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Heavy metals in sediments and soft tissues of the Antarctic clam *Laternula elliptica*: More evidence as a ? possible biomonitor of coastal marine pollution at high latitudes?

Cristian Vodopivez [a], Antonio Curtosi [a], Edda Villaamil [b], Patricia Smichowski [c], Emilien Pelletier [d], Walter P. Mac Cormack [a,e,*]

[a] *Instituto Antártico Argentino, Balcarce 290, C1091AAF Buenos Aires, Argentina*
[b] *Cátedra de Toxicología, Facultad de Farmacia y Bioquímica, Universidad de Buenos Aires, Junín 956, C1113AAD Buenos Aires, Argentina*
[c] *Unidad de Actividad Química, Comisión Nacional de Energía Atómica, Av. Gral Paz 1499, 1650 San Martín, Buenos Aires, Argentina*
[d] *Institut des Sciences de la Mer de Rimouski (ISMER), Université du Québec à Rimouski, 310 Allée des Ursulines, Rimouski G5L 3A1, Canada*
[e] *Instituto de Nanobiotecnología NANOBIOTEC (UBA-CONICET), Facultad de Farmacia y Bioquímica, Universidad de Buenos Aires, Junín 956, C1113AAD Buenos Aires, Argentina*

HIGHLIGHTS

- The potential of the Antarctic clam as biomonitor for heavy metals was evaluated.
- Levels of Cd and Cu in sediments were related to the contribution of the streams.
- Remains of paints cause high Cr and Pb levels which are randomly detected in clam tissues.
- Kidney from *L. elliptica* could be adequate for biomonitoring pollution with Cd and Zn.

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ABSTRACT

Studies on metal contamination in 25 de Mayo Island, Antarctica, yielded controversial results. In this work, we analyzed Antarctic marine sediments and Antarctic clam (*Laternula elliptica*) tissues to investigate the possible use of this mollusk as a biomonitor of metals and to identify the sources of metal pollution. Different types of paint from several buildings from Carlini Station were examined to assess their contribution to the local and random metal pollution. Five sediment samples, 105 *L. elliptica* specimens (40.2–78.0 mm length) and four types of paint were analyzed to quantify Cd, Cr, Cu, Fe, Mn, Pb and Zn using inductively coupled plasma-optical emission spectrometry. Metal concentrations in sediments were lower than the global averages of the earth's crust, with the exception of Cd and Cu. These results were related to the contribution of the local fresh-water runoff. The different varieties of paint showed low levels of Cu, Mn, Fe and Zn, whereas a broad range of values were found in the case of Cr and Pb (20–15,100 $\mu g \cdot g^{-1}$ and 153–115,500 $\mu g \cdot g^{-1}$ respectively). The remains of the paint would be responsible for the significant increases in Cr and Pb which are randomly detected by us and by other authors. High levels of Fe and Cd, in comparison to other Antarctic areas, appear to be related to the terrigenous materials transported by the local streams. Accumulation indexes suggested that kidney tissue from *L. elliptica* could be an adequate material for biomonitoring pollution with Cd, Zn and probably also Pb. In general, relationships between size and metal contents reported by other authors were not verified, suggesting that this issue should be revised.

1. Introduction

The isolation from great industrial centers, the scarce population, the absence of natural resource exploitation activities and the dominant wind patterns that reduce, to some extent, the arrival of pollutants from industrial centers justify the consideration that the Antarctica is one of the last pristine regions of the planet. Although this is true for most of the inner zones in continental Antarctica, which remain unexplored, the coastal areas have received the impact of the establishment of human settlements since the beginning of the 20th century. With eight stations from different countries operating permanently, 25 de Mayo Island exhibits the highest human presence in Western Antarctica.

* Corresponding author at: Instituto Antártico Argentino, Balcarce 290, C1091AAF Buenos Aires, Argentina. Tel.: +54 11 4964 8269.
E-mail address: wmac@ffyb.uba.ar (W.P. Mac Cormack).

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Some of the studies dealing with metal contamination associated to human activities in 25 de Mayo Island reported evidence of metal enrichment in surface sediments (Alam and Sadiq, 1993; Santos et al., 2005), whereas others suggested that the detected levels in abiotic and biotic matrixes correspond to the basal levels (Ahn et al., 1996, 2004; Andrade et al., 2001; Farías et al., 2002; Abele et al., 2008).

In Potter Cove, the metal input to the coastal marine ecosystem results from combination of two main phenomena: 1) The natural contribution from the coastal rockeries, through surface runoff and subglacial melt-water input and 2) contribution from local anthropogenic sources associated to logistic and scientific activities in Carlini Station. Chemicals from this station are introduced to the coastal marine environment through wastewater, leakages from dumpsites, ship operations and deposition of particles produced during station activity. Studies with marine sediments from Potter Cove basin in the mid-90s suggested that the levels of heavy metals represented basal levels (Andrade et al., 2001; Vodopivez et al., 2001). However, more recent works reported evidence of contamination in sediments near Carlini Station, where Igeo class 2 (moderately polluted area) was reported for Pb, Fe and Cd (Curtosi et al., 2010). Results showed that Pb enrichment could be directly associated with anthropogenic sources of pollution, while Cd and Fe enrichment could be related to the natural input of particulate material carried by melt-water runoff during the summer season.

It is known that the mobilization of trace elements of eco-toxicological interest (As, Cd, Cu, Hg, Pb, Se, Zn), or transition metals (Fe, Mn), either in soluble forms or linked to particulate matter, affect the concentration of these elements in the tissues of marine organisms (Ahn et al., 2004; Philipp et al., 2008, 2011). For this reason, the identification of potential sentinel species for environmental pollution monitoring in Antarctica has been considered a crucial issue by the Scientific Committee on Antarctic Research (SCAR/COMNAP, 1996; SCAR, 1999). In this respect, two Antarctic bivalves, the scallop *Adamussium colbecki* (Smith, 1902) and the clam *Laternula elliptica* (King and Broderip, 1831) have been identified as suitable for this purpose. Whereas *A. colbecki* has been extensively studied in the coasts of the eastern Antarctica (Berkman and Nigro, 1992; Nigro et al., 1997; Dalla Riva et al., 2004), *L. elliptica* has been mainly studied in western Antarctic coasts (Ahn et al., 1996; Ahn et al., 2001; Lohan et al., 2001). The clam *L. elliptica* has proved to be useful for estimating basal values of contaminants and has been suggested as a possible biomonitor of metal levels in the coastal marine environment (Ahn et al., 1996; Nigro et al., 1997; Dalla Riva et al., 2004). This bivalve meets the prerequisites needed to propose an organism as a metal biomonitor in the Antarctic marine coastal environment (Phillips, 1990): a broad distribution around the Antarctic continent (Linse et al., 2006), longevity of more than 36 years (Philipp and Abele, 2010), great availability of tissue for analysis and the existence of studies proving bioaccumulation and detoxification (Choi et al., 2007). In addition, simple relationships were reported for metal concentration in gill and digestive gland and body size (Ahn et al., 2001). A Previous study performed with bivalves from Potter Cove, reviewed the concept about the use of *L. elliptica* for evaluation of changes associated to the increased input of particulate material caused by glacier retraction. This study concluded that an elevated sediment ablation does not *per se* result in higher metal accumulation in *L. elliptica*, and suggested that higher metal accumulation in gills and digestive glands could be associated with the uptake of planktonic or detritic food enriched with heavy metals, or with the uptake of dissolved metals (Poigner et al., 2013). Another study (Dick et al., 2007) showed that the incorporation of several elements (including Fe, Mn, Cu, Pb and others) into the umbo matrix of *L. elliptica* is primarily coupled to respiration mass, and no change related to global warming or anthropogenic activity could be discerned.

