



# Biomonitoring Assessment of Toxic and Trace Elements in *Sterechinus neumayeri* Sea Urchins from the Comandante Ferraz Station in Antarctica

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## Abstract

In the present study, sea urchin *Sterechinus neumayeri* tissues were used for the passive biomonitoring of toxic and trace elements at the Comandante Ferraz Station, Antarctica and compared to a pristine region (Botany). As, Ba, Br, Ca, Co, Cr, Fe, K, Na, Rb, Sc, Se and Zn concentrations were determined by instrumental neutron activation analysis (INAA), while toxic metals (Cd, Hg, Ni and Pb), and Cu were determined by atomic absorption spectrometry (GF-AAS). The findings were compared to other organisms commonly applied for biomonitoring purposes and to the sediment concentrations of each sampling region. Urchins from the Ferraz Station area presented higher Br, Co, Cr, Cs, K, Se and Zn levels than the pristine location. The results obtained herein suggest *S. neumayeri* can be applied to the biomonitoring of Cr and Zn. The present study also contributes to knowledge of the mineral composition of the sea urchin *S. neumayeri*.

**Keywords** Antarctica · Sea urchin · Biomonitoring · Toxic and trace elements · Environmental contamination

The Antarctic region used to be considered preserved from human activities, especially concerning soil and water contamination. However, from the late 90 s, it was found that this region is also vulnerable to human actions, both locally, due to the presence of scientific stations, which perform garbage incineration, fuel storage and use and sewage discharges, and globally, by the global warming phenomenon and the transport of pollutants by winds and sea currents (Majer et al. 2014). Because of this, increased levels of Hg, Pb, organochlorines and plastics have been reported in this region (Santos et al. 2005). As a result, benthic Antarctic organisms located near research stations are more

susceptible to contamination by trace and potentially toxic elements, due to low fertility and growth rates (King and Riddle 2001; Santos et al. 2005).

The sea urchin *Sterechinus neumayeri* (Meissner 1900) is the most abundant species in shallow Antarctic waters, extending from the coast to about 400 m in water depth (Brey and Gutt 1991). These organisms are omnivorous, feeding on the substrate surface, including sediment, although they may seasonally become scavengers, especially in the face of food shortages and low ocean temperatures (McClintock 1994). This species lack of mobility and feeding mode, are considered premises for assessing local marine conditions, especially chemical element bioaccumulation. Therefore, *Sterechinus neumayeri* may meets the conditions to be applied as a biomonitor, similar to other frequently applied organisms, such as bivalves, oysters, crabs and macroalgae (Alves et al. 2017a). This sea urchin has, in fact, been used as a model organism in the reproductive biology, embryology, ecology and bioaccumulation fields (Grotti et al. 2008; Majer et al. 2014) and toxicology (King and Riddle 2001).

The King George Island region (Fig. 1) is located at the end of the Antarctic peninsula. This island contains the highest density of research stations in the entire Antarctica

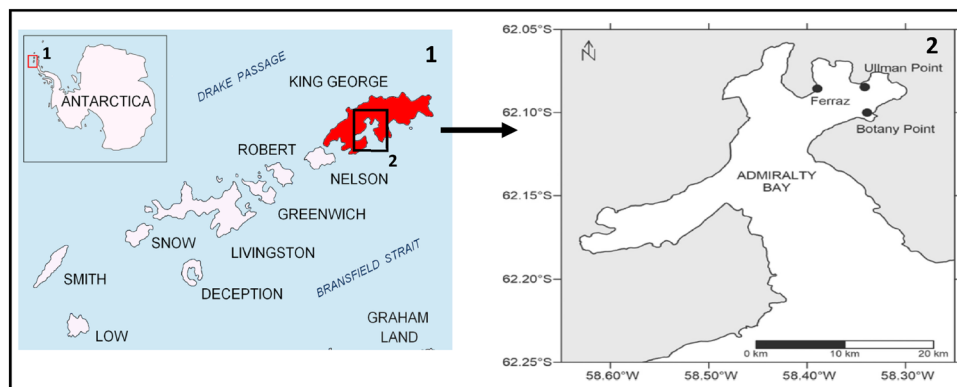
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**Fig. 1** Sampling sites of *S. neumayeri* urchins in Antarctica (adapted from Ribeiro et al. 2011)



peninsula, which may be related to the increasing environmental impacts observed in this region (Amaro et al. 2015). A region known as SSSI 8, “Site of Special Scientific Interest”, was created on the west coast of the island, where tourism is prohibited, and many environmental assessments are conducted. King George Island contains the Admiralty Bay, where the Brazilian environmental Antarctic Comandante Ferraz Station is located (Santos et al. 2005). This station was partially destroyed by a fire in February 2012, which consumed about 70% of installations. Some studies have pointed out possible sediment and biota contamination by anthropic activities in this region, especially after the 2012 fire, where high levels of Cu, Pb and Zn were found in surrounding soils (Majer et al. 2014).

