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Soil Contamination by Toxic Metals Near an Antarctic Refuge in Robert Island, Maritime Antarctica: A Monitoring Strategy

Elias de Lima Neto · Marcelo Braga Bueno Guerra · André Thomazini · Mayara Daher · André Medeiros de Andrade · Carlos Ernesto G. R. Schaefer

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Abstract The anthropogenic effects of Antarctic refuge buildings and research stations on the surrounding soils are scarcely investigated, especially when the structures are small-sized, and sporadically used or visited. The Coppermine Peninsula (Robert Island, South Shetland Islands archipelago) possesses one of the richest flora in Antarctica, being classified as an Antarctic Specially Protected Area (ASPA). There, a small refuge (Luis Risopatrón) has been seasonally occupied for scientific purposes since 1957, although no studies on the anthropic disturbances in the surroundings soils are reported. The aim of this study was the determination of the potentially toxic metals (Cd, Cr, Cu, Mn, Ni, Pb, V, and Zn) mass fractions in surface soils ($n = 40$) collected at the surroundings of the Luis Risopatrón refuge. Enrichment factors (EF) and geoaccumulation index (I_{geo}) were also calculated, using Zr as the reference element, in order to evaluate the anthropogenic impacts of these small buildings in the studied area. The main contaminants were Pb and Zn, which presented EF and I_{geo} values ranging from 1.0 to 18.3 and from −1.8 to 3.5. The mass fractions of these elements determined after an aqua regia extraction varied from 5.4 to 102 mg kg^{-1} Pb and from 43 to 210 mg kg^{-1} Zn. These results highlight that a small refuge can show environmental disturbance from low to moderate, with few hotspots with heavily contaminated soils. Environmental monitoring strategy for similar refuges anywhere in Antarctica is recommended.

Keywords Enrichment factor · Geoaccumulation index · Contamination · Soil · Antarctica · Toxic metals

E. de Lima Neto · A. Thomazini · M. Daher · C. E. G. R. Schaefer
Departamento de Solos, Universidade Federal de Viçosa, Avenida Peter Henry Rolfs, Viçosa, MG CEP 36570-900, Brazil

M. B. B. Guerra
School of Natural Sciences, Black Hills State University, 1200 University St., 57799 Spearfish, SD, USA

A. M. de Andrade
Instituto de Ciências Agrárias, Universidade Federal dos Vales do Jequitinhonha e Mucuri, Avenida Vereador João Narciso, 1380, Bairro Cachoeira, Unaí, MG CEP 38610-000, Brazil

Present Address:
E. de Lima Neto (✉)
Departamento de Hidráulica e Saneamento, Escola de Engenharia de São Carlos, Universidade de São Paulo, Avenida Trabalhador São-carlense, 400 - Parque Arnold Schimidt, São Carlos, SP 13566-590, Brazil
e-mail: eliasneto87@hotmail.com

1 Introduction

The Antarctic continent plays a key role in the global climate dynamics, expressed as atmospheric and oceanic circulations, having the greatest reservoir, containing 90% of the world's available freshwater. This continent has 14 million square kilometers, but only 0.5% are ice-free areas, where biological and human activities are concentrated (Campbell and Claridge 1987).

Although Antarctica is seen as the last unexplored region on Earth and as a worldwide conservation symbol, it is not free from anthropogenic impacts, either by

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atmospheric, long-range pollutants, or promoted by local activities, such as those related to logistic operations, and scientific stations (Bargagli 2005; Braun et al. 2012; De Moreno et al. 1997; Guerra et al. 2013; Tin et al. 2009).

The Protocol on Environmental Protection to the Antarctic Treaty, better known as the Madrid Protocol, was signed in 1991 as a legal agreement between the countries towards the mitigation of anthropogenic impacts in Antarctica. More specifically, this instrument also provides guidelines for regulating human activities through environmental monitoring and solid waste management. Another important attribute of the Madrid Protocol is the designation of restricted sites, known as the Antarctic Specially Protected Areas (ASPAs), where more rigid rules are imposed given their environmental, scientific, historical, and/or aesthetic values (Ministry of the Environment Government of Japan 2003).

Several studies have dealt with the environmental monitoring in Antarctica (Cabrerizo et al. 2016; De Moreno et al. 1997; Guerra et al. 2011a; Jerez et al. 2013; Poblet et al. 1997; Préndez and Carrasco 2003), and a substantial part of them have elected soil as the target compartment (Amaro et al. 2015; Guerra et al. 2011b, c, 2012, 2013; Santos et al. 2005; Sheppard et al. 2000) given its peculiar characteristic of being the main sink of contaminants released into the terrestrial ecosystems by anthropogenic activities (Wuana and Okieimen 2011). In these studies, the principal sites investigated are those in the neighborhood of the scientific stations.

