctic species allows for longer periods of bioaccumulation, in addition to the exposure to high natural metal concentrations.

Concentrations of Cu and Fe in *O. validus* were notably higher in Ryder Bay, compared to concentrations identified in *Asterias rubens* in the Netherlands, but those of Cr, Pb, and Zn were of the same order of magnitude (Danis et al., 2004; Temara et al., 1997b). Similar trends were identified in comparison with *Luidia clathrata*, a sub-tropical seastar from the Gulf of Mexico (Lawrence et al., 1993) and the echinoid *Diadema setosum* from Singapore (Flammang et al., 1997): Cr, Pb, and Zn concentrations were all within similar ranges to those in *O. validus*, but Cd and Cu were higher by at least one order of magnitude. Given that total metal extractions from Ryder Bay sediments were within similar orders of magnitude for Cd, Cu and Fe, it implies that *O. validus* accumulates these metals to a greater degree over the course of its longer lifespan than the temperate seastars.

4.4. Comparison of the three species as biomonitors

Both *N. concinna* and *L. elliptica* have been suggested before as biomonitors in the Antarctic (Ahn et al., 1996, 2004; Suda et al., 2015; Vodopivez et al., 2015), and while *N. concinna* is easy to collect in the near shore environment, *L. elliptica* is time-consuming to collect from sediments due to its prolific burrowing ability (Peck et al., 2004), and indeed this study was limited by the number of *L. elliptica* available at each site (3–5 individuals) due to collection difficulty. Species must have several characteristics to be good trace metal biomonitoring organisms, i.e. they are relatively sedentary, abundant, easy to collect, identify and transport, are large enough for analysis, and accumulate metals in concentrations high enough for detection when they are present (Rainbow and Phillips, 1993). *Laternula elliptica* and *N. concinna* meet many of these requirements (Ahn et al., 1996, 2002); however, *N. concinna* individuals in this study were too small to adequately dissect into different soft tissues and so whole-body concentrations were used instead. As a surface-sediment dweller and ubiquitous in the Antarctic marine environment (McClintock et al., 1988), *O. validus* also meets many of these requirements: i.e., it is generally of large enough size for ease of dissection and organ identification, shows high abundance at depths down to c. 200 m, and has a circumpolar distribution around the Antarctic continent and surrounding land-masses (McClintock et al., 1988). It is also easily collected by divers from the nearshore to deep waters, and with large numbers living on hard substrata gives the chance to compare food webs from soft and hard substratum communities. In a study by Grotti et al. (2008), concentrations of most metals in a digested arm of *O. validus* were equivalent to those of the different body tissues isolated here. However, digestion of a whole arm instead of separation into individual tissue components did not detect elevated Ni in the internal


Lagoon Island
Hangar Cove
South Cove
Cheshire Island
Cd (mg kg-1)
Co (mg kg-1)
Cr (mg kg-1)
Cu (mg kg-1)
Fe (mg kg-1)
Mn (mg kg-1)
Ni (mg kg-1)
Pb (mg kg-1)
Zn (mg kg-1)
Gonad
CDT
Internal Structure
Cardiac Stomach