Based on all the above mentioned (and sometimes controversial) antecedents and as trace and minor elements in biota from extreme regions of the planet (Antarctic, Arctic and related areas) play a pivotal role to assess global pollution and evaluate the effects of climate changes (Caroli and Bottoni, 2010), the objectives of the present study were: 1. To review the results obtained during the 2005–2006 Antarctic summer expedition regarding the samples of marine sediments and mollusks bivalves collected close to Carlini Station, in the site where a moderated pollution for Cd and Fe had been previously reported (Curtosi et al., 2010). 2. To assess the accumulation trend in three key organs (gill, digestive gland and kidney) from specimens of *L. elliptica* with different body sizes, to test the simple relationship between body size and metal content and to compare our results with other reports from other Antarctic areas. 3. To investigate the potential contribution of the outdoor paint from different buildings of Carlini Station to the high level of metals detected in some samples of soil, marine sediment and tissues of marine organisms.

2. Materials and methods

2.1. Studied area and sampling methods

Marine sediments and bivalves were collected on the south-eastern coast of Potter Cove, nearby the Carlini (formerly Jubany) Scientific Station during the 2005/06 Summer Antarctic Campaign. Two main turbid melt-water streams flow into the cove during spring and summer. These streams, which transport melt-water from terrigenous ice fields and submerged glaciers, collect substantial amounts of lithogenic particles that are discharged into the Potter Cove basin (Fig. 1). One of the streams, Potter Creek, transports melt-water from Fourcade glacier directly into the innermost part of the cove, whereas the other, Matías Creek, transports water from ice free areas located near the "Tres Hermanos" hill and is fed mainly by snow precipitation. The studied area is directly impacted by the action of Matías Creek and only to a lesser extent by the Potter Creek.

Surface sediments and bivalve sampling area consisted in an imaginary 250 m long and 50 m wide rectangle (Fig. 1). This area corresponds to that named as site 6 by Curtosi et al. (2010) during 2004/05 which was reported as moderately polluted with Cd and Fe. The area ranges from 5 to 10 m deep and represents a site with a high bivalve population density (up to 370 ind/m^2 at 5 m deep), as was reported by Urban and Mercuri (1998).

2.1.1. Surface marine sediments

Four sediment samples, corresponding to the vertexes of the imaginary rectangle, and an additional one from the central zone were taken manually by scuba divers using 500 mL high-density polyethylene flasks previously washed with nitric acid and rinsed with ultrapure water (resistivity 18 MΩ·cm). Each sample was taken (and further processed) by quintuplicate. Immediately after collection, samples were transported to Carlini Station, homogenized and fractionated into two aliquots of 250 g approximately (one for texture and organic matter content analysis and the second one for trace element quantification). Both aliquots were frozen at −20 °C and subsequently freeze-dried to constant weight (approximately 48 h). Once frozen-dried, each sample was homogenized, sieved (1 mm mesh), distributed in five glass vials of 25 mL each and stored at −20 °C until processing.

2.1.2. L. elliptica

Specimens of *L. elliptica* were manually collected by scuba divers and placed in 20 L plastic containers with seawater for transportation to Carlini Station. Once at the station, specimens were kept for 72 h in an aquarium, at 0 °C with continuous aeration. Specimens used for metal quantification ($n = 105$) were grouped according their shell length in ranges differing 10 mm. Twenty one samples, composed by 5 individuals each, were obtained. The samples were distributed as follows: <50 mm (2 samples), 50–60 mm (4 samples), 60–70 mm (10 samples), 70–80 mm (4 samples) and >80 mm (1 sample). Specimens from each sample were dissected and gills, digestive gland and kidney were separated. Because of the gelatinous nature of these bivalves, a brief freezing