The present study analyzed soft *Sterechinus neumayeri* tissues from the Antarctic Comandante Ferraz Station and Botany regions, by Instrumental neutron activation analysis (INAA), for micronutrients, and Atomic Absorption Spectrometry (AAS) for toxicological elements (Cd, Hg, Ni and Pb) and Cu, in order to contribute with valuable data concerning the nutritional and toxic constituents of this species. In addition, we intended to confirm whether this sea urchin can be used as a test organism for environmental biomonitoring, as scarce data in the literature on the use of these species as biomonitors are available. A passive biomonitoring was performed, which consists in collecting the organisms directly from their environment and processing them according to scientific interest (Market et al. 1999).

## Material and Methods

The *Sterechinus neumayeri* samples were obtained during the summer of 2014/2015, with 10 organisms collected close to the Comandante Ferraz Station effluent disposal outlet (62.05224–62.05035 S to 58.23381–58.23370 W), a region likely to be influenced by human activities (impacted site). Another 10 organisms were also collected from a pristine region, Botany Point (Fig. 1) (62.05400–62.05556 S to

58.18127–58.18612 W). Sampling was performed by dragging and transferring the specimens to nylon canvas bags and later to 30 L gallons of water with intermittent aeration for transport to the laboratory.

Subsequently, biometry was performed and each individual was dissected, the soft tissues (digestive tract and gonads) were removed and later homogenized in order to obtain a tissue pool. The tissues were stored in tubes and frozen at  $-20^{\circ}\text{C}$ . For the chemical analyses, the samples were dried in a ventilated oven at  $40^{\circ}\text{C}$ , for 7 days, homogenized and sieved through a 0.250 mm (60 mesh) nylon sieve and adequately properly.

Concerning the INAA technique, up to 0.15 g of each sample was weighed. Due to the small amount of sample available, only one sample from each organism was analyzed. Next, synthetic mono and multi-elementary standards were prepared, which included the following elements: As, Ba, Br, Ca, Co, Cr, Cs, Fe, K, Na, Rb, Sb, Sc, Se, Th, U and Zn. The standards were prepared by diluting of certified standard solutions (SPEX CERTIPREP, USA). About 0.15 g of certified reference materials (CRM) Mussel Tissue – NIST SRM 2976 and Oyster Tissue – NIST SRM 1566b and Peach Leaves – NIST SRM 1547 were weighed and prepared in the same way as sea urchin tissues. One replicate of each CRM was prepared for each irradiation. The dried sea urchin samples, certified reference materials and synthetic standards were inserted into an aluminum casing for irradiation of a daily 6 to 7-h cycle under a flow of thermal neutrons from  $1$  to  $5 \times 10^{12} \text{ n cm}^{-2} \text{ s}^{-1}$  in the IEA-R1 nuclear research reactor at the IPEN-CNEN/SP. The samples and standards were counted on a gamma ray spectrometer consisting of a hyper pure germanium semiconductor crystal detector (HPGe) associated to a CANBERRA electronic data acquisition system, with a resolution of 1.21 and 2.23 keV for the  $^{57}\text{Co}$  and  $^{60}\text{Co}$  photopeaks, respectively. Details of the analytical procedure have been previously described in Alves et al (2017a).

For the AAS technique, approximately 200 mg of each sea urchin tissue and from the certified reference materials

Oyster Tissue (SRM 1566b), Mussel Tissue SRM 2976 and Fish Tissue (IAEA 2010) were weighed, packaged in MARS-ONE TOUCH™ Teflon® tubes. Subsequently, 10 mL of concentrated HNO<sub>3</sub> (Merck™) were added to the samples and the mixtures were digested at room temperature overnight. Two analytical blanks containing only digested HNO<sub>3</sub> were also prepared. The following day, the samples, reference materials and analytical blanks were submitted to the “animal tissue” program in a MARS 6 microwave oven (CEM Corporation) for acid digestion. After cooling, the tubes were opened and the contents were transferred to Falcon™ tubes, made up to 50 mL with Milli-Q water and stored 5°C, for further analysis by CV-AAS for Hg and GF-AAS for Cd, Cu, Ni and Pb. For the CV-AAS analysis, a PERKIN ELMER™ Flow Injection Mercury System 100 was used, with SnCl 2.1% (m/v) as the reducing agent at a flow rate of 6.4 mL/min and 3% HCl (v/v) (carrier solution), at a flow rate of 10.4 mL/min. A hollow Hg cathode lamp at 253.7 nm was used and absorptions were measured using the Winlab 32 software from the same manufacturer. An AAnalyst 800 PERKIN ELMER spectrometer was used for the GF-AAS analyses. Standard solutions, sea urchin samples, CRMs, chemical modifiers, an HNO<sub>3</sub> diluent solution and analytical blanks were placed in injection sample containers in the AAS oven. An NH<sub>4</sub>H<sub>2</sub>PO<sub>4</sub> at 0.5% (m/v) and Mg(NO<sub>3</sub>)<sub>2</sub> at 0.03% (m/v) mixture was used as the chemical modifier for the GF-AAS Cd, Cu and Pb analyses, while a Pd + Mg(NO<sub>3</sub>)<sub>2</sub> at 0.03% (m/v) mixture was used for Ni determinations (Skoog et al. 2014). The following wavelengths (nm) were used: Cd-228.8; Cu -324.8; Ni-232.0 and Pb-283.3.

