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Concentration and Trophic Transfer of Copper, Selenium, and Zinc in Marine Species of the Chilean Patagonia and the Antarctic Peninsula Area

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Abstract

Patagonia and Antarctica are biodiverse regions in the Southern Hemisphere, but little is known about the levels of trace elements in marine organisms from these remote coastal ecosystems. In this study, selenium (Se), copper (Cu), zinc (Zn), and stable isotopes of nitrogen ($\delta^{15}N$; relative trophic level) were measured in 36 marine species collected from two locations of the Chilean Patagonia and two locations of the Antarctic Peninsula area to determine whether biomagnification of these trace elements occurs in the food webs. Results indicated that Cu, Se, and Zn levels were slightly lower than those in similar species from elsewhere, and the highest metal levels were found in marine macroinvertebrates compared with fishes. There was evidence of Cu, Se, and Zn biomagnification but only within the lower-trophic-level organisms. When assessing whole food webs, levels of these elements typically decreased from macroinvertebrates to fishes or birds, suggesting lower risks of metal toxicity to higher-level consumers.

Keywords Bioaccumulation · Biomagnification · Heavy metals · Trace elements · Marine food webs · Patagonia · Antarctica

Introduction

Although Cu, Se, and Zn are essential elements, human activities tend to increase their levels in coastal marine environments even in remote and cold regions [1, 2]. Since the 2003 banning of tributyl-tin (TBT)-based paints on ships, Cu concentrations in marine environments are likely increasing because of its elevated use as a biocide on ship hulls [3]. Industrial and agricultural activities have released Se from geological sources and increased its levels in aquatic ecosystems worldwide [1]. Zinc is used for the growing galvanizing industry, and (as most of elements), it can be transported to cold regions from industrial areas, being linked to major human activities present in South Shetland Islands, Antarctic Peninsula [4, 5].

Elevated exposures to Cu, Se, or Zn can damage the function of cells and cause physiological disorders and disease [6]. Studies on aquatic species have shown that, for example, Cu can affect biochemical and structural hepatic functions of fish [7, 8]. Selenium may impair normal function and lead to toxicity when found at high concentrations in gonads of sea stars and the flesh of fish [9]. Elevated concentrations of Zn can affect the endocrine system of vertebrates [10] and produce adverse effects on growth, survival, and reproduction in mollusks, crustaceans, echinoderms, fish, and amphibians [11].

It remains controversial whether trace metals biomagnify through food webs. When biomagnification occurs, the elevated metal concentrations in higher-trophic-level species could pose a threat to the organisms themselves or to human consumers [12]. In the past, it was believed that only Hg biomagnified [13], and many subsequent food web studies have shown a consistent increase in Hg with trophic level [14]. However, more recently, there is some evidence that

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Cd, Cu, Ni, Pb, Se, Ta, and Zn may also biomagnify through aquatic food webs [15–18]. However, there is still ongoing debate as to whether these metals biomagnify and, if so, under what conditions. It may be that some of these metals show greater biomagnification in colder, high-latitude systems as has been found for Hg [14]. High-latitude food webs are simpler and characterized by low species diversity, which may lead to higher trophic transfer of metals [14, 17]. Chilean Patagonia and Antarctica are high latitude environments that are currently minimally impacted by local developments, although both are being affected by global anthropogenic activities [19, 20]. Information on the concentration of metals in tissue of marine organisms that inhabit pristine areas of Chile and Antarctica is almost non-existent [17, 18, 21], yet it is crucial to assess their baseline levels given the increasing human presence in these remote regions. Consequently, the objectives of this study were to assess the concentrations of Cu, Se, and Zn as well as the relative trophic levels (using stable nitrogen isotopes or $\delta^{15}N$) of marine organisms from the coastal zones of Chilean Patagonia and the Antarctic Peninsula and determine whether these metals biomagnify through these systems.

