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Metal accumulation in sea urchins and their kelp diet in an Arctic fjord (Kongsfjorden, Svalbard)

In-Young Ahn *, Jungyoun Ji, Hyun Park

Korea Polar Research Institute of Korea Ocean Research and Development Institute (KORDI), Songdo Technopark, 7-50 Songdo-dong, Yeonsu-gu, Incheon 406-840, Republic of Korea

The Arctic marine environment is a significant repository of anthropogenic pollutants, including heavy metals (Bard, 1999; Muir et al., 1999; AMAP, 2002, 2005). Elevated concentrations of some toxic metals such as Hg, Pb, Se, and Cd have been reported from several marine birds and mammals (Ronald et al., 1984; Wagemann et al., 1996; Bard, 1999; Muir et al., 1999; Fant et al., 2001; AMAP, 2002, 2005; Dehn et al., 2006). Studies on metal accumulation in prey organisms in Arctic waters have been limited to some major pelagic species such as zooplankton and fish (Ritterhoff and Zauke, 1997; Dehn et al., 2006), despite the fact that a variety of prey organisms, including benthic invertebrates, constitute a major part of the diet for many Arctic marine mammals (Bustamante et al., 2004; Dehn et al., 2006, 2007). Several studies have already reported higher concentrations of Cd in Arctic seals that prey on benthic invertebrates rather than fish (Bustamante et al., 2004; Dehn et al., 2005).

Sea urchins are an important prey item of predatory organisms at higher trophic levels, such as fish, seals, and whales (Muir et al., 1999), and are thus considered to contribute significantly to the transfer of metals and other pollutants to higher trophic levels. Apparently, by virtue of their commercial importance, most studies on sea urchins related to metals have focused on metal toxicity to sea urchin embryos or larval development (Radenac et al., 2001; Kobayashi and Okamura, 2005; Gopalakrishnan et al., 2008), effects on adult reproduction (Au et al., 2001), and development of molecular biomarkers to detect metal exposure (Aspholm and Hylland, 1998; Riek et al., 1999; Geraci et al., 2004). Few studies have examined metal accumulation in natural sea urchin populations (Bohn, 1979; Sadiq et al., 1996; Aspholm and Hylland, 1998; Strorelli et al., 2001; Deheyn et al., 2005), despite their abundance and wide distribution. Therefore, further study to elucidate metal accumulation through the food web is warranted.

Sea urchins of the genus *Strongylocentrotus* have a wide geographic distribution, occurring in the North Atlantic, North Pacific, and Arctic Oceans (Bohn, 1979; Bazhin, 2002; Gagnon et al., 2004; Addison and Hart, 2004, 2005), including the Svalbard Islands, a key area in the Arctic Monitoring and Assessment Programme (AMAP, 1996). The green sea urchin *S. droebachiensis* is reportedly a key species on shallow rocky subtidal substrata in Kongsfjorden on West Spitsbergen, Svalbard (Hop et al., 2002; Kaczmarek et al., 2005; Beuchel and Gulliksen, 2008). Hop et al. (2002) reported that the coverage of laminarian kelps fluctuated widely in this location, and heavily grazed areas devoid of kelps were commonly associated with high densities of *S. droebachiensis*. The morphologically similar species *S. pallidus* occurs concomitantly in such areas, but is less abundant (Hop et al., 2002).

This study aimed to assess the metal accumulation of the sea urchins *Strongylocentrotus* spp., and further to improve the understanding of metal transfer at lower trophic levels in Arctic marine ecosystems. Sea urchins (*S. droebachiensis, S. pallidus*) were collected from shallow subtidal waters (5–15 m) of Kongsfjorden in two consecutive summers, late July to early August 2003 and late June 2004, from three stations (A, B, and C) along the shoreline (Fig. 1). Kongsfjorden (79°N, 12°E) is a glacial fjord that is influenced by both Atlantic and Arctic water masses, and contains a mixture of boreal and Arctic flora and fauna (Hop et al., 2002). As an important feeding ground for marine mammals and seabirds, Kongsfjorden has received extensive research interest, and is currently regarded as a suitable site for investigating impacts of global climate change. Hydrographic and oceanographic features of the fjord are described in detail in Svendsen et al. (2002). The sampling stations were chosen to represent varying degrees of glacial runoff influence, as reflected in surface water temperature and salinity regime (Svendsen et al., 2002; Kang et al., 2003). Station A was adjacent to the pier, had a medium degree of melt-water influence, and was likely to be the most polluted. Station B, near the inlet of the fjord, was least influenced by melt-water, and was likely to be least influenced by anthropogenic activities. Station C was closest to melt-water runoff sources and submerged glaciers and was most influenced by melt-water.