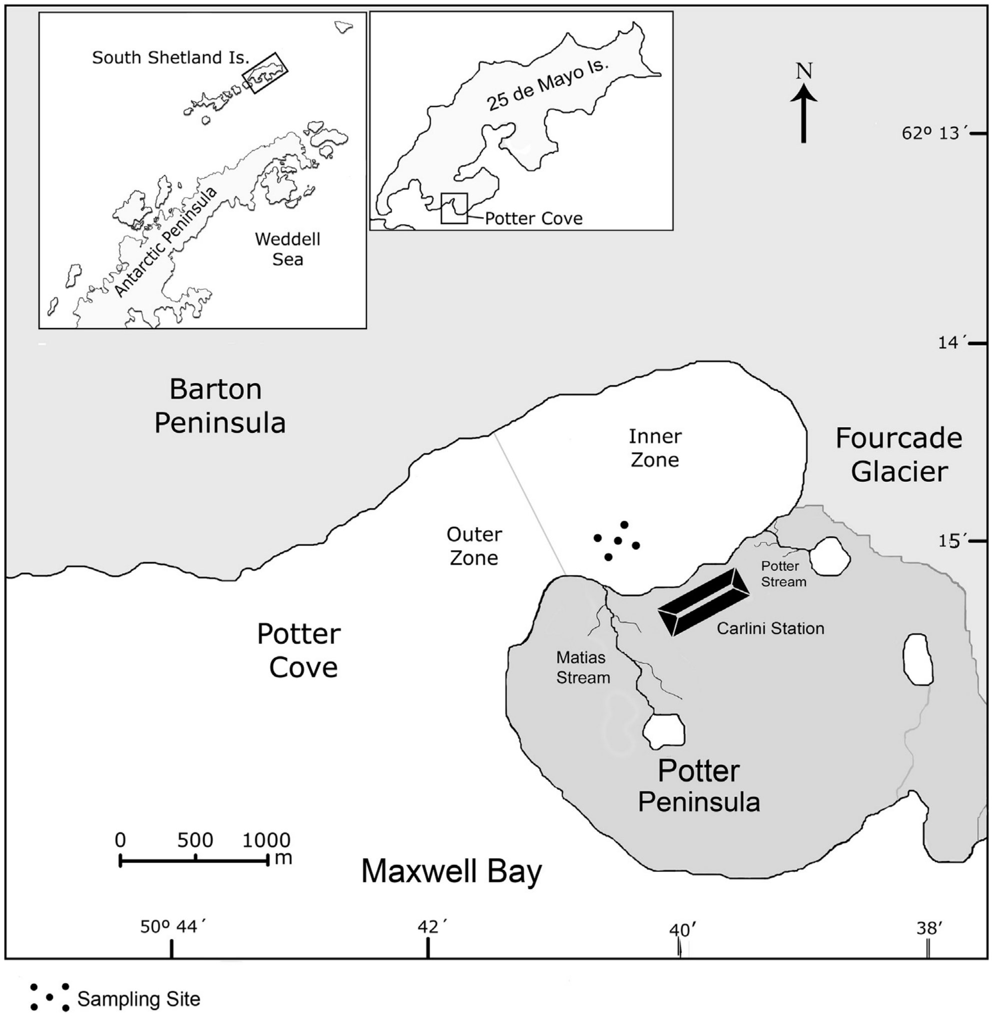

Fig. 1. Geographic location of Potter Cove. Position of the sampling site, the two main streams that outflow into the cove and Carlini Station are indicated.

period was applied (90 min at −20 °C) in order to facilitate handling. Gills from the five specimens corresponding to each sample were pooled in one glass vials (25 mL), frozen and freeze-dried to constant weight (48–72 h). Subsequently, the freeze-dried material was ground and mixed using a glass rod. The same protocol was applied to digestive glands and kidneys.

Specimens (n = 12) used to analyze length–dry weight relationship had shell lengths ranging between 40.2 and 78.0 mm and fresh weights ranging between 1.047 and 6.118 g. The age estimated by von Bertalanffy growth function ranged from 6 to 25 years old. The whole amount of the soft tissue from each specimen was freeze-dried to constant weight. Weighing was performed with an analytical balance (Mettler, 0.0001 g precision). The valves' length was established by measuring the major axis with a caliber (precision: 0.1 mm).

2.1.3. Exterior paints

Regarding the exterior paint sampling, this was carried out on February 2008, under the frame of the Argentinean Program of Environmental Monitoring at Carlini Station when the influence of peeling of paint on the coastal environment was examined. Results were taken into account in order to explain the presence of high values of some metals in sediments and gills tissue samples.

Four random types of orange paint were selected based on their different appearance and date of use. The paint layers selected exhibited signs of deterioration, evidencing the occurrence of previous peelings. Sampling was performed using a stainless steel clip, and the samples (n = 5 for each paint type) were placed in nitric acid pre-treated glass vials (25 mL) and stored at room temperature until processing.

2.2. Sample processing and analytical methods

The analytical method applied represents a modification of the previously proposed by Farías et al. (2002). Validation of this method was carried out according rules of IUPAC (Thompson et al., 2002) using for the evaluation of the initial performance the CRM MURST-ISS-A2 (Antarctic krill) from Istituto Superiore di Sanita, Rome. The study found a quarterly linear range for all the examined elements between 0.1 and 1000 μg/g.

The limit of detection (LOD) and limit of quantification (LOQ) were calculated following the IUPAC rules (Thompson et al., 2002) on the basis of the 3 and 10 σ criteria respectively from 10 replicate measurements of a blank control solution. LOD values varied between 0.05 μg/g (Mn) and 0.3 μg/g (Cr). Instruments and materials used are described in Sections 2.2.1 and 2.2.2. Sediments and bivalve samples were processed and analyzed between October 2006 and April 2007 whereas paint samples were analyzed on March 2008.

2.2.1. Acid digestion of the samples

For sample digestion a MLS-2000 (Milestone-FKW, Sorisole, Bergamo, Italy) microwave (MW) device equipped with ten Teflon-PFA (perfluoroalkoxy) vessels was used. All samples (marine sediments, paint and bivalve tissues) except kidney tissue were treated according to the following procedure: 0.3 ± 0.03 g portion of dried material was transferred into the Teflon vessel and 7.0 ± 0.1 mL of HNO_3 70% (J.T. Baker, USA, for trace metal analysis quality) was added. Due to the scarce mass of the kidneys (0.150–0.200 g) the whole organ mass was weighed. After that, samples were treated in the MW device (power applied during the digestion step varied from 250 to 600 W). The extract was allowed to cool down, transferred into 25 mL volumetric flask (A class), 1.0 mL of HNO_3 was added, and adjustment to volume was achieved through the use of ultra-pure water. With both, organic and inorganic matrixes, certified reference materials (CRMs) were processed in order to evaluate the accuracy of the analytical method. Standard solutions were also included. Sediment and paint samples were processed by quintuplicate and the tissues by triplicate except for the kidney samples, which permitted one measurement only.

2.2.2. Analytical determinations

For metal quantification, a Perkin-Elmer (Norwalk, CT) ICP Optima 3100 XL (axial view) simultaneous inductively coupled Ar plasma optical emission spectrometer was used.

Calibration curves were obtained with multi-elemental standards prepared in 0.7 mol/L HNO_3. To assess the accuracy of the analytical method, one portion of the digested CRM was subjected to the same analytical procedure. The CRM materials used were MURST-ISS-A1 (Antarctic Sediment) and MURST-ISS-A2 (Antarctic Krill). In all cases, recovery values ranging from 90 to 108% were obtained, and they were considered acceptable based on the values stated by the Council of Managers of National Antarctic Programs (COMNAP/SCAR 2000). Relative Standard Deviation (%RSD) for the MURST-ISS-A1 ranged between 4.3 (Fe) and 15.1 (Pb) whereas %RSD for MURST-ISS-A2 ranged between 0.4 (Fe) and 4.2 (Cd). Reference and experimental concentration values for Cd, Cr, Cu, Fe, Mn, Pb and Zn in the CRM are shown in Table 1.

Sediment samples for texture analysis were treated with 30% H_2O_2 to remove OM, washed with distilled water to remove all soluble salts and then dispersed with a sodium hexametaphosphate solution (5.5 g/L). The gravel/sand fraction was separated from silt/clay fraction using a 62.5 μm screen (4 phi). Grain size analysis for particles finer than 4 phi was performed using a Sedigraph CILAS 1180.

2.3. Statistical analysis

Comparison of metal levels and OM content between sediment samples was carried out using one-way ANOVA and a posteriori Tukey–Kramer test. Metal concentration in samples of a specific organ was related to its shell length, and the regression lines were fitted by the least squares method. The same procedure was used to relate soft tissue dry-weight to shell-length. The differences between metal content in the three analyzed tissues were tested using nonparametric ANOVA test (Kruskal–Wallis) followed by Dunn test in order not to remove the outliers. Spearman's correlation coefficients were calculated for each pair of metals and for each tissue. All data were analyzed using statistical program InStat 3.05, GraphPad Software Inc., USA.