Z-Score criteria were adopted for precision and accuracy verifications of the INAA analytical technique (Bode 1996; INMETRO 2017). Details of these criteria and how they were calculated have been previously described (Alves et al. 2017a). Measurement uncertainties were calculated for each Z-Score-validated element. The INMETRO (2017) analytical method validation procedure was followed for the AAS technique, expressed as trend/recovery in % and in the expanded uncertainties for each element.

To statistically evaluate concentrations variations, the Shapiro–Wilk test was performed concerning data normality and the Levene test was applied for homoscedasticity assessments ( $p < 0.05$ , 95% CI). The means were tested by the *t*-Student test for independent samples (by variables) where  $p < 0.05$  at 95% CI, in order to indicate concentration differences between the sampling sites, while the Mann–Whitney test was applied for nonparametric data. The Grubbs test (95% CI) was performed to detect outliers. A linear correlation matrix with linear *r* (Pearson) and *p* value  $< 0.05$  for significance was applied, and an exploratory PCA was applied to integrate concentration data. The Excel® and Past3 software programs were used for all analysis.

## Results and Discussion

If  $|Z| < 3$ , the individual result of the control sample (certified reference material) lies within the 99% confidence interval of the target value. Z-score values for As, Ba, Br, Ca, Cr, Cs, Fe, K, Na, Rb, Sc, Se and Zn were all in this interval of ( $|Z| < 3$ ), indicating good INAA precision and accuracy.

Table 1 displays the results for the certified reference material analyses as detected by the AAS technique, the CV for AAS-determined Hg and for GF- AAS-determined Cd, Cu, Ni and Pb. Recovery values (%) in the order of magnitude ranging from 100 to 10,000 ng g<sup>-1</sup> must lie between 80 to 110% (INMETRO 2017). At least one CRM met the validation conditions for the analyzed elements (Table 1).

Most elements from both regions displayed normal distribution by the Shapiro–Wilk test, while K concentrations in both regions, Cu in the Botany region and Ni in the Ferraz Station region exhibited *p* values  $< 0.05$ , characterizing non-normal distributions. Thus, K, Cu and Ni were subjected to the non-parametric Mann–Whitney test, to verify differences in the medians for the Botany and Ferraz Station areas.

The *Sterechinus neumayeri* tissue element determination results by both the AAS techniques and the INAA technique are presented in Table 2, expressed as means and standard deviation with 95% significance on a dry basis at both sampling sites. The limits of quantification (LoQ), relative standard deviation (RSD), number of individuals (*n*), *t* test *p* values for K, Cu and Ni and Mann–Whitney *p* values are also presented.

As, Ba, Cd, Cu, Fe, K, Na, Ni, Pb, Rb and Sc were not significantly different between the Botany (non-impacted) and Ferraz Station (possibly impacted) areas, according to a *t*-test at a 95% CI ( $p < 0.05$ ), and according to the Mann–Whitney non-parametric test, under the same conditions.

On the other hand, Br ( $220 \pm 20$  mg kg<sup>-1</sup> and  $300 \pm 60$  mg kg<sup>-1</sup>); Co ( $260 \pm 50$  ng g<sup>-1</sup> and  $330 \pm 40$  ng g<sup>-1</sup>); Cr ( $0.5 \pm 0.1$  mg kg<sup>-1</sup> and  $0.8 \pm 0.2$  mg kg<sup>-1</sup>); Zn ( $80 \pm 10$  mg kg<sup>-1</sup> and  $120 \pm 30$  mg kg<sup>-1</sup>); Cs ( $32 \pm 7$  ng g<sup>-1</sup> and  $60 \pm 20$  ng g<sup>-1</sup>) and Se ( $2.1 \pm 0.3$  mg kg<sup>-1</sup> and  $2.9 \pm 0.5$  mg kg<sup>-1</sup>) at the Botany and Ferraz Station regions, respectively, were significantly different by the *t*-test, at a 95% CI ( $p < 0.05$ ). These elements were higher at the Comandante Ferraz Station region, which is possibly impacted. Ca and Hg were below the limit of quantification and were, therefore, excluded from this study.