Laminarian kelps (*Laminaria saccharina, L. digitata*, and *Alaria esculenta*) and seawater samples were also collected from the sea urchin habitats to elucidate metal accumulation through a food web. Laminarian kelps are preferred foods of sea urchins in shallow rocky subtidal habitats (Miller and Mann, 1973; Vadas, 1977; Keats et al., 1984; Lemire and Himmelman, 1996; Minor and Scheibling, 1997; Gagnon et al., 2004; Wessels et al., 2006), and are also reported to have high rates of growth and reproduction (Vadas, 1977; Keats et al., 1984; Lemire and Himmelman, 1996; Minor and Scheibling, 1997; Lyons and Scheibling, 2007). Wessels et al. (2006) found that *S. droebachiensis* in Kongsfjorden have a significant preference for leathery seaweeds like *Laminaria* and *Alaria*.

Collected sea urchins were dissected and freeze-dried in the lab at Ny-Ålesund. Test diameter of each individual sea urchin was determined to the nearest 0.01 mm with vernier calipers. The soft

* Corresponding author. Tel.: +82 (0)32 260 6150; fax: +82 (0)32 260 6109.
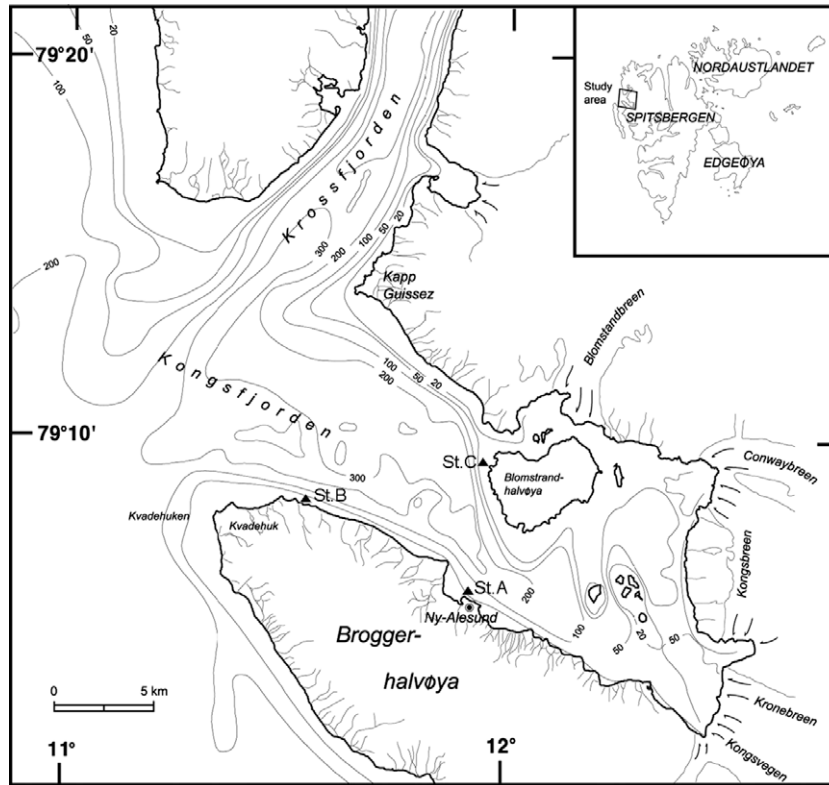*E-mail address:* iahn@kopri.re.kr (I.-Y. Ahn).

Fig. 1. Location of Kongsfjorden, on the island of Spitsbergen of Svalbard, and the sampling stations.

tissue of each individual was divided into the gonad and the rest (viscera). Each tissue part was determined to the nearest 1 mg. Excised sea urchin tissue samples were freeze-dried for about 48 h. For seaweeds, fronds above the meristematic region (young and soft part) were used for metal analysis, given that sea urchins actively (preferentially) graze on kelp blades (softer part), leaving behind the bases of stipes (Bohn, 1979; Gagnon et al., 2004). Subsamples of fronds, free from visible epiphytes, particulates, and animals, were washed once or twice with 0.2-μm filtered seawater to remove remaining particulates. Seaweed samples were then briefly rinsed with deionized water to remove salt, and freeze-dried at the station before later analysis in Korea.

Freeze-dried sea urchin tissue and seaweed samples were ground and homogenized, and then digested with concentrated nitric acid (Suprapur®, Merck) following the procedures described by Ahn et al. (2002). Concentrations of 10 metals (Cd, Zn, Cu, Pb, Cr, Mn, Fe, Co, Ni, and As) were determined in the digested samples by ICP/MS (Perkin–Elmer Elan 6100). The accuracy of the analytical method used on the sea urchin tissues was tested using standard reference materials (SRMs) for oyster (SRM 1566a, National Institute of Standards and Technology, USA) and mussel (CRM 278, Institute for Reference Materials and Measurements, Belgium). Recovery rates from the oyster and mussel tissues were 90–110%. Metal concentrations in seawater were determined separately in the dissolved and particulate fractions, following the procedures described by Ahn et al. (2004a). Blanks and SRMs (CASS-3, MESS-2) for quality assurance testing were processed in the same way. Recovery rates of SRMs ranged between 92% and 113%. All data were analysed using the statistical program MINI-TAB 13 (MINITAB Inc).