Material and Methods

From the coast of the Chilean Patagonia, ten species of macroinvertebrates and eight species of fishes were collected near the Marchant River Mouth (44° 5′ S, 73° 5′ W) and off of Yalac Island (44° 01′ S, 73° 14′ W) (Sector 1; Fig. 1). From the Antarctic Peninsula (Sector 2, Fig. 1), six species of macroinvertebrates, three species of fishes, and feathers from two species of birds were collected at Paradise Bay, west coast of Graham Land (64° 51′ S, 62° 54′ W); four species of macroinvertebrates and feathers from three species of birds were sampled at Cape Shirreff, South Shetland Islands (62° 28′ S, 60° 46′ W). Details of species and sample size are indicated in Table 1. The samples were obtained in February 2014. The fishes were captured by means of harpoon and nets, anesthetized with 5% benzocaine (BZ-20, Veterquimica), the spinal cord severed, and then muscle samples were obtained. Soft tissues of mollusks were completely removed from the shells, while feather samples were collected individually in polyethylene bags from adult seabirds. All samples were stored at − 20 °C until their arrival to the laboratory.

In the lab, samples were washed with ultrapure water (18.2 MΩ cm^{-1}), dried at room temperature, and then ground with IKA A11 Basic Auto-miller for sieving (24 mesh dm^{-2}). Subsamples (0.02 and 0.45 g, according to availability) were microwave digested using 2 mL high-purity-grade nitric acid (70%), 2 mL hydrochloric acid (37%), and 1 mL perchloric acid (30%) (Suprapur, Merck). The concentrations of Se were determined by electrothermal atomic absorption spectrometry (ET-AAS, Analytik Jena AG-AAS ZEEnit 60, equipped with Zeeman background corrector). The concentrations of Cu and Zn were obtained using flame atomic absorption spectrometry (Varian spectrometer AAS 240FS, equipped with deuterium background corrector). All metal concentrations were determined at the Biophysics Institute of the Federal University of Rio de Janeiro, Brazil. Measurements were performed in triplicate and then the values averaged. Measurement quality was assessed by using a certified reference material (DOLT-4 Dogfish Liver, NRC, Canada), with elements recovery that ranged between 74 and 110%. Blanks were analyzed at the beginning of each set of samples, and the limit of detection (mg kg^{-1} dw) was 3.1 for Zn, 0.1 for Cu, and 0.2 for Se. Relative standard deviations and agreement between observed and certified concentrations of the metal reference materials were lower than 10%, while blanks were lower than 0.2% of the mean of the sample. All element concentrations are expressed as milligrams per kilogram dry weight unless otherwise stated.

Dried subsamples were also analyzed for stable nitrogen isotopes ($\delta^{15}N$), to assess relative trophic level, at the Nature Laboratory of the University of New Brunswick (Canada) using an elemental mass spectrometer Costech 4010 interfaced with Delta XP. Stable isotope measurements were reported as delta isotope δ in parts per thousand (‰) [22]. Two standards were used as reference materials: N-2 ($n = 6$) and CH-7 ($n = 6$), both certified by the International Atomic Energy Agency (IAEA) for stable isotope values [23, 24]. Additionally, certified standards of commercially available elements, acetanilide ($n = 18$) and nicotinamide ($n = 18$) were used, as well as three laboratory standards, bovine liver ($n = 18$), muskellunge muscle ($n = 42$), and protein ($n = 18$), which exhibited an average deviation of 0.03‰ from the long-term values. Replicates of each ten samples were performed, and the accuracy was 0.14 ± 0.14‰ for $\delta^{15}N$.

Levels of Cu, Se, and Zn were $\log_{10}$ transformed to meet the assumptions of normality and biomagnification was examined within macroinvertebrates only and across all species within a food web using linear regressions of each of these elements versus trophic level (TL) as in Yoshinaga et al. [25]. Consumer $\delta^{15}N$ values were converted to TL using the equation:

$$TLc = \left(\delta^{15}Nc - \delta^{15}Nb\right)/\Delta^{15}N + \lambda$$

where λ is the trophic level of the baseline organism (being 1 for primary producers and 2 for primary consumers), and $\delta^{15}Nc$ and $\delta^{15}Nb$ are isotope values of the consumer and a baseline organism, respectively. A trophic discrimination factor for $\Delta^{15}N$ of 3.4‰ was used for aquatic organisms [26, 27]. Analysis of Covariance (ANCOVA) was used to determine whether metal biomagnification was significantly different among the four food webs. Statistical analyses were performed using the JMP Scripting Language (JSL) from SAS [28].