For the elements analyzed by the INAA technique, the observed relative standard deviation (RSD) suggests a

**Table 1** Certified and observed values (ng g<sup>-1</sup>) (means ± expanded uncertainty) for the reference materials analyzed by AAS

	Cd	Cu	Hg	Ni	Pb
Oyster tissue (NIST 1566b)					
Certified	2480 ± 80	71,600 ± 1600	37.1 ± 1,3	1040 ± 90	308 ± 9
Observed	2870 ± 310	56,700 ± 3300	41.6 ± 7.1	1140 ± 380	323 ± 62
Recovery (%)	116	79	112	110	105
RSD (%)	10.8	5.8	17.1	33.3	19.2
Mussel tissue (NIST SRM 2976)					
Certified	820 ± 160	4020 ± 330	61.0 ± 3.6	930 ± 120	1190 ± 180
Observed	910 ± 100	3700 ± 220	67 ± 11	710 ± 240	1390 ± 270
Recovery (%)	111	92	110	76	117
RSD (%)	11.0	5.9	16.4	33.8	19.4
Fish tissue <sup>a</sup>					
Certified	20 ± 2	1160 ± 70	880 ± 120 <sup>b</sup>		
Observed	18 ± 2	910 ± 50			
Recovery (%)	90	78			
RSD (%)	11.1	5.5			

<sup>a</sup>MRC not published yet – IAEA RLA 2/014 PROJECT<sup>b</sup>Informative value**Table 2** Total mass fraction (mg kg<sup>-1</sup>, d.w.) with standard deviation (s.d.) from *S. neumayeri* sea urchin tissues by INAA and CV-AAS/GF-AAS, Antarctica

	Pristine site			Possibly impacted site			LoQ	<i>p</i> value <sup>e</sup>
	(Botany)			(Ferraz Station)				
	Mean (s.d.)	RSD%	n <sup>b</sup>	Mean (s.d.)	RSD%	n <sup>b</sup>		
As	9 (3)	28	10	8 (1)	17	9	2.5	0.07
Ba	9 (2)	26	6	9 (3)	34	4	11.4	0.53
Br	220 (20)	11	10	300 (60)	19	10	0.21	0.01
Ca	<LoQ	NC <sup>c</sup>		NC <sup>c</sup>	<LoQ		NC <sup>c</sup>	NC <sup>c</sup>
Co <sup>a</sup>	260 (50)	20	8	330 (40)	18	9	0.15	0.02
Cr	0.5 (0.1)	12	8	0.8 (0.2)	29	8	0.39	0.00
Fe	200 (100)	60	9	200 (50)	26	8	30	0.76
K	18,400 (1700)	9	9	25,000 (9000)	38	10	5800	0.16 <sup>d</sup>
Na	14,000 (2000)	15	10	15,000 (2000)	14	10	60	0.61
Rb	6.4 (0.6)	10	8	6 (1)	12	10	1.8	0.27
Zn	80 (10)	13	8	120 (30)	24	5	0.3	0.01
Cs <sup>a</sup>	32 (7)	21	6	60 (20)	35	6	1.5	0.01
Sc <sup>a</sup>	81	16	8	8 (4)	46	7	27	0.91
Se	2.1 (0.3)	14	9	2.9 (0.5)	17	8	4	0.00
Cd <sup>a</sup>	4700 (1700)	37	7	3300 (1300)	41	8	4,8	0.17
Cu <sup>a</sup>	5500 (2500)	46	9	6700 (2400)	35	8	182	0.42 <sup>d</sup>
Hg <sup>a</sup>	<LoQ	NC <sup>c</sup>	NC <sup>c</sup>	<LoQ	NC <sup>c</sup>	NC <sup>c</sup>	1.2	NC <sup>c</sup>
Ni <sup>a</sup>	610 (260)	42	4	800 (500)	61	8	11	0.68 <sup>d</sup>
Pb <sup>a</sup>	1100 (400)	41	5	1700 (1100)	67	5	300	0.29

<sup>a</sup>Mass fraction (ng g<sup>-1</sup>)<sup>b</sup>Number of valid results for the means calculations<sup>c</sup>Not calculated<sup>d</sup>Mann-Whitney test<sup>e</sup>*t*-test *p* value for a 95% significance

natural variability of these elements in sea urchins due to their metabolism (Marcovecchio 2004). Regarding the AAS results, Cd, Cu, Ni and Pb also exhibited high RSD values, which also suggests natural variability of these element between organisms.