The size and sexual maturity of the two sea urchin species are compared in Table 1. Only samples from Station C were used, as specimens of both species were of a similar size (a prerequisite to eliminate size effects) and could be collected in sufficient quan-

tities at that location. About 20 specimens of each species were analysed, and these ranged from 37.2 to 60.3 mm test diameter and 20.8–79.9 g total tissue wet weight (test included). The average test diameter and total tissue weight of *S. pallidus* (50.5 mm and 49.4 g, respectively) were slightly larger than those of *S. droebachiensis* (47.0 mm and 41.1 g, respectively), but not significantly so (Mann–Whitney *U*-test, $p > 0.1$ for diameter and $p > 0.4$ for total tissue weight). The two species also showed no significant differences in size parameters between males and females or in the relationship between test diameter and tissue weight.

Gonadal somatic index (GSI) was determined as percentage wet weight of the gonad to total body weight [(wet weight of gonad/wet weight of total tissue) × 100]. GSI ranged from 10 to 30 (mean = 20). These values are well within the range reported for the same species at spawning stages in other geographic regions (Himmelman, 1978), indicating that the sea urchins in this study were sampled when at sexual maturity, just prior to spawning. There were no significant differences in GSI between male and female sea urchins.

Tissue metal concentrations did not differ significantly between the two species; thus, the data were pooled for statistical analysis. The lack of differences between the two species is likely a result of both species being collected from the same habitat and therefore probably eating the same foods. Table 2 shows the comparisons of metal concentrations between the female and the male and also between the gonad and the viscera of *Strongylocentrotus* spp. All the metals but Zn showed no difference between females and males. Zn concentrations were several times higher in the female gonad than in male gonads and viscera. Zn is essential for reproduction in many marine organisms and is generally present in high concentrations in female gonads relative to other tissues during the reproductive period in many marine invertebrates (Watling and Watling, 1976; Orren et al., 1980; Latouche and Mix, 1982; Ahn et al., 2002). In the present study, the gonads of both sexes

Table 1
Size comparison of *Strongylocentrotus droebachiensis* and *S. pallidus* collected from depths of 5–15 m at Station C on 23 June 2004. Body weights are based on wet tissue. ww: wet weight, gonadal somatic index (GSI) = (gonad ww/total tissue ww) × 100.

	n	Test diameter (mm)	Total tissue ww (g)	Gonad ww (g)	Viscera ww (g)	GSI
S. droebachiensis						
Male	15	47.78 ± 3.59	43.43 ± 8.44	8.17 ± 2.92	8.59 ± 2.56	18.53 ± 4.76
Female	5	44.72 ± 7.78	34.22 ± 16.14	6.38 ± 3.16	7.51 ± 5.26	18.62 ± 4.19
Pooled	20	47.02 ± 4.91	41.13 ± 11.14	7.72 ± 3.01	8.32 ± 3.30	18.55 ± 4.51
S. pallidus						
Male	9	48.34 ± 4.72	42.87 ± 14.69	8.57 ± 3.91	8.01 ± 3.53	19.88 ± 5.68
Female	11	52.18 ± 7.39	54.69 ± 20.60	11.83 ± 6.00	11.37 ± 5.36	20.84 ± 5.59
Pooled	20	50.46 ± 6.48	49.37 ± 18.72	10.36 ± 5.31	9.86 ± 4.83	20.41 ± 5.50
Pooled (S. droebachiensis + S. pallidus)						
Male	24	47.99 ± 3.96	43.22 ± 10.89	8.32 ± 3.25	8.37 ± 2.90	19.04 ± 5.05
Female	16	49.85 ± 8.08	48.30 ± 21.18	10.13 ± 5.79	10.16 ± 5.47	20.15 ± 5.16
Pooled	40	48.74 ± 5.93	45.25 ± 15.77	9.04 ± 4.46	9.09 ± 4.16	19.48 ± 5.06

Table 2
Comparison of metal concentrations ($\mu g\,g^{-1}$ tissue dry mass) between the female and the male and also between the gonad and the viscera of *Strongylocentrotus* spp. (pooled data from *S. droebachiensis* and *S. pallidus*). The data (except Zn) were pooled for both sexes for statistical analysis between the two tissue parts. The figures in bold face indicate significantly higher ($p < 0.001$) values in the viscera than in the gonad, and figures in italic indicate higher values in female gonads than in male gonads and viscera. The Mann–Whitney U-test was used to test the effects of sex and body part.