Table 1
Metal concentration in the certified reference materials for sediments (CRM MURST ISS-A1) and biological tissues (CRM MURST ISS-A2). Values represent mean ± standard deviation from 5 independent replicates.

Element	CRM MURST ISS-A1 Concentration (μg/g)		CRM MURST ISS-A2 Concentration (μg/g)	
	Certified	Experimental value	Certified	Experimental value
Cd	0.538 ± 0.027	0.49 ± 0.04	0.73 ± 0.06	0.72 ± 0.03
Cr	42.1 ± 4.4	39.5 ± 3.5	0.73 ± 0.14[a]	0.67 ± 0.02
Cu	6 ± 2[a]	5.4 ± 0.3	65.2 ± 2.3	64.1 ± 0.4
Fe	2440 ± 70	2300 ± 100	56.6 ± 2.3	55.7 ± 0.2
Mn	446 ± 19	425 ± 20	4.12 ± 0.10	4.1 ± 0.1
Pb	21.0 ± 2.9	19.9 ± 3.0	1.11 ± 0.09	1.2 ± 0.03
Zn	53.3 ± 2.7	52.1 ± 3.1	66.0 ± 2.0	64.6 ± 0.6

[a] Informative value.

3. Results and discussion

3.1. Surface marine sediments and paint samples

The five sediment points examined showed a great homogeneity in terms of concentration of the analyzed metals, and fraction <63 μm. In fact, one-way ANOVA showed no significant differences between the 5 sites examined, except for a subsample, for which very high values of Cr and Pb (42 μg/g and 16 μg/g respectively), were detected. These values were considered outliers (Dixon's Q test, Q 99%) and were not included in the calculation of averages.

In general, mean level of metals found in surface marine sediments from Potter Cove were lower than the global averages of the earth's crust, with the exception of Cd and Cu. Table 2 shows the global descriptive statistic obtained for the seven elements studied (Cd, Cr, Cu, Fe, Mn, Pb and Zn), the fraction <63 μm and the organic matter content from the five sediment points analyzed (each point was composed of five independent subsamples). Also the average values reported by Curtosi et al. (2010) from nine stations from Potetr Cove are included. It is important to remark that for the case of Cd, the average reported by Curtosi et al. (2010) could be slightly overestimated, because four of the values reported as lower than 0.1 μg/g were assumed as 0.1 for the calculation of the average.

The mean Cd value in the working area (0.62 μg/g), was higher than the mean values reported for Potter Cove (Curtosi et al., 2010) as well as for other areas of KGI (Ahn et al., 1996; Santos et al., 2005). In a first instance, this difference appears to be linked to the influence of the Matías Creek, which could transport soil particles enriched with this element from Potter Peninsula. In this sense, similar levels of Cd in soil samples were reported by us in a previous study (Vodopivez et al., 2008). In fact, in this previous work, we detected levels of Cd which ranged between 0.5 and 0.8 μg/g in nine samples of surface soil collected in the surroundings of Carlini Station, with a moderate increase near the incinerator area (1.1 μg/g). This Cd enrichment resembled that reported by Negri et al. (2006) for sediments from McMurdo Sound, where levels of 0.4 μg/g were detected in marine sediments directly exposed to the activity of McMurdo Station (close to a wastewater drain and about 200 m from the historical dumpsite), against the 0.12 μg/g found in sediments from the area considered as blank (Turtle Rock). Although Cd levels as high as 19.2 μg/g (Alam and Sadiq, 1993) and 10 μg/g (Lenihan et al., 1990) were reported for coastal sediments from Potter Cove and Winter Quarters Bay respectively, these values were associated with local phenomena resulting from human contamination from unidentified sources. The grain size of the sediments and soil particles transported by the Matías Creek is an important factor to take into account. In fact, Dalla Riva et al. (2004) reported that in Terra Nova Bay, the levels of Cd in sediments are strongly influenced by particle size, reporting total Cd values of 0.29 μg/g for the fraction <2000 μm but values almost 20 times higher in the fraction <63 μm (5.40 μg/g).

Table 2
Descriptive statistics for the concentration levels of the seven studied metals (μg/g), sediment fraction <63 μm (%) and organic matter content (%) in sediment samples. Mean values were calculated from five points, each one comprising five independent subsamples.

	Cd	Cr	Cu	Fe	Mn	Pb	Zn	<63 μm
Mean (n = 25)	0.62	5.6	73	33,520	695	5.4	58	75
Standard deviation (SD)	0.05	1.0	11	661	5	0.3	5	7
Range	0.13	2.3	28	1300	10	0.9	11	19
Minimum	0.56	4.2	54	32,800	690	4.9	52	66
Maximum	0.69	6.5	82	34,100	700	5.8	63	85
Average from Curtosi et al., 2010 (n = 9)	0.25	7.0	103	19,665	798	7.6	56	–

In this sense, it should be noted that in the studied area the fraction <63 μm represents 75%. A detailed study of the geochemistry of Potter Peninsula and Matías Basin soils is needed to confirm the levels of Cd and their origin.

In the same way, the enrichment with Fe in the study area compared with the average value reported by Curtosi et al. (2010) is clearly associated with the Matías Creek discharge. Fe levels (between 28,400 and 30,504 μg/g) similar to those determined for the studied area were detected in surface sediments of Matías Basin by Vodopivez et al. (2001). Moreover, reinforcing the hypothesis of the strong influence of the Matías stream on marine sediments near its outlet, the Fe/Mn and Fe/Cu ratios (48 and 459 respectively) in surface sediments obtained in this study were similar to those reported by Abele et al. (2008) for suspended particulate from Potter Cove near the outlet of Matías stream. Husmann et al. (2012) reported higher levels of Fe and Mn (>50,000 μg/g and >940 μg/g respectively) and similar levels of Cu and Zn (about 90 and 80 μg/g respectively) for sediment cores collected close to the study area. Although the samples were collected two years later, and the quantitative analysis was different (Husmann et al., 2012 used quantitative WD XRF analysis for determination of Fe, Mn, Cu and Zn), the differences observed between the two studies could also be explained by the moderate acid digestion used in our digestion procedure. As can be observed in Table 1, the concentrations found in this study for the CRMs were always 5 to 10% lesser than the certified values. Certified values have been obtained from samples completely dissolved (In accordance with the procedures required in the certification exercise) while in our acid digestion an insoluble siliceous fraction remains after the HNO_3 attack.

The high Cu level in Potter Cove has been associated with the geochemical characteristics of Barton Peninsula, where rocks are found to have high levels of Cu (Yeo et al., 2004) not attributable to a local pollution phenomenon (Ahn et al., 1996, 2004; Choi et al., 2003). Water streams enriched with Cu from Barton Peninsula are spilled into the cove during spring and summer, determining the high levels of this metal in the cove. The lower level of Cu in the study area, compared with the average value of the cove, could be attributed to a dilution effect of the Matías stream. In fact, low levels of Cu have been reported for this stream either soluble (Abele et al., 2008) or associated to the particulate matter (Vodopivez et al., 2001).