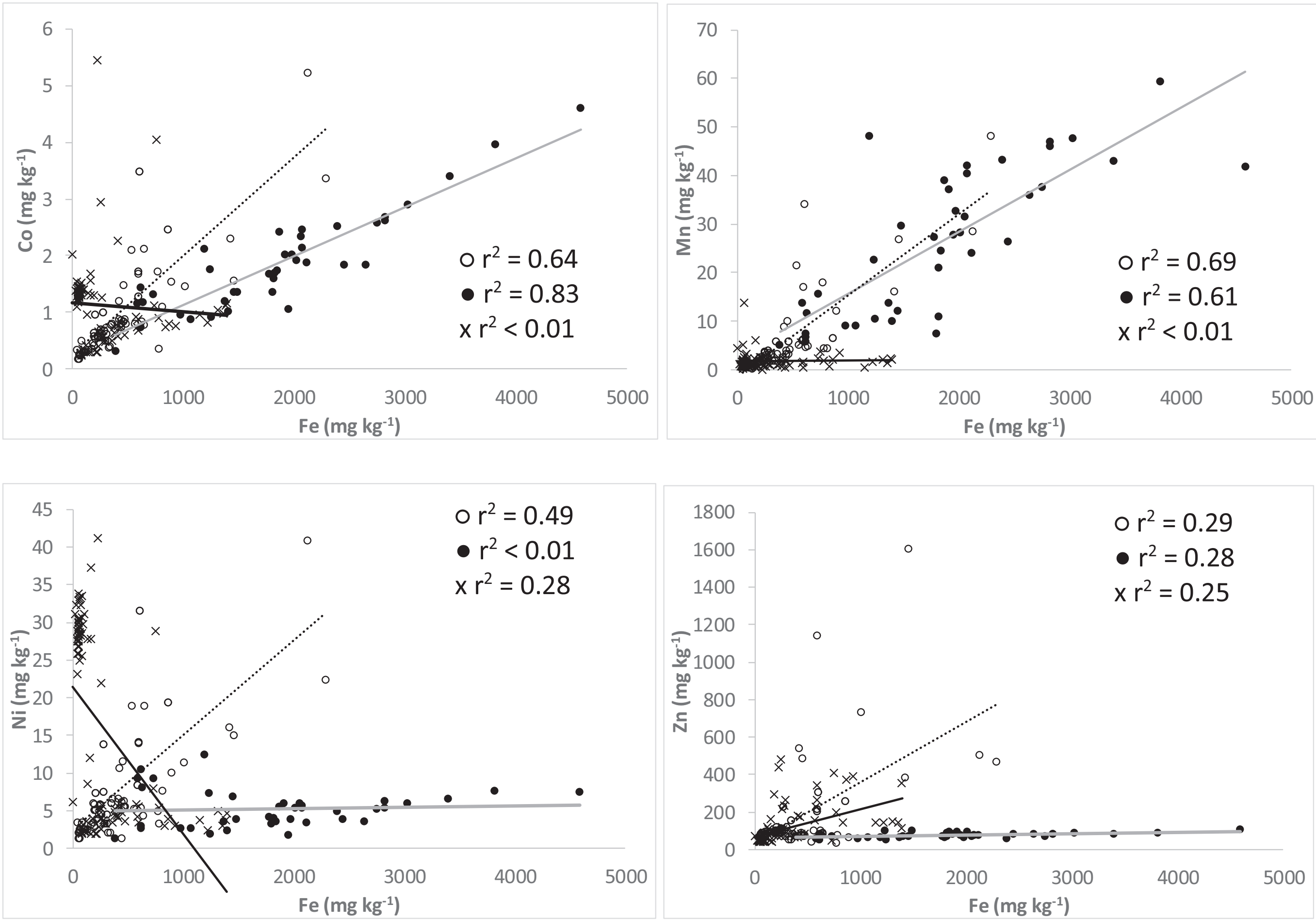


Fig. 4. Correlations between a) Co, b) Mn, c) Ni and d) Zn in relation to Fe to determine lithogenic origin of metals in the different tissues of three organisms in Ryder Bay: *L. elliptica* (o, dashed lines), *N. concinna* (•, grey lines) and *O. validus* (x, solid black lines). R^2 values for each line are given in the respective figure.

structure, nor elevated Fe in the digestive tract as this tissue was located in the central disc area rather than in the arm.

As most individuals included in this study were adults, the potential to identify relationships between body size and metal concentration was limited. Within the size range available between individuals irrespective of sampling site, none of the three organisms showed a relationship between body size and metal concentration in different organs. This study was restricted by small numbers of individuals, and no assessments was made of the stage of the reproductive cycle. It is recommended that these factors be included in the development of a biomonitoring programme.