	Gonad			Viscera			Pooled (whole tissue)
	M (n = 24)	F (n = 15)	Pooled	M (n = 24)	F (n = 15)	Pooled	n = 39
Cd	0.17 ± 0.09	0.22 ± 0.10	0.1 9 ± 0.10	2.58 ± 0.69	2.66 ± 0.92	**2.61 ± 0.78**[***]	1.14 ± 0.30
Zn	43.4 ± 42.1	*175 ± 82*[***]		73.0 ± 18.8	75.1 ± 16.2	73.8 ± 17.7	86.1 ± 54.6
Cu	3.07 ± 0.73	2.95 ± 0.51	3.02 ± 0.65	8.15 ± 2.48	6.82 ± 1.58	**7.64 ± 2.25**[***]	4.94 ± 1.08
Pb	0.14 ± 0.12	0.15 ± 0.09	0.14 ± 0.11	1.49 ± 1.02	1.49 ± 0.91	**1.49 ± 0.96**[***]	0.73 ± 0.53
Cr	1.35 ± 0.62	1.64 ± 0.67	1.43 ± 0.64	5.75 ± 3.39	5.35 ± 1.94	**5.59 ± 2.87**[***]	3.12 ± 1.16
Mn	5.23 ± 3.28	5.06 ± 1.76	5.16 ± 2.76	89.6 ± 61.7	75.9 ± 45.8	**84.3 ± 55.9**[***]	39.0 ± 29.2
Fe	230 ± 196	158 ± 111	203 ± 171	3318 ± 2281	3219 ± 1830	**3280 ± 2094**[***]	1537 ± 1179
Co	0.49 ± 0.23	*0.76 ± 0.36*[*]	0.60 ± 0.31	2.55 ± 1.52	2.56 ± 1.13	**2.56 ± 1.37**[***]	1.43 ± 0.74
Ni	0.47 ± 0.276	0.47 ± 0.15	0.47 ± 0.23	6.29 ± 3.62	5.42 ± 2.90	**5.96 ± 3.35**[***]	2.80 ± 1.78
As	23.1 ± 8.6	30.5 ± 9.1	26.0 ± 9.4	26.5 ± 8.5	24.0 ± 8.0	25.5 ± 8.3	25.7 ± 7.2

[*] $0.01 < p < 0.05$.
[***] $p < 0.001$.

were ripe, and major spawning was yet to occur. The tissue distribution of Zn would be expected to change after spawning. A seasonal study may clarify this. On the other hand, concentrations of most metals significantly differed between gonad and viscera tissues. Concentrations of all metals, except Zn and As, were higher in viscera than in gonads. As was evenly distributed among the body parts.

Spatial variation in tissue metal accumulation among stations was not investigated, as there were significant differences in sea urchin size among stations within each year; tissue accumulation commonly varies with body size and sexual maturity (Boyden, 1977). Metal concentrations in the sea urchins in this study are comparable to those of the same *Strongylocentrotus* species in other Arctic areas, although very few data are currently available on metal accumulation in natural sea urchin populations (Table 3).

Table 4 shows concentrations of metals in seaweeds from the three stations. Among species, *Alaria esculenta* had higher values than *Laminaria* spp. for most metals, particularly at Stations A and C, where the melt-water influence was greater than at Station B. In contrast, *Laminaria* spp. contained significantly higher concentrations of As than *A. esculenta* at all three stations. Among *Laminaria* spp., *L. saccharina* had higher Cd concentrations than *L. digitata* and *L. solidungula*. A previous study (Ahn et al., 2004b) reported the same patterns among algal species. The higher concentrations of most metals in *A. esculenta* is likely attributable to the blades being thinner than those of *Laminaria* spp., leading to a higher surface/volume ratio. On the other hand, the higher accumulation of As in *Laminaria* spp. is likely an inherent feature indicative of internal regulation. Ahn et al. (2004b) also reported

Table 3
Comparison of metal concentrations ($\mu g\,g^{-1}$ tissue dry mass) in *Strongylocentrotus* spp. in this study with values for the same sea urchin species from other Arctic areas.

Metal	*Strongylocentrotus* spp.			
	This study		Bohn (1979)	
	Gonad	Whole tissue	Gonad	Whole tissue
Cd	0.52–1.6	0.78–2.8	0.9–1.5	1.2–1.8
Zn	20–134	26–120	96–184	29–39
Cu	1.2–3.3	1.7–3.9	3.3–9.0	2.4–3.3
Pb	0.03–0.08	0.06–0.49	–	–
Cr	1.1–2.0	1.1–1.6	–	–
Mn	1.1–3.8	3.3–18	–	–
Fe	32–133	80–582	185–285	305–845
Co	0.12–0.45	0.14–0.56	–	–
Ni	0.22–1.2	0.43–2.4	–	–
As	8.2–24	9.0–26	6.8–16	3.4–4.2

–: Not available.

significant spatial variation in algal metal concentrations, with most concentrations higher at Stations C and A than at Station B, and attributed this to input of melt-water laden with terrigenous sediment particles (Al, Fe, Mn, Pb, etc.), and suggested the potential use of *Laminaria* spp. and *A. esculenta* as biomonitors of metal pollution in the area. In summer 2004, however, there were no distinct differences among stations, except for Fe, which was higher in kelps from Station A. This may indicate inter-annual variations in the influence of melt-water.