We mentioned above we detected the presence of anomalous values for Cr and Pb in a sediment subsample. Also in our own previous study, high levels of Cr, Fe and Mn were detected in a muscle sample of *L. elliptica* and in a sample of *Nacella concinna* (Curtosi et al., 2010). Before that, a similar finding had been reported by Vodopivez et al. (2008) for soils around Carlini Station. In our study, we reported an increase of Cr and Pb in pairs in soils from sites exhibiting high anthropogenic impact, and we suggested that these values could not be attributed to variations in regional geochemistry and seemed to be associated to surface contamination phenomena caused by particle deposition, presumably originated from remnants of exterior paint. Given that the station was established in 1953, remodeled several times and frequently painted, many paint layers of different origins and ages were identified. As can be seen in Table 3, the metal content in paints tested varied within a very broad range of up to three orders of magnitude. All paint showed low content of Cu and Mn. In general, Fe and Zn contents were also low, but varying within a wider range. Cr content varied between 20 and 15,100 μg/g, while the Pb content ranged between 153 and 115,500 μg/g. Paint no. 1 showed the lowest content of Cr and Pb, followed by paint no. 2. Paint no. 3 and paint no. 4 showed the highest contents of Cr and Pb. Paint no. 3 showed the highest Cd level (the only paint sample where Cd was detected) and Zn. Paint layers come off by the normal deterioration or when removed during painting tasks. Their subsequent dispersal by winds or by water during the thawing season could be responsible for the significant increases in Cr and Pb levels detected in the previously mentioned subsample.

3.2. *L. elliptica* samples

It was reported that bivalve mollusks typically exhibit a relationship between body mass and metal content. Boyden (1974, 1977) expressing this relationship as a linear function: $\log [TE] = \log a + b \log M$, where "[TE]" is the concentration of the trace elements in the tissue examined, "a" and "b" are constants and "M" is the body mass of the organism. However, some authors have recognized that the total soft tissue weight has a great variability, and for this reason other parameters related to size, such as weight or length of the valves have been employed. The variability of the total soft tissue weight is attributed to methodological differences and also to natural factors, mainly life cycle, because body mass is clearly affected by the spawning cycle (Páez-Osuna et al., 1995). For *L. elliptica*, and most of the Antarctic bivalves, spawning occurs between December and February, in synchronicity with the more frequent sampling periods, during summer expeditions. Regarding the methodological problems, the relationship between total soft tissue dry weight (TST DW) and shell length (SL) was tested (Fig. 2A), resulting in a linear regression for the whole lengths (40.2–78.0 mm) and masses (1.047–6.118 g) of the ranges studied. Linear regression was highly significant ($P < 0.001$) and did not deviate significantly from linearity ($P = 0.197$). Based on the presence of this correlation and because the gelatinous nature of fresh tissues could cause a rapid loss of intracellular fluids leading to a loss in body mass during the handling of samples (Ahn et al., 2001) we correlated the level of trace metals with shell length of *L. elliptica*.

The metal content in organs was evaluated in 105 specimens with an average length of 64.2 mm. Table 4 shows the descriptive statistics of the metal contents determined in gill, digestive gland and kidney whereas in Table 5 the Spearman correlation coefficients for each pair of elements analyzed and for every organ examined are shown. Two extreme Cr values detected in gills (120 and 63 μg/g) were considered as outliers and therefore eliminated from the descriptive statistics analysis using Dixon's Q test (Q 99%).

In general, statistical analysis of our data showed no significant correlation between SL and metal content. Exceptions ($P < 0.01$) are shown in Fig. 2B, C (significant correlation between Cd content and SL in gills and DG respectively, both with positive slopes) and 2D (significant correlation between Mn and SL in DG showed a significant correlation, but with a negative slope). Significant regressions between SL and TST DW, SL and Cd in gills and SL and Mn in DG agree with those reported by Ahn et al. (2001) for Marian Cove. In addition, both works are also coincident in the absence of significant regression in kidney for all metals examined, the prevalence of positive slopes for Cd, Cr, Fe, Mn in gill and negative slopes for Cd, Zn and Mn in DG. Husmann et al. (2012), reported that metal accumulation (Cd and Fe) in

Table 3
Metal content (μg/g) in four different exterior paints used in Carlini Station. Values represent means ± SD from five replicates.

Paints[a]	Cd	Cr	Cu	Fe	Mn	Pb	Zn
1	<0.5	20 ± 2	4.2 ± 0.4	12,600 ± 600	145 ± 7	153 ± 8	7800 ± 400
2	<0.5	4600 ± 200	<0.5	500 ± 25	24 ± 1	5600 ± 300	4800 ± 250
3	146 ± 10	15,100 ± 700	6.9 ± 0.7	3700 ± 200	300 ± 15	114,500 ± 5500	12,250 ± 650
4	<0.5	8500 ± 400	6.8 ± 0.7	1400 ± 100	130 ± 7	115,500 ± 5500	110 ± 6

[a] Paint 1: aquarium coating. Paint 2: liquid nitrogen generation facility coating. Paint 3: refrigeration chamber coating. Paint 4: radio building coating.

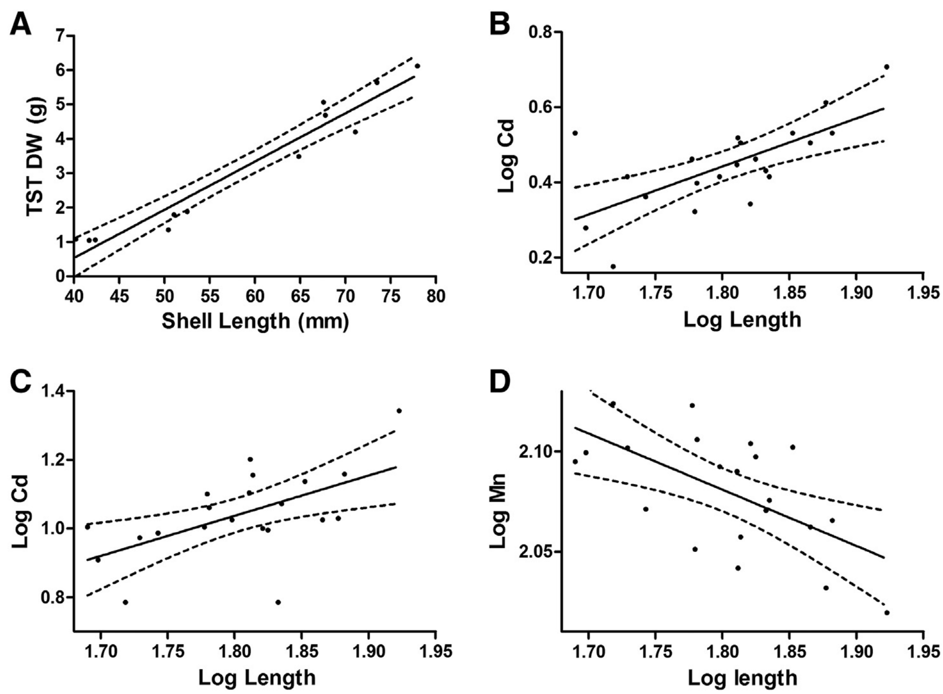

Fig. 2. A. Relation of shell length (mm) to total soft tissue dry weight (g) of *L. elliptica*: a = 5.077, b = 0.140, r^2 = 0.969. Relationships between shell length to metal content for Cd in gill (B, a = −1.858; b = 0.682; r^2 = 0.465), Cd in digestive gland (C, a = −1.068; b = 1.170; r^2 = 0.325) and Mn in digestive gland (D, a = 2.586; b = −0.281; r^2 = 0.366). Doted lines represent the 95% confidence interval.