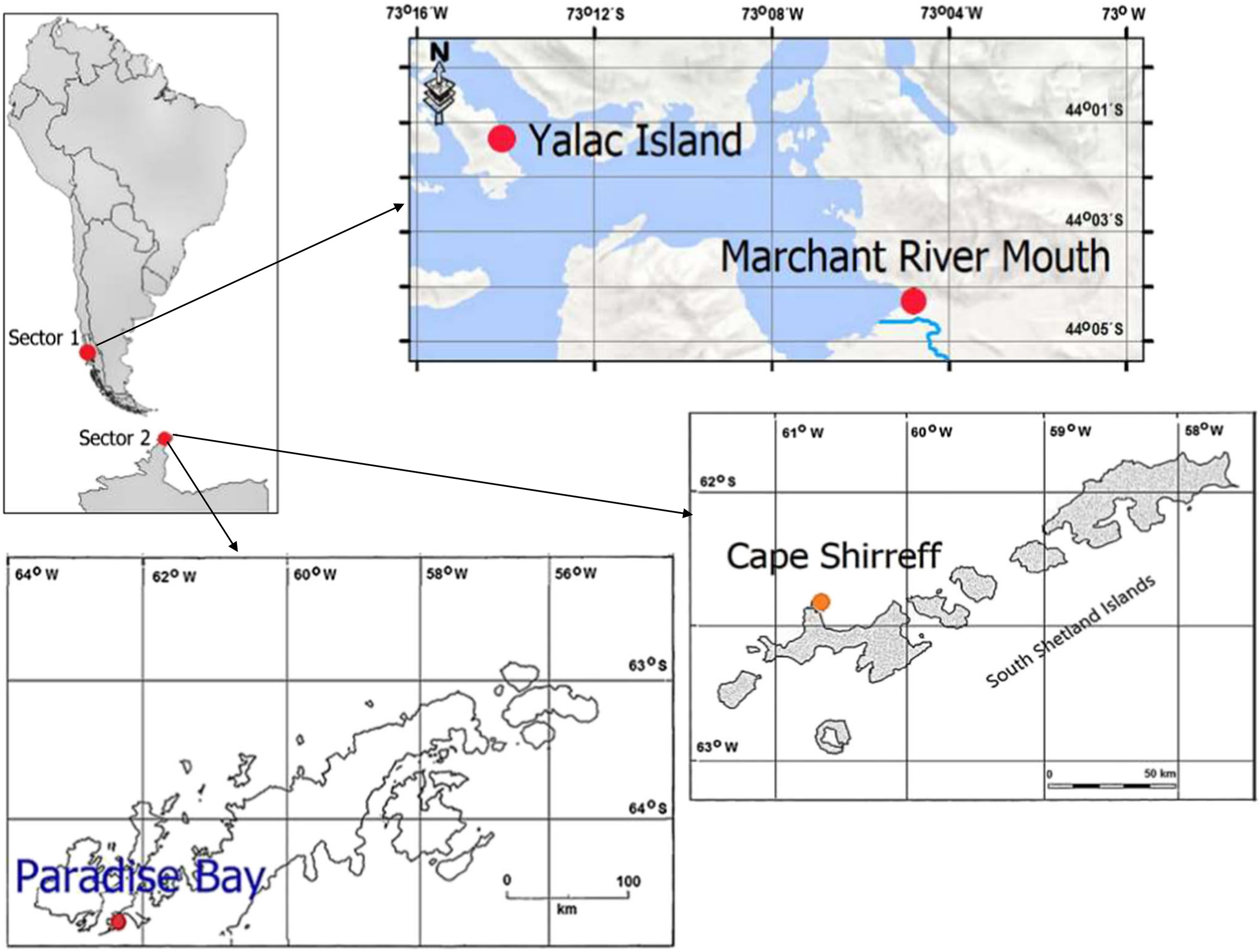

Fig. 1 Locations of the marine food webs studied from Chilean Patagonia (Sector 1) and Antarctic Peninsula area (Sector 2)

Results

In Patagonia, Cu, Se, and Zn concentrations ranged from 0.01 to 93.9, 0.2 to 4.5, and 11.9 to 107.5 mg kg^{-1}, respectively, across all species (Table 1). The highest Cu levels were found in the benthic carnivorous sea star *Stichaster striatus* at Marchant River Mouth, while the highest Se and Zn levels were found in the herbivorous marine snail *Tegula atra* at Yalac Island. In contrast, the lowest Cu levels were found in the benthopelagic carnivorous fish *Macruronus magellanicus* at Marchant River Mouth, while the lowest Se and Zn levels were found in the carnivorous mollusk *Concholepas concholepas* at Yalac Island and in the carnivorous pelagic fish *Merluccius australis* at Marchant River Mouth, respectively.