Table 5 shows the concentrations of metals in seawater and seaweed, and sea urchin gonad, viscera, and total soft tissues (gonad

Table 4
Comparison of metal concentrations ($\mu g\ g^{-1}$ tissue dry mass) in the brown macroalgal species that are the preferred diet of *Strongylocentrotus* spp. The macroalgae were collected from the three stations at depths of 5–15 m on 23–26 June 2004. The figures in bold face indicate significantly higher values in *Laminaria* spp. than in *A. esculenta*, and those in italic indicate higher values in *Laminaria* spp.

	L. saccharina (n = 5)	*L. digitata*	*L. solidungula* (n = 4)	*Laminaria* spp. (pooled, n = 9)	*A. esculenta* (n = 5)
St. A					
Cd	*1.48 ± 0.38* *	–	0.220 ± 0.051	0.919 ± 0.718	1.43 ± 0.681 **
Zn	4.55 ± 0.69	–	4.708 ± 0.219	4.618 ± 0.516	**7.27 ± 1.396** **
Cu	0.66 ± 0.09	–	0.504 ± 0.080	0.590 ± 0.112	**1.11 ± 0.337** *
Pb	0.10 ± 0.04	–	0.080 ± 0.011	0.093 ± 0.030	**0.15 ± 0.040** *
Cr	0.24 ± 0.04	–	0.173 ± 0.020	0.211 ± 0.048	0.25 ± 0.050 **
Mn	2.37 ± 0.22		2.09 ± 0.24	2.242 ± 0.256	**3.42 ± 1.043** **
Fe	61.7 ± 25.2	–	50.6 ± 7.68	56.8 ± 19.35	**114 ± 21.97** **
o	0.08 ± 0.01	–	0.085 ± 0.032	0.083 ± 0.021	0.086 ± 0.028 **
Ni	0.56 ± 0.04	–	0.57 ± 0.055	0.560 ± 0.045	**0.79 ± 0.087** *
As	44.6 ± 6.28	–	44.8 ± 5.5	**44.65 ± 5.59** *	27.9 ± 10.65
	(n = 5)	(n = 5)		(pooled, n = 10)	(n = 5)
St. B					
Cd	*1.52 ± 0.27* *	0.347 ± 0.133	–	0.93 ± 0.65	0.82 ± 0.08
Zn	4.56 ± 1.183	7.155 ± 2.039	–	5.86 ± 2.08	5.78 ± 0.60
Cu	0.673 ± 0.203	0.827 ± 0.102	–	0.75 ± 0.17	1.06 ± 0.18
Pb	0.185 ± 0.144	0.154 ± 0.146	–	0.17 ± 0.14	0.22 ± 0.07
Cr	0.261 ± 0.110	0.272 ± 0.043	–	0.27 ± 0.08	0.24 ± 0.02
Mn	1.98 ± 0.459	*2.69 ± 0.35* *		2.34 ± 0.53	2.76 ± 0.62 **
Fe	43.76 ± 6.314	45.766 ± 5.783	–	44.8 ± 5.8	**70.5 ± 17.5** **
Co	0.076 ± 0.022	0.12 ± 0.02	–	0.10 ± 0.03	0.08 ± 0.02 **
Ni	0.435 ± 0.097	0.485 ± 0.098	–	0.46 ± 0.10 **	**0.97 ± 0.23** **
As	45.4 ± 11.7	53.9 ± 10.6	–	**49.6 ± 11.4** **	19.2 ± 2.86
	(n = 5)	(n = 3)	(n = 4)	(pooled, n = 12)	(n = 5)
St C					
Cd	*1.10 ± 0.20* *	0.304 ± 0.202	0.212 ± 0.11	0.60 ± 0.46	**1.59 ± 0.84** *
Zn	3.8 ± 0.51	*5.22 ± 1.45* *	*4.97 ± 0.99* *	4.54 ± 0.92	**5.64 ± 0.99** **
Cu	0.47 ± 0.03	0.630 ± 0.067	0.49 ± 0.08	0.52 ± 0.08	**1.17 ± 0.11** **
Pb	0.07 ± 0.02	0.045 ± 0.005	0.06 ± 0.01	0.06 ± 0.02	**0.22 ±0.11**
Cr	0.18 ± 0.02	0.164 ± 0.020	0.16 ± 0.05	0.17 ± 0.02	**0.30 ± 0.09** **
Mn	1.98 ± 0.16	2.52 ± 0.21	1.90 ± 0.15	2.10 ± 0.29	**3.79 ± 0.90** **
Fe	46.0 ± 5.75	39.5 ± 2.6	38.5 ± 2.5	41.8 ± 5.27	**75.0 ± 15.7** **
Co	0.08 ± 0.01	0.102 ± 0.018	0.06 ± 0.01	0.08 ± 0.02	0.09 ± 0.02 **
Ni	0.47 ± 0.12	0.397 ± 0.04	0.39 ± 0.03	0.42 ± 0.09	**0.98 ± 0.16** *
As	30.4 ± 2.53	42.0 ± 3.7	39.6 ± 9.0	**36.38 ± 6.66** *	24.7 ± 6.93

Table 5
Ranges of metal concentrations ($\mu g\ L^{-1}$ for seawater, $\mu g\ g^{-1}$ tissue dry mass for other values) in seawater, seaweed, and sea urchin gonads, viscera, and whole tissues (gonad and viscera pooled). Sea urchins (n = 23, 45.6 ± 4.20 mm test diameter, 36.9 ± 10.4 g total wet weight, 9.3 ± 3.9 g gonad wet weight) were collected on 1 August 2003 from Station B. Numbers with asterisks indicate significantly higher values in sea urchins than in seaweeds. The Mann–Whitney *U*-test was used to test the effects of sex and tissue part.