No statistically significant differences between areas studied (*t* test,  $p < 0.05$ , CI 95%) were observed for Ba ( $9 \pm 2$  and  $9 \pm 3$  mg kg<sup>-1</sup>); Fe ( $200 \pm 100$  and  $200 \pm 50$  mg kg<sup>-1</sup>); Na ( $14,000 \pm 2000$  and  $15,000 \pm 2000$  mg kg<sup>-1</sup>); Rb ( $6.4 \pm 0.6$  and  $6 \pm 1$  mg kg<sup>-1</sup>) and Sc ( $8 \pm 1$  and  $8 \pm 4$  ng g<sup>-1</sup>), at Botany and Ferraz Station, respectively. Comparing these results to other organisms (Catharino 2008), the sea urchin species evaluated herein is rich in Na, but this element is not of interest in environmental biomonitoring, due to its association with salinity. Ba concentrations in sediments at Admiralty Bay range at about 363 mg kg<sup>-1</sup> (Fávaro et al., 2012). Therefore, the detected Ba contents in the sea urchins are

probably a reflection of the availability of this element in sediments ingested during the feeding process. Fe, Rb and Sc exhibit average concentrations of 5200, 56 mg kg<sup>-1</sup> and 23.8 µg kg<sup>-1</sup>, respectively, in sediments (Fávaro et al. 2012). Thus, it is very likely that the content of these elements in *S. neumayeri* is also due to the availability of these elements in the sediment, as the concentration of these elements in sediments is much higher than in the evaluated organisms.

For a better understanding of the correlation between the chemical elements detected in sea urchins and their role concerning environmental issues, especially regarding marine pollution and biomonitoring, a Correlation matrix (Table 3) for urchins in Ferraz Station and exploratory Principal Component Analysis (PCA) was applied for both regions (Fig. 2).

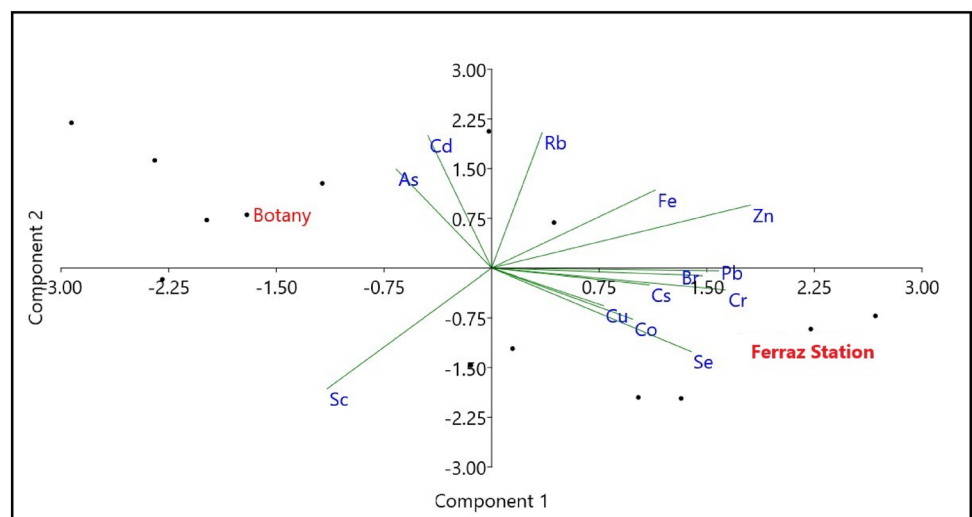
For the Botany region, a linear correlation matrix was performed which exhibited that Rb had a positive correlation with As ( $p = 0.02$ ,  $r = 0.73$ ) and Br ( $p = 0.01$ ,  $r = 0.79$ )

**Table 3** Correlation matrix for *S. neumayeri* sea urchin tissues in Ferraz Station region

	Pool (weight)	As	Br	Co	Cr	K	Na	Sc	Zn	Cd	Cu
Pool (weight)		0.85	0.20	0.69	<b>0.03</b>	<b>0.01</b>	0.16	<b>0.00</b>	0.88	<b>0.00</b>	0.47
As	0.07		0.84	0.38	0.51	0.27	0.48	0.74	<b>0.01</b>	0.32	0.43
Br	0.44	0.07		0.72	0.19	<b>0.02</b>	0.90	0.08	0.97	0.31	0.36
Co	-0.15	-0.31	-0.13		0.80	0.47	<b>0.04</b>	0.84	0.76	0.57	0.07
Cr	<b>0.70</b>	-0.24	0.45	0.09		0.10	0.62	<b>0.03</b>	0.53	0.11	0.99
K	<b>0.78</b>	0.39	<b>0.70</b>	-0.26	0.55		0.30	<b>0.01</b>	0.62	<b>0.01</b>	0.89
Na	-0.48	-0.26	0.04	<b>0.66</b>	-0.18	-0.37		0.56	0.63	0.18	<b>0.03</b>
Sc	- <b>0.83</b>	0.12	-0.58	0.07	- <b>0.70</b>	- <b>0.78</b>	0.21		0.31	<b>0.01</b>	0.86
Zn	-0.05	<b>0.78</b>	-0.01	0.11	-0.22	0.18	-0.18	0.36		0.78	0.27
Cd	<b>0.94</b>	0.35	0.36	-0.21	0.54	<b>0.78</b>	-0.46	- <b>0.76</b>	0.10		0.71
Cu	0.26	-0.28	-0.32	-0.60	0.00	-0.05	- <b>0.70</b>	-0.07	-0.39	0.14	

The highlighted values above diagonal indicates  $p$  values  $< 0.05$  and below indicates  $r \geq |0.70|$  in Pearson  $r$  correlation coefficient

**Fig. 2** PCA Components 1 and 2 for the elements analyzed in the present study in *Stereochinus neumayeri* sea urchins



and the element Zn has positive linear correlation with K ( $p=0.01$ ,  $r=0.79$ ). Other elements had no significant linear correlation.