In the Antarctic Peninsula (Table 2), metal concentrations ranged from 1.5 to 57.1 mg kg^{-1} for Cu, from 0.2 to 31.1 mg kg^{-1} for Se, and from 14.2 to 166.9 mg kg^{-1} for Zn. The highest Cu and Zn levels were found in the Antarctic shrimp (*Lyssianasid amphipod*) and in the benthic omnivorous shrimp *Chorismus antarcticus* at Paradise Bay, respectively; the highest Se levels were found in the sea star predator *Diplasteria brucei* at Cape Shirreff. In contrast, the lowest Cu, Se, and Zn levels were all found in the cod *Trematomus bernacchii* at Paradise Bay.

There was some evidence of the biomagnification of Cu, Se, and Zn in the food webs of Chilean Patagonia and Antarctica, but this was only found when considering a subset of species. In Paradise Bay, there was an increase in Cu levels (biomagnification) with TL among macroinvertebrate species (slope = 0.69; $p = 0.008$) but a significant decrease in Cu (biodilution) through the whole trophic web (slope = − 0.39; $p = 0.003$; Table 3). Biomagnification of Cu was observed for fishes from Marchant River Mouth (slope = 3.13; $p = 0.01$), but the opposite occurred for macroinvertebrates (slope = − 1.87; $p = 0.04$) and the whole food web (slope = − 1.95; $p = 0.001$) at Yalac Island. For Se, there was biomagnification among macroinvertebrate species at Marchant River Mouth (slope = 0.49; $p = 0.003$) but significant biodilution through the food web of Paradise Bay (slope = − 0.24; $p = 0.01$; Table 4). Similarly for Zn, biomagnification was found for macroinvertebrates from Paradise Bay (slope = 0.51; $p = 0.05$) but not for

Table 1 Concentration of Cu, Se, and Zn (mg kg^{-1} dry weight), feeding habit (FH), values of δ^{15}N (‰), and trophic level (TL) in aquatic organisms from sites in Chilean Patagonia

Location	Group	Species	FH	*N*	Sample	Cu	Se	Zn	δ^{15}N[a]	TL
MRM	MI	*Stichaster striatus*	bp	3	Soft tissue	93.9 ± 27.1	2.5 ± 0.7	86.6 ± 27.8	12.9 ± 0.3	3.7 ± 0.1
		Aulacomya ater	ff	3	Soft tissue	6.1 ± 1.3	1.9 ± 0.5	69.9 ± 7.6	9.7 ± 0.5	2.7 ± 0.1
		Hemigrapsus granulosus[b]	bg	3	Whole body	57.7 ± 10.2	0.4 ± 0.1	54.9 ± 5.6	8.2 ± 1.0	2.3 ± 0.3
		Loxechinus albus	bg	3	Soft tissue	4.7 ± 0.4	1 ± 0.4	72 ± 47.7	10.5 ± 0.7	3 ± 0.2
	Fish	*Eleginops maclovinus*	bpp	3	Muscle	0.7 ± 1.1	0.3 ± 0.2	12.7 ± 9.2	13.6 ± 0.5	3.9 ± 0.2
		Genypterus blacodes	bp	3	Muscle	23.9 ± 29.7	1.8 ± 0.5	23.2 ± 7.9	16.3 ± 0.2	4.7 ± 0.1
		Macruronus magellanicus	bpp	1	Muscle	0.01	1.3	13.8	12.6	3.6
		Merluccius australis	bpp	1	Muscle	1.4	1.7	11.9	14.7	4.2
		Salitota australis	bp	1	Muscle	1.4	1.5	13	16.1	4.6
		Schroederichthys chilensis	bp	2	Muscle	1.4 ± 2.0	3.5 ± 1.3	42.9 ± 19.7	15.5 ± 0.4	4.4 ± 0.1
Yalac Is.	MI	*Chorus giganteus*	bp	3	Soft tissue	0.01 ± 0.004	0.8 ± 1.0	43.7 ± 3.4	14.9 ± 0.6	4 ± 0.2
		Concholepas concholepas	bp	3	Soft tissue	2.2 ± 2.0	0.2 ± 0.1	20.9 ± 5.9	12.6 ± 0.6	3.3 ± 0.2
		Fisurella sp.	bg	3	Soft tissue	3.7 ± 0.7	0.81 ± 0.07	32.9 ± 1.0	11.6 ± 0.3	3.1 ± 0.1
		Nacella magellanica	bg	3	Soft tissue	0.5 ± 0.8	0.43 ± 0.06	21.1 ± 0.3	11.5 ± 0.2	3 ± 0.1
		Cliona chilensis[b]	ff	1	Soft tissue	3	1.93	34.3	9.9	2.5
		Tegula atra	bg	3	Soft tissue	93 ± 132.2	4.5 ± 2.7	107.5 ± 74.2	10.6 ± 2.2	2.8 ± 0.7
	Fish	*Paralabrax humeralis*	bpp	1	Muscle	0.01	0.6	14.1	16.2	4.4
		Panguipes chilensis	bpp	3	Muscle	0.02 ± 0.004	0.5 ± 0.3	12.4 ± 0.6	16.4 ± 0.3	4.4 ± 0.1