	Sea water		Laminarian kelps			Sea urchins (n = 23)		
	Dissolved (n = 2)	Particulate	*Laminaria* spp. (n = 6)	*Alaria esculenta* (n = 3)	Pooled (n = 9)	Gonad	Intestine	Whole tissue
Cd	0.013 ± 0.004	0.013 ± 0.011	1.65 ± 0.91	2.83 ± 0.21	2.05 ± 0.94	0.97 ± 0.30	3.21 ± 1.13	1.67 ± 0.48
Zn	0.285 ± 0.132	0.077 ± 0.017	7.05 ± 2.48	10.5 ± 2.3	8.20 ± 2.85	**62.7 ± 40.8** ***	**54.9 ± 10.3** **	**61.0 ± 30.4** ***
Cu	0.103 ± 0.028	0.044 ± 0.001	1.07 ± 0.19	1.24 ± 0.02	1.13 ± 0.17	**2.03 ± 0.41** ***	**2.79 ± 0.47** ***	**2.29 ± 0.34** ***
Pb	0.010 ± 0.005	0.035 ± 0.009	0.07 ± 0.05	0.09 ± 0.02	0.08 ± 0.04	0.05 ± 0.01	**0.31 ± 0.23** ***	**0.14 ± 0.09** **
Cr	-	-	0.202 ± 0.049	0.19 ± 0.03	0.20 ± 0.04	**1.38 ± 0.12** ***	**1.49 ± 0.32** ***	**1.42 ± 0.15** ***
Mn	0.019 ± 0.027	0.495 ± 0.067	2.06 ± 0.26	3.65 ± 0.14	2.59 ± 0.83	2.22 ± 0.73	**13.9 ± 5.9** ***	**6.08 ± 2.48** ***
Fe	-	46.9 ± 12.1	39.4 ± 6.9	59.8 ± 7.5	46.2 ± 12.2	61.3 ± 26.3	**558 ± 328** ***	**230 ± 144** ***
Co	0.012 ± 0.004	0.007 ± 0.002	0.250 ± 0.047	0.242 ± 0.045	0.25 ± 0.04	0.21 ± 0.09	**0.51 ± 0.19** ***	0.31 ± 0.11
Ni	0.363 ± 0.306	0.208 ± 0.082	0.463 ± 0.126	0.744 ± 0.173	0.56 ± 0.19	0.61 ± 0.27	**1.99 ± 0.98** ***	**1.09 ± 0.48** ***
As	-	-	**67.5 ± 11.7** ***	**53.1 ± 0.8** ***	62.7 ± 11.7	12.4 ± 3.6	16.0 ± 3.9	13.6 ± 3.5

-: Not determined.
** 0.001 < p < 0.01.
*** p < 0.001.