Data from linear correlation matrix for the Ferraz Station is shown in (Table 3). Only data that with Pearson's  $r$  values  $>0.71$  and  $p < 0.05$  are shown. Cd, Cr and K had a strong linear correlation with the tissue pool weight, especially Cd with  $r=0.94$ , while the Sc had a strong negative correlation tissue pool weight, Cd, Cr and K. Zn had positive correlation with As and Na had a positive correlation with Co, but negative with Cu; K had a positive correlation with Br.

The PCA tests was performed with the following characteristics: all values were normalized by logarithm, missing data within each group were filled with the average values of each group, elements not relevant to environmental issues (i.e. Na and K) were excluded, as they are abundant in marine environments, in addition Ba, Ca, Hg and Ni were excluded due to the low number of results in both regions and/or the fact that they were below the LoQ; Cu element was excluded due the non-normal distribution. For the PCA analysis was considered enough factors to explain 75.8% of the data variance. Despite the recommendation considering factorial loads above 0.4 for each component (Field 2009, Nory 2018), the chemical elements with the highest factor load values, in module, were considered as load factors.

The exploratory PCA grouped the chemical elements into three main factors explaining 75.8% of the total data variance. The case projection graphs exhibited in Fig. 2 indicate that Component 1, under higher loads, and component 2, under less loads, were responsible for grouping the elements that separate Botany and Ferraz station areas as not impacted and possibly impacted, respectively (Santos et al. 2006). Elements widely known as potentially toxic (Santos et al. 2006; Negri et al. 2006; Fávares et al. 2012; Majer et al. 2014) were more grouped and located closer to Ferraz Station when compared to the Botany region. Thus, the concentrations of the most common elements in environmental contamination studies presented in Table 2 and the  $t$  test applied to verify differences between means are in line with the PCA results.

Component 1, which explains 43.5% of the total data variance, associates Br, Cr, Pb and Zn to the Ferraz Station region (impacted) with factor load values of 0.34, 0.38, 0.37 and 0.42, respectively. In addition, Cr, Pb and Zn are well grouped in the Ferraz Station area (Fig. 2). Table 4 presents a comparison of results reported by other authors for other species and sampling sites concerning elements with relevant load factors for this PCA component.

Br concentrations were higher at the Ferraz Station area ( $300 \pm 60$  mg kg<sup>-1</sup>) compared to the non-impacted Botany region ( $220 \pm 02$  mg kg<sup>-1</sup>). Br is present in seawater at around 67 mg kg<sup>-1</sup> and in sediment at around 76 mg kg<sup>-1</sup> in both study regions, respectively (Fávares et al. 2012). Differences in concentrations may be related to the availability of

this element within the *S. neumayeri* food chain as is more evident due the positive correlation with K (Table 3) (Grotti et al, 2008). There is evidence that *S. neumayeri* naturally accumulates Br, given the high concentrations detected at both sites, since Br concentrations are generally high in benthic organisms, according to other assessments carried out with *Perna perna* mussels (Seo et al. 2013). In addition, Br concentration in the present study was detected at the same order of magnitude as in *L. variegatus* sea urchins (Alves et al. 2017a). Since Br concentrations in *S. neumayeri* are statistically different between the sampling points, further studies with a higher number of individuals are required in order to verify whether this difference is anthropic in origin.

Regarding Cr, concentrations at the Ferraz Station region were practically two-fold than those detected in the Botany region ( $0.8 \pm 0.2$  mg kg<sup>-1</sup> and  $0.5 \pm 0.1$  mg kg<sup>-1</sup>, respectively). The observed values were of the same order of magnitude as those observed in *S. neumayeri* sea urchins in the Terra Nova region (Grotti et al. 2008), and lower than in *A. ingens* sea urchins from the Casey Station region (Duquesne and Riddle 2002). *A. ingens* sea urchins also exhibited higher Cr concentrations in the contaminated region (more than two-fold higher than in the non-impacted region, at Casey Station, while the macroalgae *D. menziensis*, probably a food source for *S. neumayeri* sea urchins (McClintock 1994), contained almost threefold higher Cr content at the Ferraz Station region compared to the non-impacted Botany region, probably due to anthropic coal and oil burning and the production of non-ferrous metals (Santos et al 2005; Trevisani et al. 2018). Shinagawa (2016) reported that Cr sedimental content at Ferraz Station is threefold higher than in the control region (Table 4), which may be the result of the 2012 fire. Based on the results of this study, *S. neumayeri* sea urchins bioaccumulated higher Cr contents at Ferraz Station region compared to the preserved Botany area, in addition Cr had a positive correlation with the weight of tissue pool (gonads and digestive tract) and a negative with Sc (Table 3), which may be a consequence of the greater Cr content in the environment (Table 2). Cr bioaccumulation trends observed herein are similar to that observed for *L. variegatus* sea urchins on the coast of Brazil, considered adequate biomonitors (Alves et al. 2017a, b). Based on this, the present study suggests that *S. neumayeri* may prove to be adequate Cr biomonitors.