MRM, Marchant River Mouth; MI, macroinvertebrate; *bp*, benthic predator; *ff*, filter-feeder; *bg*, benthic grazer; *bpp*, benthic pelagic predator

[a] Previously reported by Espejo et al. [18]

[b] Species used as baseline for TL calculations

Table 2 Concentrations of Cu, Se, and Zn (mg kg^{-1} dry weight), feeding habit (FH), values of δ^{15}N (‰), and trophic level (TL) of aquatic organisms from the Antarctic Peninsula area

Location	Group	Species	FH	*N*	Sample	Cu	Se	Zn	δ^{15}N[a]	TL
Paradise Bay	MI	*Diplasterias brucei*	bp	2	Soft tissue	36 ± 1.7	5.5 ± 1.3	121 ± 3.3	7.2 ± 0.01	2.9 ± 0.004
		Chorismus antarcticus	bg	1	Soft tissue	35.6	6.5	167	7.6	3
		Lyssianasid amphipod	dsg	3	Whole body	57.1 ± 9.2	1.5 ± 0.5	48.4 ± 5.4	7.4 ± 0.3	2.9 ± 0.1
		Nacella concinna[c]	bg	3	Soft tissue	9 ± 1.3	2 ± 0.3	36.2 ± 26.1	5.1 ± 0.7	2.2 ± 0.2
		Euphausia superba	gf	3	Whole body	27.3 ± 3.5	3 ± 0.5	64.7 ± 18.2	5.8 ± 0.9	2.4 ± 0.3
		Haplocheira sp.	os	3	Whole body	26.6 ± 1.3	1 ± 0.3	54.2 ± 17.2	6.8 ± 0.02	2.7 ± 0.01
	Fish	*Harpagifer antarcticus*	bp	3	Muscle	1.6 ± 1.3	0.2 ± 0.4	27.4 ± 3.5	11.5 ± 0.6	4.1 ± 0.2
		Trematomus bernacchii	bp	1	Muscle	1.5	0.2	14.2	11.8	4.2
		Trematomus hansoni	bp	2	Muscle	1.6 ± 0.6	0.6 ± 0.3	16 ± 0.2	11.6 ± 0.81	4.2 ± 0.2
	Seabird[b]	*Catharacta maccormicki*	pp	3	Feather	13.9 ± 3.7	2.6 ± 1.4	77.4 ± 21.2	11.4 ± 0.9	4.1 ± 0.3
		Pygoscelis papua	pp	3	Feather	14.5 ± 2.4	1.9 ± 0.4	82.1 ± 11	10.5 ± 4.4	3.8 ± 1.3
Cape Shirreff	MI	*Diplasteria brucei*[c]	bp	1	Soft tissue	46.1	31.1	49	6.6	0.06
		Macroptychaster sp.	bp	1	Soft tissue	30.2	2.2	111.1	6.6	0.07
		Nacella concinna	bg	3	Soft tissue	10.7 ± 1.9	0.8 ± 0.6	50.2 ± 14.2	8.5 ± 0.1	0.6 ± 0.03
		Odontaster validus	os	1	Soft tissue	54	7.2	70.4	7.91	0.45
	Seabird[b]	*Pygoscelis antarctica*	pp	1	Feather	22.4	2	87.7	15.7	2.73
		Pygocelis papua	pp	1	Feather	23.7	1.8	80.5	12.5	1.80
		Catharacta maccormicki	pp	3	Feather	13.6 ± 3.1	2.5 ± 2.2	82.4 ± 28.3	13.9 ± 2.6	2.2 ± 0.8