Although individually all three species seem to meet most of the criteria for bioindicator organisms, different feeding strategies and metal accumulation pathways in each species provide insight into different aspects of the food web and environment. Concentrations of Cu, Cr, Pb and Co were similar in all three species; however, *N. concinna* had concentrations of Fe and Mn over three times higher than recorded in *L. elliptica* and *O. validus* at all locations. *L. elliptica* contained the highest concentration of Zn and *O. validus* the highest concentrations of Cd and Ni. Ahn et al. (2002) originally suggested *N. concinna* was a good bioindicator in the intertidal zone where *L. elliptica* is absent; however, these two species showed different spatial trends between the different metals, as discussed previously, probably due to differences in feeding and metal storage methods. As a scavenger, *O. validus* arguably gives a better overview of the entire food web due to its consumption of many different food sources, including *N. concinna* and *L. elliptica*, and indeed top predators are often used as biomonitors due to their magnification of contaminants in the marine environment (De Moreno et al., 1997). In order to develop a good biomonitoring programme in Antarctica, it is suggested that all three species are analysed initially, along with a suitable algal species (Dalla Riva et al., 2004), and further sediment analyses at a range of sites around any research station or location of interest.

5. Conclusions

Laternula elliptica, *O. validus* and *N. concinna* were all confirmed as good examples of biomonitors for trace metal contamination, in support of previous studies (Ahn et al., 2002; Lohan et al., 2001) and showed limited variation in metal concentrations at each site. *Odontaster validus* can now also be included in that role, with the advantage of a large body size and ease of collection, as well as providing a more integrated metal concentration from the biological community from its highly varied diet.

Future studies into metal concentrations at Ryder Bay should incorporate:

Fig. 3. Mean concentrations (mg kg^{-1} ± standard error) of a) Cd, b) Co, c) Cr, d) Cu, e) Fe, f) Mn, g) Ni, h) Pb and i) Zn in four tissues (gonad, central digestive tract (CDT), internal structure and cardiac stomach) from *O. validus*. Samples were collected from four sites in Ryder Bay, Antarctica: the control site Lagoon Island (black bars), Hangar Cove (white bars), South Cove (light grey bars) and Cheshire Island (dark grey bars).

1. Sampling in the vicinity of glacier fronts (dissolved and suspended metals, sediment and biomonitors) to identify potential metal concentration gradients resulting from glacial runoff.
2. Biogenic utilization of metals and bioavailability of metals from glacier sources need to be assessed in laboratory exposure studies primarily using microbial, phytoplankton and microphytobenthos organisms.
3. Comparisons of glacier fines from glaciers overlying different bedrock types are needed with assessments of marine invertebrate metal uptake to assess if metal availability to the ecosystem varies with source rock type.

There was little evidence of metal contamination above background levels in Ryder Bay emanating from the scientific and logistical activities at Rothera Research Station. Generally, high metal concentrations within the Ryder Bay marine environment were attributed to metal influx from glacial runoff, due to physical processes working on the underlying, metal-rich bedrock. Benthic invertebrates living in the Antarctic coastal zone may therefore already be adapted to high concentrations of these metals and similar findings have been reported for cold water environments in the Arctic (Chapman, 1993). Increasing rates of polar melt as climate change progresses could significantly alter the metal concentration and bioavailability around polar waters (Lee et al., 2017). Metal toxicity is influenced by changes in temperature, salinity and pH (Riba et al., 2004), suggesting that climate change may decrease tolerance of Antarctic benthic invertebrates to high metal concentrations. Furthermore, increasing Antarctic water temperatures could impair metabolic processes regulating metal concentrations within the organism (Sokolova and Lannig, 2008), and potentially increase mortality. This is a relatively unexplored potential impact of climate change.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.scitotenv.2019.134268.

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