and viscera pooled). Concentrations of most metals in gonads were similar to (Mn, Fe, Co, and Ni) or lower than (Cd, Pb, and As) those in the kelps. For the viscera and whole tissue, however, most metals concentrations were several times higher than in kelps; concentrations in the latter being 10^2–10^4 times higher than those of the ambient seawater. For As, however, the concentrations were four to five times higher in seaweeds than in both sea urchin gonads and viscera. Cd concentrations in seaweeds were also higher (0.001 < p < 0.01, Mann–Whitney *U*-test) than those in sea urchin gonads, and similar to those in the viscera and whole tissue. The higher concentrations of most metals in sea urchins than in their preferred algal food might suggest metal biomagnification even
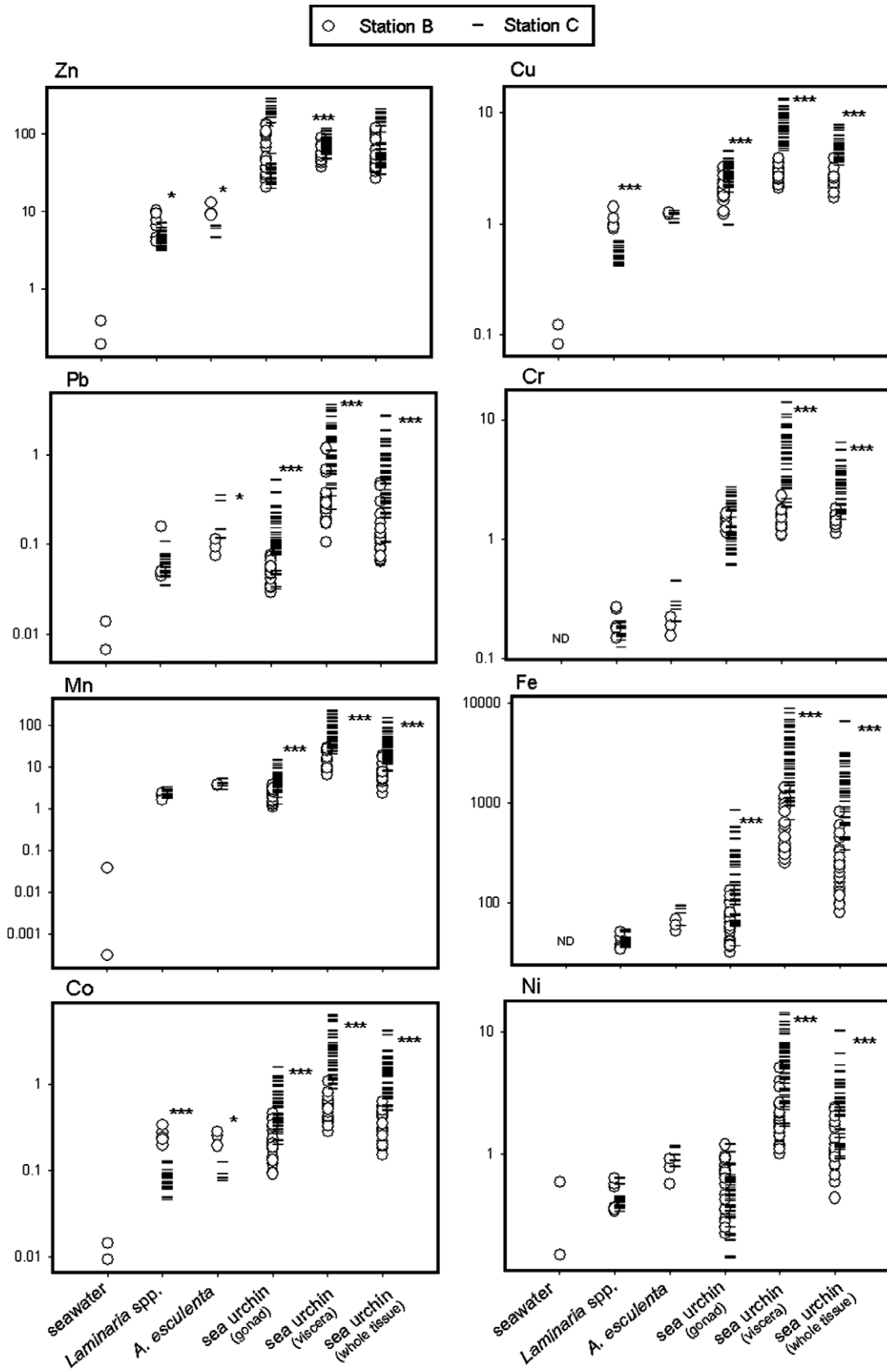
Fig. 2. Metal concentrations [$\mu g\,L^{-1}$ for seawater (dissolved), $\mu g\,g^{-1}$ tissue dry mass for other measurements] in seawater, brown seaweeds (*Laminaria* spp. and *Alaria esculenta*), and sea urchin tissues from Stations B and C. The data are presented as vertical points. Sea urchin size and sexual maturity were similar between the two stations. Refer to Table 5 for Station B data, and Tables 2 and 4 for Station C data.

at this low level of the Arctic marine food web. Higher concentrations of most metals in the visceral mass than in the gonads indicate that significant amounts are taken up in the diet.

However, comparison with the values from Station C, the site closest to melt-water runoff sources and submerged glaciers, indicates the presence of other pathways of metal transfer to sea urchins; sea urchins from Station C in late June 2004 (Table 1) were similar in size and sexual maturity to those collected from Station B on 1 August 2003 (Table 5), and a comparison was made between these two groups. Concentrations of most metals in sea urchin tissues (including gonads) were several times higher at Station C than at Station B, while the concentrations in seaweed were similar (Cr, Mn, Fe, and Ni) or lower (Zn, Cu, and Co) at Station C than at Station B (Fig. 2). Only Pb concentrations were higher at Station C in both seaweed (only *A. esculenta*) and sea urchin tissues. This difference in accumulation patterns between sea urchins and their preferred diet was prominent for Mn, Fe, and Co, for which concentrations in sea urchins from Station C were almost one order of magnitude higher than those from Station B. As mentioned above, this result strongly indicates the presence of other pathways of metal transfer to sea urchins, most likely consumption of lithogenic particles laden with these metals that are introduced into seawater together with glacial runoff from terrigenous sources. Ahn et al. (2004a) reported a similar trend in an Antarctic limpet from an Antarctic fjord; they found that tissue concentrations of Cu, Mn, Fe, and Pb in *Nacella concinna* varied significantly among sampling stations, with a strong tendency to increase with proximity to the source of glacial discharge. Thus, we found wide spatial variation in baseline concentrations of some metals from lithogenic sources, likely associated with varying degrees of glacial runoff. The amount and composition of glacial runoff likely varies temporally and spatially, causing fluctuations in natural background metal levels in the surrounding seawater, and subsequently in the baseline levels of biomonitor organisms. This should be taken into consideration when conducting future monitoring in the region and in other Arctic fjords.