MI, macroinvertebrate; *bp*, benthic predator; *bg*, benthic grazer; *dsg*, detritivore-scavenger-grazer; *gf*, grazer/filtering consumer; *os*, omnivorous scavenger; *pp*, pelagic predator

[a] Previously reported by Espejo et al. [18]

[b] The rules for the protection of threatened or endangered animals such as penguins make almost impossible to work with samples such as muscle or internal organs; however, some works have shown a direct relationship between feathers and muscle tissues for trace elements in seabirds [43–45]

[c] Species used as baseline for TL calculations

Table 3 Linear regressions between Cu concentrations and trophic levels according to location and food web studied

Region	Location	Food web	Slope	Intercept	R^2	*p* value	References
Antarctica	Paradise Bay	Macroinvertebrate	0.69	− 0.40	0.59	0.008*	Own studies
		Fish/bird	− 0.16	1.29	0.02	0.62	
		Whole	− 0.39	2.35	0.30	0.003*	
	Cape Shirreff	Macroinvertebrate	− 0.93	1.71	0.57	0.08	Own studies
		Bird	0.09	1.02	0.14	0.52	
		Whole food web	− 0.07	1.36	0.07	0.43	
Patagonia	Marchant River M.	Macroinvertebrate	0.24	0.59	0.05	0.49	Own studies
		Fish	3.13	− 13.91	0.48	0.01*	
		Whole	− 0.53	2.28	0.07	0.20	
	Yalac Island	Macroinvertebrate	− 1.87	5.43	0.27	0.04*	Own studies
		Fish	− 0.87	0.78	0.01	0.88	
		Whole	− 1.95	5.68	0.45	0.001*	
East Asia	Yellow River Delta (China)	Macroinvertebrate/fish/bird	− 0.12	1.37	0.15	0.6	[46]
	Pearl River Estuary (China)	Mollusk/crab	0.181	n/i	0.785	0.001*	[47]
	Deer Island (China)	Macroinvertebrate	0.020	0.766	0.017	0.654	[48]
Southeast Asia	Mekong Delta (Vietnam)	Macroinvertebrate	− 0.043	2.011	0.382	0.118	[49]
		Fish	0.027	− 0.600	0.321	0.225	
		Whole	− 0.102	2.070	0.227	0.182	
Mediterranean Sea	Beal Station (Spain)	Macroinvertebrate	0.171	1.313	0.074	0.1047	[50]
		Fish	− 0.408	2.089	0.133	0.080	
	Ciervo Station (Spain)	Macroinvertebrate	0.298	1.052	0.129	0.084	[50]
		Fish	0.882	− 2.238	0.183	0.037*	
Southern Asia	Sulu Sea (Philippines)	Pelagic fish	0.06	0.27	0.887	0.017*	[51]
** North America	Estero de Urías (Mexico)	Macroinvertebrate	0.31	0.39	0.67	0.05*	[52]

*Statistically significant value; **Gulf of California

the entire food webs of Marchant River Mouth (slope = − 0.23; $p = 0.01$) and Yalac Island (slope = − 0.19; $p = 0.05$; Table 5).

Discussion

There is little information regarding the levels and fate of trace elements within cold ecosystems of the Southern Hemisphere, which makes it difficult to discuss our data. Elements such as Cu, Se, and Zn can be harmful to aquatic organisms and humans if they exceed certain thresholds [26, 27], which can be related to the bioaccumulation and biomagnification of these elements through the aquatic food web.