Zn, detected at  $80 \pm 10$  and  $120 \pm 30$  mg kg<sup>-1</sup> at the Botany and Ferraz Station areas, respectively, was detected at same order of magnitude as in *S. neumayeri* and *A. ingens* sea urchins in other studies (Table 4) (Duquesne and Riddle 2002; Majer et al. 2014). Zn concentrations in Ferraz station region sediments ranged from 100 to 148 mg kg<sup>-1</sup> before the 2012 fire (Favaro et al. 2012). Shortly after the fire, the concentration of this metal increased to 2800–3500 mg kg<sup>-1</sup> (Shinagawa 2016). Studies conducted on *L. elliptica*

**Table 4** Total mass fraction results (interval or means  $\pm$  dispersion) (mg kg<sup>-1</sup>) in sea urchins, other organisms and sediments in Antarctica, with their respective references

	Preserved site	Impacted site	Organism	Specie	Study area	References	
As	9.3 $\pm$ 0.2	7.5 $\pm$ 0.3	Sea urchin	<i>S. neumayeri</i>	Ferraz station	This study	
		5.0 $\pm$ 0.3			Admiralty Bay	Majer et al. (2014)	
Cd <sup>a</sup>	4690 $\pm$ 790	4–6	Sediment	*	Ferraz station	Santos et al (2006)	
		8–33			Admiralty Bay	Majer et al. (2014)	
		8.5	Sea urchin	<i>S. neumayeri</i>	Ferraz station	This study	
		39,000	3260 $\pm$ 550			Admiralty Bay	Majer et al. (2014)
Cr	0.48 $\pm$ 0.02	980 $\pm$ 20			Terra Nova Bay	Grotti et al. (2008)	
		3880 $\pm$ 80			Cape Evans	Grotti et al. (2008)	
		4420 $\pm$ 80	Sediment	*	Ferraz station	Fávaro et al. (2012)	
		0.8 $\pm$ 0.2	Sea urchin	<i>S. neumayeri</i>	Ferraz station	This study	
		10.4 $\pm$ 1.1				Casey station	Duquesne & Riddle (2002)
		0.68 $\pm$ 0.05				Terra Nova	Grotti et al. (2008)
		3	9.3 $\pm$ 2.7	Algae	<i>D. menziensis</i>	Ferraz station	Trevisani et al. (2018)
Cu <sup>a</sup>	5460 $\pm$ 580	36–45	Sediment	*		Santos et al. (2006)	
		10.2				Shinagawa (2016)	
		6720 $\pm$ 720	Sea urchin	<i>S. neumayeri</i>	Ferraz station	This study	
		3600 $\pm$ 30				Admiralty Bay	Majer et al. (2014)
		5610 $\pm$ 200				Cape Evans	Grotti et al. (2008)
Pb <sup>a</sup>	1064 $\pm$ 200	71,000	Sediment	*	Ferraz station	Shinagawa (2016)	
		1400 $\pm$ 400	Sea urchin	<i>S. neumayeri</i>	Ferraz station	This study	
						Casey station	Duquesne & Riddle (2002)
		8930 $\pm$ 910				Admiralty Bay	Majer et al. (2014)
		6000	Sediment	*	Admiralty Bay	Majer et al. (2014)	
Zn	83 $\pm$ 2	5500			Ferraz station	Shinagawa (2016)	
		117 $\pm$ 5	Sea urchin	<i>S. neumayeri</i>	Ferraz station	This study	
		55.4 $\pm$ 5.4				Casey station	Duquesne & Riddle (2002)
		354 $\pm$ 7				Admiralty Bay	Majer et al. (2014)
		81–95	87–134	Sediment	*	Ferraz station	Santos et al (2006)
			63			Admiralty Bay	Majer et al. (2014)
	61			Ferraz station	Shinagawa (2016)		

<sup>a</sup>Mass fraction (ng g<sup>-1</sup>)

\*Not applicable

bivalves, considered good biomonitors (Negri et al. 2006), indicate higher Zn concentrations in impacted sites, but did not hypothesize on anthropic sources of this element (Majer et al. 2014). The aforementioned authors assessed the possible Zn increases at the Ferraz Station due to the 2012 fire and suggested continuous biomonitoring evaluations. Trevisani et al. (2018) concluded that the amount of Zn in benthic organisms may be related to the availability of this element in sediment.