L. elliptica specimens from Potter Cove was generally higher in larger individuals compared to smaller ones, indicating an irreversible accumulation of heavy metals throughout the animal's lifetime. Conversely, levels of Mn, Zn and Cu were reported higher in some tissue of the younger specimens. The prevalence of positive slopes for the relationship size–metal content is probably due to the fact that when growth predominates over metal absorption, a dilution effect of the metal content occurs. In almost all species, younger organisms (smaller size) grow faster than adults, thereby inducing a greater dilution effect reflected in a positive slope. Also, positive slopes have been associated with very low rates of metal excretion and absence of regulatory mechanisms of metal uptake. In these cases, the accumulation of metals occurs throughout the life of the organism, thus higher metal content is expected in older individuals. In Antarctica, marine organisms are characterized by slow growth rates compared with similar organisms from temperate regions. *L. elliptica*'s shell reaches 100 mm length in more than 30 years (Philipp et al., 2008), while a clam of similar characteristics in temperate regions usually requires no more than four years to reach that size. It is possible that the prevalence of positive slopes in size–metal content relationship in *L. elliptica* could be associated with its slow growth and longevity. Furthermore, both Ahn et al. (2001) and Husmann et al. (2012) suggested that negative slopes

Table 4
Descriptive statistics of metal contents in gill, digestive gland and kidney of *Laternula elliptica*. Values are expressed in μg/g dry weight. n = 21 for all examined samples except for Cr in gills (n = 19), every sample is a pool of 5 individual each.

	Cd	Cr	Cu	Fe	Mn	Pb	Zn
Gill							
Mean	2.9	0.78	8.6	1100	18	0.70	107
Standard deviation (SD)	0.8	0.5	5.5	550	13	0.30	17
Range	3.6	1.8	25.6	2550	58	0.97	55
Minimum	1.5	0.5	6.2	600	9	0.19	84
Maximum	5.1	2.3	31.8	3150	67	1.16	139
Digestive gland							
Mean	11	2.1	73	856	7.4	1.4	120
Standard deviation (SD)	3	2.4	14	263	3.0	0.6	8
Range	16	8.9	57	872	10.5	2.1	28
Minimum	6	0.5	52	541	4.6	0.4	105
Maximum	22	9.4	108	1413	15.1	2.5	133
Kidney							
Mean	129	0.9	7.3	3150	240	68	2650
Standard deviation (SD)	27	0.6	3.8	2150	76	97	750
Range	95	2.3	17	9100	304	460	3200
Minimum	88	0.5	4.5	900	106	29	1300
Maximum	183	2.8	21.5	10,000	410	489	4500

Table 5
Spearman correlation coefficient for each pair of metals in the different organs examined in *L. elliptica*. DG: digestive gland.

	Cd	Cr	Cu	Fe	Mn	Pb	Zn
Gill							
Cd	1	0.363	0.152	0.596*	0.132	0.117	−0.435**
Cr		1	0.558*	0.732*	0.513**	0.427**	−0.171
Cu			1	0.449**	0.400**	−0.009	0.069
Fe				1	0.756*	0.378**	−0.265
Mn					1	0.081	−0.131
Pb						1	−0.306
Zn							1
DG							
Cd	1	0.118	0.154	0.529*	−0.298	0.336	−0.567*
Cr		1	−0.348	0.376	−0.196	−0.528*	−0.184
Cu			1	0.127	0.261	0.156	−0.177
Fe				1	0.271	−0.191	−0.738*
Mn					1	−0.456	−0.211
Pb						1	0.207
Zn							1
Kidney							
Cd	1	0.148	−0.236	0.071	0.606*	0.222	0.740*
Cr		1	0.131	0.039	−0.019	−0.033	0.151
Cu			1	0.194	−0.061	−0.176	−0.442**
Fe				1	0.375	−0.124	−0.039
Mn					1	0.000	0.555*
Pb						1	0.348
Zn							1

* P < 0.01.
** P < 0.05.

found for Cu, Mn and Zn (in the present study these trends are reflected most clearly for Mn and Zn) may be associated with higher filtration rates of smaller individuals. This fact suggests that these elements could be linked to diet and/or particulate matter intake.

As is shown in Table 4, when metal content in all three organs was compared, kidney, showed significantly higher content ($P < 0.01$) of Cd, Fe, Mn, Pb and Zn, while in digestive gland higher levels of Cu were found. Statistical analysis of metal content in the three organs showed significant differences for almost all elements examined. The distribution of metals in the organs is in agreement with previous reports (Fattorini et al., 2008; Ahn et al., 1996, 2001; Lohan et al., 2001; Husmann et al., 2012), for which trends were as follows: for Cd and Pb, kidney > DG > gill; for Cu, DG > gill ≅ kidney; for Fe, kidney > gill ≅ DG; for Mn, kidney > gill > DG and for Zn, kidney > gill ≅ DG.

The accumulation of some elements in the kidney was notorious compared to the levels found in shallow marine sediments (SMS). The highest accumulation coefficients (metal concentration in kidney/ metal concentration in SMS) were found for the toxic metals Cd and Pb (208 and 13 respectively), and for Zn (46). For the rest of the studied metals, accumulation rates were always <1, varying between Cu = 0.1, Fe = 0.09 and Mn = 0.3. These differences suggest the existence of concentration regulatory mechanisms. The high levels of Cu in the sediments were not reflected either in gill or in kidney tissues but in DG, indicating preferential accumulation in this organ. Similar accumulation patterns were observed in whole specimens of *L. elliptica* collected around McMurdo and Scott stations (Negri et al., 2006).

When accumulation in kidney with respect to the other tissues was evaluated by means of the accumulation coefficients (Table 6), Kidney/ Gill relationship showed the highest values for Cd and Pb (44 and 97 respectively). Cu was the only metal that showed values <1 for both ratios (kidney/gill = 0.8 and kidney/DG = 0.1), indicating a preferential accumulation in DG. This accumulation could be related to the incorporation of this metal through particulate material. In this sense, studies on mussels exposed to Cu have shown that, if Cu is associated to particulate material it is preferably concentrated in digestive gland, while soluble Cu is accumulated on gill (Viarengo et al., 1993).