Mean Cu and Zn concentrations found in macroinvertebrates from Patagonia were 4.8 times higher and 34% lower than those previously reported in benthic organisms from southern Chilean Patagonia, respectively [21], and the latter were much lower than those found previously in marine gastropods and bivalves from Eastern Argentinian Patagonia [29]. Except for Cu, the maximum Se and Zn levels found in macroinvertebrates from Antarctica were lower than those previously reported by Deheyn et al. [9] in benthonic organisms (bivalves, brittlestars, sea urchins) from Deception Island (South Shetland Islands). In addition, the highest Cu and Zn levels found herein in macroinvertebrates are below those reported in whole marine benthic invertebrates of Southern Ocean [30] and from Northern Hemisphere [31]. Copper levels found in our macroinvertebrates from Patagonia were lower, while those from Antarctica were higher than those reported in benthic marine organisms from contaminated sites of northern Chile [32]. The higher Cu levels in our samples from Antarctica are consistent with the high Cu levels present in Antarctic fauna [33, 34]. Our maximum levels of Cu and Zn found in *Nacella magellanica* are lower than those levels of Cu (15.2 mg kg^{-1}) and Zn (96.2 mg kg^{-1}) reported by Conti et al. [35] in the same species from Cape Horn (Southern Patagonia). Previously, Comoglio et al. [36] reported lower Cu levels (7.6 mg kg^{-1}) and Zn (102.6 mg kg^{-1}) levels from Tierra del Fuego (Southern Patagonia) and the same species (whole body). Our Se levels (0.2–31.1 mg kg^{-1}) were lower than the toxic effect thresholds (700 mg kg^{-1}) for impacts on food-chain organisms, and those levels from field studies showing that benthic invertebrates can accumulate 20 to 370 mg Se kg^{-1} without deleterious effect on reproduction [37].

Table 4 Linear regression between Se concentrations and trophic levels according to location and food web studied

Region	Location	Food web	Slope	Intercept	R^2	*p* value	References
Antarctica	Paradise Bay	Macroinvertebrate	0.05	3.22	0.0026	0.85	Own studies
		Fish/bird	− 0.10	3.30	0.01	0.70	
		Whole	− 0.24	3.93	0.22	0.01*	
	Cape Shirreff	Macroinvertebrate	− 1.04	3.60	0.28	0.28	Own studies
		Bird	0.58	1.86	0.32	0.32	
		Whole	0.03	3.12	0.0041	0.85	
Patagonia	Marchant River Mouth	Macroinvertebrate	0.49	1.62	0.60	0.003*	Own studies
		Fish	0.77	− 0.29	0.25	0.11	
		Whole	0.16	2.45	0.07	0.20	
	Yalac Island	Macroinvertebrate	− 0.20	3.34	0.03	0.55	Own studies
		Fish	0.91	− 1.38	0.04	0.79	
		Whole	− 0.11	3.08	0.02	0.58	
East Asia	Deer Island (China)	Macroinvertebrate	− 0.008	0.325	0.002	0.875	[48]
Southeast Asia	Mekong Delta (Vietnam)	Macroinvertebrate	0.014	− 0.815	0.236	0.345	[49]
		Fish	0.029	− 1.035	0.205	0.447	
		Whole	0.066	− 1.599	0.443	0.007*	
	Sulu Sea (Philippines)	Pelagic fish	0.09	− 0.58	0.828	0.032*	[51]

*Statistically significant value

In fish, the highest muscle concentrations of Cu were found in the demersal carnivorous species *Genypterus blacodes* at Marchant River Mouth, while the highest Se and Zn levels were found in the redspotted catshark *Schroederichthys*

Table 5 Linear regression between Zn concentrations and trophic levels according to location and food web studied

Region	Location	Food web	Slope	Intercept	R^2	*p* value	References
Antarctica	Paradise Bay	Macroinvertebrate	0.51	0.40	0.25	0.05*	Own studies
		Fish/bird	− 0.09	1.96	0.03	0.62	
		Whole	− 0.06	1.87	0.02	0.47	
	Cape Shirreff	Macroinvertebrate	− 0.28	1.89	0.22	0.34	Own studies
		Bird	0.12	1.64	0.38	0.26	
		Whole	0.07	1.75	0.20	0.17	
Patagonia	Marchant River Mouth	Macroinvertebrate	0.13	1.44	0.23	0.11	Own studies
		Fish	0.35	− 0.26	0.21	0.15	
		Whole	− 0.23	2.35	0.24	0.01*	
	Yalac Island	Macroinvertebrate	0.01	1.53	0.00012	0.96	Own studies
		Fish	0.05	0.89	0.02	0.87	
		Whole	− 0.19	2.11	0.19	0.05*	
East Asia	Yellow River Delta (China)	Macroinvertebrate/fish/bird	0.15	1.42	0.32	0.24	[46]
	Pearl River Estuary (China)	Mollusk/crab	− 0.044	n/i	0.057	0.569	[47]
		Macroinvertebrate/fish	− 0.0206	n/i	0.319	0.009*	
	Deer Island (China)	Macroinvertebrate	0.023	1.818	0.103	0.262	[48]
Southeast Asia	Mekong Delta (Vietnam)	Macroinvertebrate	0.022	1.110	0.249	0.318	[49]
		Fish	− 0.025	1.602	0.337	0.202	
		Whole	0.031	0.781	0.252	0.138	
Mediterranean Sea	Beal Station (Spain)	Macroinvertebrate	− 0.784	5.024	0.480	0.001*	[50]
		Fish	− 0.371	3.081	0.254	0.012*	
	Ciervo Station (Spain)	Macroinvertebrate	− 0.403	3.228	0.103	0.102	[50]
		Fish	− 0.117	1.708	0.018	0.533	
** North America	Estero de Urías (Mexico)	Macroinvertebrate	− 0.09	1.36	0.13	0.05*	[52]