Pb values in *S. neumayeri* sea urchins were of 1100  $\pm$  400 and 1700  $\pm$  1100 ng g<sup>-1</sup> at the Botany and Ferraz Station areas, respectively. However, this difference was non-significant ( $p > 0.05$ ), which may suggest that the Pb content is more related to natural biological variability (Amaro et al. 2015; Cabrita et al. 2017). In 2013, one year after the 2012

fire, a study concerning the bioaccumulation of toxic elements in *S. neumayeri* sea urchins was carried out, at Pb concentrations were about 40-fold higher in relation to the non-impacted sampling area (Table 4) (Majer et al. 2014) suggesting acute contamination, probably related to the fire. Shinagawa (2016) evaluated sediments and reported higher Pb concentrations at Ferraz Station compared to the non-impacted region (Table 4). Higher Pb concentrations were also detected at Casey Station, which is considered contaminated. Although the results of this study do not point to Pb contamination, the other biomonitoring studies presented in Table 4 suggest possible anthropic Pb sources, such as coal and oil combustion (Majer et al. 2014; Trevisani et al. 2018). On the other hand, the result of this study for Pb suggests its spread throughout the collection sites, especially in the

preserved region since significant increases in Pb concentrations *S. neumayeri* sea urchins were observed.

PCA Component 2, which explains 23.1% of the total data variance, positively associated Cd, Rb, with factor load factors of 0.46 and 0.47, respectively, while Sc was negatively associated, with a factorial load of -0.42. Rb ( $6.4 \pm 0.4$  and  $6.0 \pm 0.4$  mg kg<sup>-1</sup>) and Sc ( $8 \pm 1$  and  $8 \pm 4$  ng g<sup>-1</sup>) at the Botany and Ferraz Station areas, respectively, were not significantly different ( $p < 0.05$ ) by the *t* test. An indication that these elements are isolated is noted in Fig. 2, which may suggest that the evaluated sea urchins probably accumulate these elements naturally, regardless of the study region conditions.

Cd concentrations were of  $4700 \pm 1700$  and  $3300 \pm 1300$  ng g<sup>-1</sup> at the Botany and Ferraz Station areas, respectively, the same order of magnitude reported by Grotti et al. (2008) for other regions (Table 4). The significant difference between means ( $p = 0.01$ ) suggests potential *S. neumayeri* contamination by this element in the Botany region, as this metal is not essential. In contrast, the PCA diagram (Fig. 2) indicates that this difference is probably not associated to the study regions. In addition, Cd contents at the Ferraz station were almost threefold higher compared to the results reported by Majer et al. (2014) (Table 4) for the same species and region. Some studies in another antarctica regions suggest soil contamination by Cd, while also considering that this element may be associated to the benthic community food chains (Zhang et al. 2009; Majer et al. 2014).

The exploratory PCA Factor 3, which explains 9.3% of the total data variance, associates only Cu to the Ferraz Station region. Cu concentration were of  $5500 \pm 2500$  and  $6700 \pm 2400$  ng g<sup>-1</sup> at the Botany and Ferraz Station areas, respectively, with a factor load factor of - 0.67. On the other hand, according to the t-test, no significant differences between the means of both regions were detected. However, the high coefficient of variation may suggest a natural variability of this element in the studied sea urchins. The low number of analyzed individuals must also be considered, which can lead to high coefficient of variation values in biological samples. Majer et al. (2014) reported concentrations of around 34 mg kg<sup>-1</sup> of Cu in soil close to the location of the Ferraz Station ruins. The authors suggested that this element may be accessible to the local ecosystem due to seasonal melting. Another study associated Cu to the sediment conditions of the Admiralty Bay region, where it may be associated to chalcopyrite and rock erosion (Machado et al. 2001; Trevisani et al. 2018).

The present study contributed towards knowledge of the mineral composition of *S. neumayeri* sea urchins, indicating that this species is rich in Na and K compared with other marine organisms.

Br, Cr, Cs, K, Se and Zn were higher at the Ferraz Station, considered an impacted site, compared to the less impacted

control Botany region. This indicates a certain degree of environmental impacts in the former, especially concerning Cr and Zn, which may be related to the 2012 fire. The other analyzed metals were not significantly different between the two study regions. The observed differences were confirmed by statistical comparisons between means.

The PCA assessment, in addition to comparative studies with other organisms, suggest the possibility of passive biomonitoring for Cr and Zn, indicating that this organism may be a good passive biomonitor candidate for coastal environments. However, studies in active biomonitoring need to be made to confirm if *S. neumayeri* can be used as biomonitor for other elements. In addition, the Comandante Ferraz Station region, despite the 2012 fire, did not show any signs of significant contamination by potentially toxic metals, except for Cr.

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## Declarations

**Ethical Approval** The authors declare that all animals were collected under an ICMBio license (SISBIO n.30422) and in accordance to Brazilian legislation (BRASIL, 2014, 2015). This study was also approved by the USP Biomedical Institute Ethics Committee on Animal Use.

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