The comparison of our results with those reported by Ahn et al. (2001) from 75 mm *L. elliptica* specimens (Table 6) showed very similar concentrations for all tested metals, evidencing a relatively constant pattern of accumulation in the three tissues for similar size/age specimens. By contrast, coefficients calculated from the results reported by Ahn et al. (1996) for 86 mm SL of *L. elliptica*, showed a marked decrease in the accumulation coefficients of all metals, mainly for Cd and Pb, suggesting that in specimens older than 30 years, some kind of excretion or regulation mechanisms could be present. In this sense, Ahn et al. (2001) reported stabilization or even a decrease in the levels of some metals for specimens over 80 mm. Even though the observed trends in the distribution of metals in the organs examined were similar in all these studies, average levels of metal contents differ markedly between specimens collected in different locations. A review of the levels of metals detected in the three organs examined for specimens from different Antarctic sites (KGI, Adelaide Island and Terra Nova Bay) can be found in Lohan et al. (2001).

In relation to the high levels of Cd in kidney tissue, it could be associated to the presence of metallothioneins or with calcium phosphate granules. Both mechanisms play relevant roles in the accumulation and detoxification processes of metals. It was observed that renal concretions of calcium phosphate (in scallops and clams) have longer half-lives (six months or more) than those observed in other organs (Viarengo et al., 1993; Lohan et al., 2001). In addition, Choi et al. (2003) confirmed the presence of metallothioneins in gill, digestive gland and kidney of *L. elliptica* whereas Choi et al. (2007) reported a metal-binding protein induced upon experimental Cd exposure in the gill and digestive gland of *L. elliptica*. Ahn et al. (1996) also suggested that high levels of Cd in kidney could be related to the presence of metallothioneins, this evidence being supported by the finding of significant correlations between Cd and Zn ($r = 0.696$, $P < 0.05$), Cd and Pb ($r = 0.660$, $P < 0.05$) and Cd and Mn ($r = 0.694$, $P < 0.05$) (r = Pearson correlation coefficient). Lohan et al. (2001) reported significant correlations between Cd and Zn ($r^2 = 0.946$, $P < 0.01$) and between Cd and Pb ($r^2 = 0.525$, $P < 0.01$) and suggested the same mechanisms. In agreement with these previous reports, in the present study significant correlations were found in kidney between Cd and Mn ($r = 0.606$, $P < 0.01$) and between Cd and Zn ($r = 0.740$, $P < 0.01$).

As was mentioned above, in the present study two outlier values for Cr (120 and 63 μg/g) were detected in gills. It is possible that these high values may be related with an anthropogenic emission source, for example some kind of paint with high Cr content, but low concentrations of the other tested metals.

Finally, we compared our results with those reported for tissues of *L. elliptica* obtained from other Antarctic locations but having similar shell lengths: Marian Cove (75 mm, Ahn et al., 2001), Adelaide Island (65.7 mm, Lohan et al., 2001) and Terra Nova Bay (65.0–90.0 mm, Nigro et al., 1997). For this purpose we used values from gills, because it was reported as the tissue exhibiting the lesser seasonal and life-cycle related variations (Ahn et al., 2001). In this comparison, Cr (due to the high contents found in some of our samples) and Cu (due to the high levels reported by Lohan et al. (2001), which were attributed to local contamination processes) were excluded from the analysis. Notwithstanding the above limitations, the comments in the following sections can be made for each analyzed metal.

3.2.1. Cadmium and zinc

The specimens collected in the Antarctic Peninsula showed lower concentrations of Cd and Zn than those from the East Antarctica (Terra Nova Bay). The high content of Cd in bivalves from Terra Nova Bay has been associated with the high bioavailability of this metal determined by the upwelling of trace elements enriched waters (Nigro et al., 1997). Cd in Antarctic waters would be a “recycling” element (elements that show positive correlation with micronutrients), correlating positively with phosphate concentration. Bargagli et al. (1996), who

Table 6
Comparison of the metal accumulation coefficients calculated from kidney tissues of *Laternula elliptica* by Ahn et al. (1996, 2001) and the present work. Average values are expressed as (μg/g).

Metal	Present study (ASL 64.2 mm) Estimated age vBGF = 15 years			Ahn et al. (2001) (ASL 75 mm) Estimated age vBGF = 20 years			Ahn et al. (1996) (ASL 86 mm) Estimated age vBGF > 30 years		
	Kidney (average)	Kidney/gill	K/DG	Kidney (average)	Kidney/gill	K/DG	Kidney (average)	Kidney/gill	K/DG
Cd	129	44	12	174	63	9.3	41.9	5.8	3.6
Cu	12.6	0.8	0.1	21	2.6	0.3	33.3	1.6	0.9
Fe	3150	2.9	3.7	6210	4.9	4.3	4318	2.2	2.2
Mn	240	13	32	260	18	35	190	4.3	10.2
Pb	68	97	48	87.8	98	25	37.7	13.6	6.9
Zn	2650	25	22	4155	33	35	1687	8.2	11

ASL: average shell length.

reported high levels of Cd in marine organisms from Terra Nova Bay, related it to the enrichment of surface waters caused by the upwelling and to the high coastal primary production rates. Cd incorporation by phytoplankton, together with the phosphate required for the normal development, would be the critical steps needed to transfer this element to other organisms. In addition, Dalla Riva et al. (2004) reported that in the marine sediments of Terra Nova Bay, a high fraction of Cd is bound to the labile phase in both, the pelitic fraction (52.8%), and the sediment with grain size <2000 μm (55.1%). They suggested that this trend of Cd may explain the high levels of this metal in the benthic organisms of this area, especially in detritivorous, suspensivorous and opportunistic bivalves (*L. elliptica*, *A. colbecki*). Regarding Cd found in the marine coastal environment of KGI, Ahn et al. (2004) reported that concentrations of suspended particulate matter (SPM), Al, Fe, Cu, Mn, Pb and Zn were notably high in areas near to melt-water sources. These concentrations sharply decreased when the distance from such melt-water sources decreased as well. Furthermore, substantial portions (40% to >90%) of all the metals, except Cd (<6%), were associated with SPM. Contrary to that, Cd was detected predominantly (>94%) in the dissolved form.

In relation to Zn, the specimens collected in the Antarctic Peninsula showed a similar trend to that observed for Cd, but varying within a narrower range.