*Statistically significant value; **Gulf of California *chilensis* at the same location. These Zn levels are much lower than those previously reported by Santos et al. [38] in the demersal dusky rockcod fish *Trematomus newnesi* (99.1 mg kg^{-1}) and the rockcod *Notothenia* spp. (64.6 mg kg^{-1}) from Antarctica. In fish, Se can bioaccumulate and cause negative impacts. The Se levels in fish muscle found herein (0.2–3.5 mg kg^{-1}) were far below those (14 mg kg^{-1}) in the striped bass (*Morone saxatilis*) from Northern Hemisphere, a level linked to mortality on fish [37] and lower than 7.9 mg kg^{-1} related to deformities observed on splittail (*Pogonichthys macrolepidotus*) in San Francisco Bay [39]. Concentrations of Cu, Se, and Zn in Patagonian and Antarctic fishes were lower than the guidelines for human consumption (80 for Cu, 5 for Se, and 150 μg/g dw for Zn) stated in literature in muscle of fish [15, 40].

Levels of Cu, Se, and Zn in feathers of Antarctic seabirds were slightly higher than those reported previously also in Antarctica by Jerez et al. [34] and Szopińska et al. [2]. Feather Se levels were higher in skuas than penguins, which makes sense because skua feeds at trophic levels higher than penguin.

While lab and field studies and biokinetic modeling have shown that Cu and Zn generally do not biomagnify through freshwater and marine food webs consisting of primary producers, macroinvertebrates, and fish [16], our results suggest these elements biomagnify within specific compartments (macroinvertebrates or fishes) of marine food webs in cold and pristine environments of Patagonia and Antarctica. The biomagnification of Cu and Se observed here in Antarctic macroinvertebrates or Patagonian fishes has also been noted in different aquatic ecosystems of the Northern Hemisphere (see Tables 3 and 4). Our study found only one case of possible biomagnification of Zn in Patagonian macroinvertebrates, which contradicts the biodilution of this metal in along the food webs of different aquatic ecosystems elsewhere (see Table 5). Results from the current study support previous findings from pristine locations in Antarctica and Patagonia showing that the trophic transfer of Cd is highly dependent on the species considered [18, 41], unlike for Ta which biomagnified across all species and sites [17].

In summary, the marine food webs in Chilean Patagonia and Antarctica had Cu, Se, and Zn levels that were lower than similar species from elsewhere and some evidence of Cu, Se, and Zn biomagnification through a subset of the food web that appears to be species and site specific. We did not find any evidence of the biomagnification of these metals through whole food webs. Dietary habits, seasonality, and certain physicochemical factors (such as pH, temperature, and dissolved organic carbon) influence the bioaccumulation and biomagnification of metals [14, 42]. The trophodynamics (i.e., the study of trophic transfer of trace elements in food chains) of Cu, Se, and Zn of the cold regions of the Southern Hemisphere such as Patagonia and Antarctica can have important implications on wildlife and human health. Although the current risk to human health from the consumption of shellfish and fish contaminated with Cu, Se, and Zn appears low, this situation could change as climatic conditions change and with increased human activity. More studies are needed to understand the factors that are influencing the trophic transfer of metals in these remote and cold areas, and thus to evaluate their possible effects on animals and humans.

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Compliance with Ethical Standards

Conflict of Interest The authors declare that they have no conflict of interest.

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