Acknowledgements

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Monitoring of trace metals in coastal sediments from sites around Sardinia, Western Mediterranean

M. Schintu *, B. Marras, A. Maccioni, D. Puddu, P. Meloni, A. Contu

Università di Cagliari, Dipartimento di Sanità Pubblica, Via G.T. Porcell 4, 09124 Cagliari, Italy

Sardinia (Italy) (pop. 1,670,000) is the second-largest island in the Mediterranean Sea and covers an area of 24,090 km². Its economy is largely based on tourism, agriculture and animal husbandry; however, several industrial areas are present and act as localised sources of metals and organic contaminants in the coastal environment (Schintu and Degetto, 1999; De Luca et al., 2004). In this study the authors explore, for the first time, monitoring data on trace metals collected from coastal superficial sediments of the island from 2001 to 2006. Coastal sediments are considered a major sink and a secondary source of pollutants. Since trace metal concentrations in sediments are orders of magnitude higher than in the overlying water, sediments are preferable monitoring tools, as they allow a more consistent assessment of spatial and temporal contamination (Solomons and Förstner, 1984). The distribution and the accumulation of trace metals are influenced by sediment texture, mineralogical composition, reduction/oxidation state, adsorption and desorption processes and physical transport (Förstner, 1989). Therefore the relative influence of natural and anthropogenic sources on the geochemistry of marine sediments is not always clear. The objectives of this study were (i) to obtain a dataset of trace metal concentrations in this region of the Western Mediterranean based on a prolonged period, providing a resource for future monitoring comparisons, and (ii) to interpret sediment quality and show anthropogenic influence.

Eight sampling sites representative of areas at different levels of exposure to contaminants were selected (Fig. 1, Table 1). S2 (Asinara) and S5 (Capo Carbonara) were located in marine protected areas (MPAs). Several stations were located in the vicinity of commercial and passenger ports (S3, S4, S6, and S8) or industrial harbours (S7 is 10 km south of Portoscuso). The coasts of Alghero (S1), Olbia (S3), and Arbatax (S4) are tourist areas with no major industrial development. Sampling station S6 was intended to monitor anthropogenic inputs from Cagliari and its hinterland (about 500,000 inhabitants). Terrigenous sediments come mainly in the Gulf of Cagliari from the refluxes of the lagoon of Santa Gilla, which has been heavily polluted by Hg (Degetto et al., 1997). S8, in the Gulf of Oristano, was located near the mouth of the Tirso River (152 km), the drainage basin of which includes agricultural areas and a few industrial activities, such as a plastics factory in central Sardinia.

Sediments were collected twice a year, in April and September, from 2001 to 2006. Sampling and analyses were carried out according to the methods suggested by ICRAM (2001). A Van Veen grab whose penetration was typically 10–20 cm, was used. The topmost sediment (2 cm) was carefully removed with a plastic spoon and transferred to plastic vessels. Composite samples were made from the surface sediment of three grabs at each station. The samples were kept in iceboxes until they reached the laboratory. Grain size distribution was measured by wet sieving and the following fractions were determined: sand (2 mm > x > 63 μm); silt (63 μm > x < 4 μm); clay (<4 μm) (Shepard, 1954). The clay fraction (<4 μm) was only measured at S8. Organic carbon (OC) and metal contents were all determined in the <2 mm fraction.

OC was determined by using a CHN elemental analyser (LECO, model CHN-2000) on sediments previously acidified with 1 N HCl in order to remove carbonates (Hedges and Stern, 1984). The limit of detection (LOD) and the limit of quantitation (LOQ) were 0.07% and 0.10%, respectively. Accuracy and precision were checked by analysing 10 replicates of the standard reference materials Soil 1 (OC% = 2.613) and Soil 4 (OC% = 0.328) supplied by EuroVector (Italy). Accuracy was within 12% of the certificated values. Precision, expressed as relative standard deviation (RSD), was lower than 2%.

Concentrations of Al, As, Cd, Cr, Cu, Fe, Hg, Pb, and Zn were determined after total digestion of the samples. Aliquots of 0.5–1 g of homogenised wet sediments were placed in Teflon bombs with 3 ml of HCl, 9 ml of HNO₃ and 2 ml of HF. After each addition, samples were left to rest for 15–20 min. The bombs were then

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* Corresponding author. Tel.: +39 0706758307; fax: +39 0706758986.
E-mail address: schintu@unica.it (M. Schintu).