3.2.2. Iron and manganese

The specimens collected in the Western Antarctic Peninsula showed the highest values. In addition, specimens from KGI evidenced higher concentrations than those found in Adelaide Island. The high levels detected in specimens from Marian Cove and Potter Cove are consistent with Fe values found in the geochemical studies carried out in Barton and Potter peninsulas and may be associated with the entry of Fe-enriched particles transported during the summer runoff (Ahn et al., 2004; Abele et al., 2008). A similar trend was observed for Mn. Recently, Poigner et al. (2013), reviewed this assumption. These authors considered the differences in sedimentation of terrigenous lithogenic material as insufficient for a complete explanation about Fe and Mn accumulation pattern in Potter Cove and attributed the high variability of Fe and Mn accumulation in tissues of *L. elliptica* around Antarctica to differences in the geochemical environment of the sediment and the resulting Fe and Mn flux across the benthic boundary. They also pointed out that Fe(II) discharged by anoxic subglacial waters into oxic seawater or surface freshwaters, is rapidly oxidized to ferrihydrite nanoparticles. Apparently bivalves would assimilate Fe nanoparticles via endocytosis by specific epithelial cells in gills and viscera. In contrast to the Fe behavior, Mn remains primarily as free Mn^{2+} and $MnCl^{+}$ in the water column (Roitz et al., 2002). Since silicate bound Mn is not bioavailable to the bivalves, dissolved Mn around the benthic boundary would constitute the major Mn source for *L. elliptica*. In summary, according to Poigner et al. (2013), at Potter Cove Mn would be assimilated as dissolved species, whereas Fe would precipitates as ferrihydrite nanoparticles prior to assimilation by the bivalve. The same authors recognize a potential influence of melt-water inlets on the Fe and Mn tissue contents in specimen located close to the coast, at less than 10 m deep. This could be a possible explanation for the high variation of Fe and Mn content in tissues of *L. elliptica* observed in this study.

3.2.3. Lead

The specimens collected in the KGI showed higher concentrations than those found in Adelaide Island and the East Antarctica. A possible Pb input to coastal waters in Potter Cove was attributed to Carlini

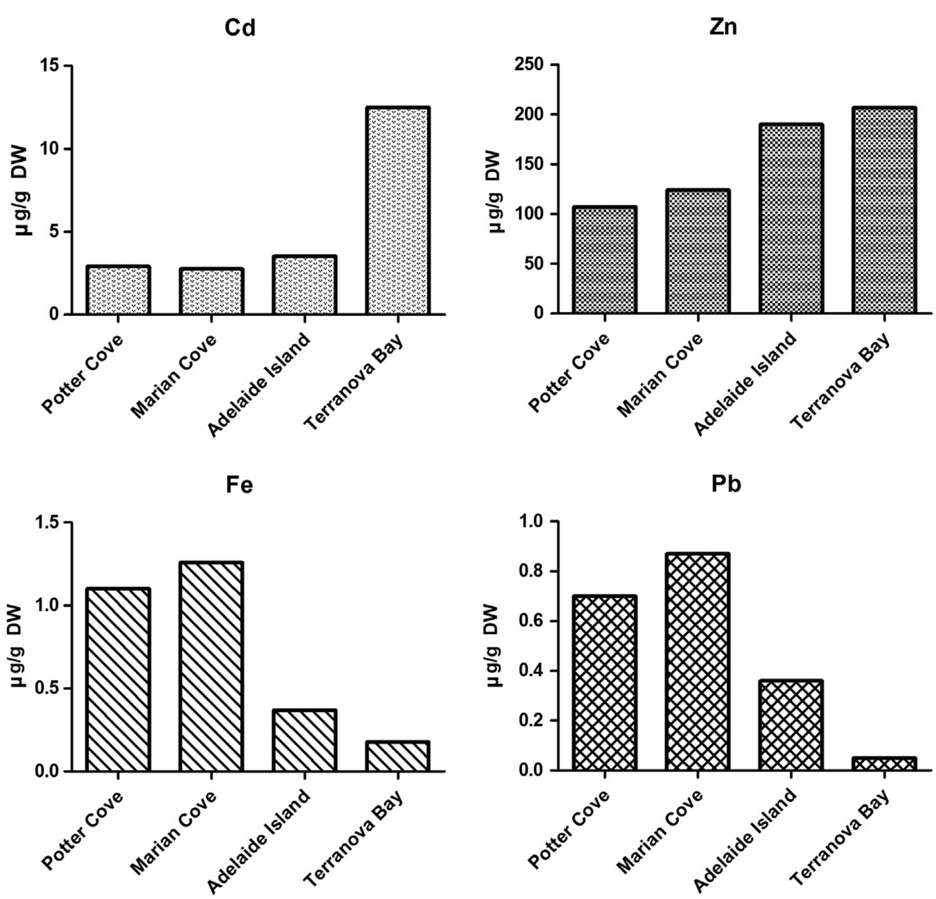

Fig. 3. Cd, Zn, Fe and Pb levels in gill tissue of *L. elliptica* obtained from Potter Cove (this work), Marian Cove (Ahn et al., 2001), Adelaide Island (Lohan et al., 2001) and Terra Nova Bay (Nigro et al., 1997).

Station activity and especially to the outboard engines of the inflatable boats used in the cove (Curtosi et al., 2009). For this reason, levels of Pb in *L. elliptica* detected close to KGI may be reflecting the input of terrigenous material transported by the glacier runoff, the anthropogenic contribution associated to the station or both. Concentration levels for Cd, Zn, Fe and Pb reported from the four compared sites are shown in Fig. 3.

3.3. Conclusions

The present study showed that *L. elliptica* tissues reflect the availability of metals in the study coastal marine area of Potter Cove. The high levels of Fe and Cd in the three tissues examined appear to be related to the contribution of Matías stream.

Regarding the relationship between body size and metal content, the trends previously reported by other authors were not verified, except for Cd in gill and Mn in DG, suggesting that this issue should be revised. Perhaps the metal content vs size/age could be improved, if growth band is used to determine age more precisely instead using shell length.

The peeling of exterior paint particles could be responsible of the high levels of Cr in gill tissue of *L. elliptica*. This point merits particular attention because values usually considered as outliers could be evidencing contamination in a random pattern distribution. Even though these data should not be included in the estimation of the mean values, they should not be ignored as they could represent a sign of anthropogenic contamination.

Accumulation indexes suggest that kidney from *L. elliptica* could be an adequate biomonitor species for Cd, Zn and probably also for Pb.

While the ability of this organism (and other possible biomonitor such as *A. colbecki*) to reflect availability of metals in the coastal environment is evident, knowledge of environmental conditions in the area under study is critical, because a simple comparison of mean values of specimens of the same species and size, but from different locations has a limited value. Therefore, a clear knowledge of the local geochemical characteristics, the influence of the ocean streams in the area, the local hydrographic conditions and coastal ecosystem functioning it is necessary for a proper interpretation of the meaning of the measured levels. In Potter Cove, the geochemical characteristics of the area, the transport of metals as particulate or soluble fraction from the terrestrial to the marine environment and the interaction between sediments and benthic organisms should be further investigated in a deeper and integrated way.

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