Tin et al. (2009) reviewed the scientific literature on the anthropic impacts in the Antarctic ecosystem. They highlighted that the most commonly found contaminants are those related to fuel spills, potentially toxic elements (arsenic, cadmium, copper, lead, mercury, and zinc), and polychlorinated biphenyls (PCBs). A long list of persistent organic pollutants (POPs) also deserves special attention such as flame-retardants, polycyclic aromatic hydrocarbons (PAHs), polybrominated diphenyl ethers (PBDEs), and polychlorinated dibenzodioxins (PCDDs). The main sources of such chemicals are most likely to be the runoff from abandoned waste disposal sites, sewage systems, and emissions from burning fuel.

Moreover, Szopińska et al. (2016) highlighted that the assessment of metals deposition over the Antarctic region is becoming a particularly important research field given the ever-increasing human presence by either scientific activities or tourism. They also confirmed that the most affected areas are concentrated near historic sites and polar stations, where fossil fuels, solid wastes, and sewage can potentially contaminate soil.

Some catastrophic events also have strongly increased the impact over the Antarctic environment. Serious fire-related incidents (Dickhut et al. 2012; Ward 2001), such as the one that recently destroyed the Brazilian Antarctic Station in 2012 (Colabuono et al. 2015; Guerra et al. 2013), sparks the attention by both the devastation caused and the massive emission of pollutants.

Among the contaminants arising from human presence in Antarctica, the potentially toxic elements are of special concern. In contrast to the organic compounds, which can be microbiologically oxidized to carbon dioxide, these elements are persistent in the environment and their presence can promote a myriad of harmful conditions (Giller et al. 1998; Kizilkaya et al. 2004; Wuana and Okieimen 2011), such as phytotoxicity, food chain imbalances, inhibition of organic pollutants biodegradation (Sandrin and Maier 2003), among others.

The neighborhoods of the Antarctic stations are not the only threatened sites by local anthropogenic contamination. Also threatened are the lesser-known and smaller refuges, which support logistical scientific operations, and may lead to human disturbances. To the best of the authors' knowledge, there are no systematic studies on the soil contamination by potentially toxic metals near Antarctic refuges. Given the demand established by the Madrid Protocol regarding the assessment of anthropic disturbances on Antarctica, this subject becomes of utmost relevance.

The aim of this study was the analysis of soil samples collected around a small refuge (Luis Risopatrón) in the Coppermine Peninsula (Robert Island, Maritime Antarctica) for the determination of potentially toxic metals (Cd, Cr, Cu, Mn, Ni, Pb, V, and Zn) mass fractions as a way to evaluate possible anthropogenic impacts and providing data for the environmental monitoring of the area.

2 Experimental

2.1 Site Description and Soil Sampling Protocol

The Coppermine Peninsula is located in the western part of Robert Island (South Shetland Islands archipelago) between Nelson and Greenwich Islands (Fig. 1a). The region has one of the largest continuous vegetation cover of mosses and *Deschampsia antarctica* anywhere

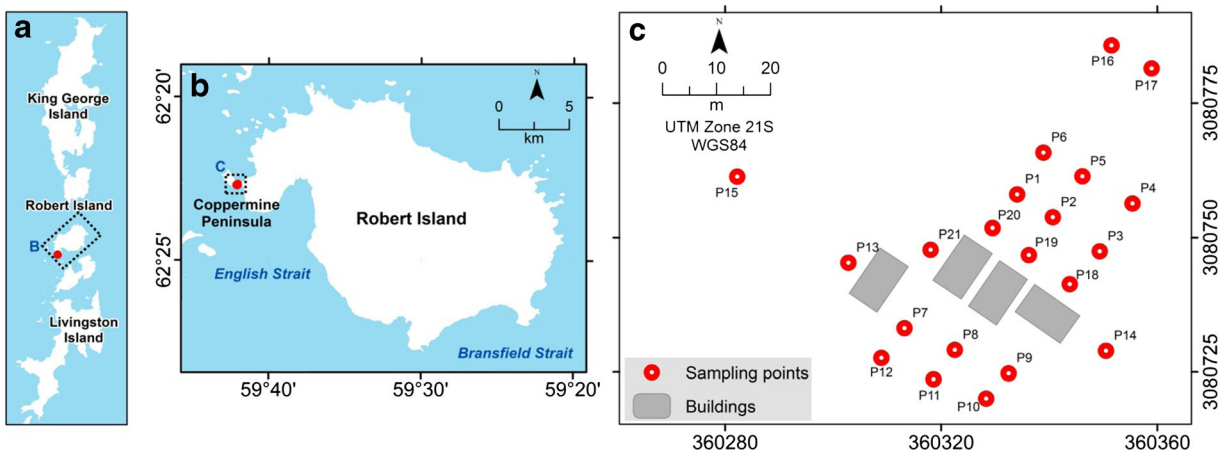

Fig. 1 **a** South Shetland islands. **b** Robert Island. **c** Sampling sites near the Luis Risopatrón refuge

in Antarctica (Torres-Mellado et al. 2011). Its geology is mostly composed of dark olivine-basalt rocks, in contrast to the dominant greenish andesites of the other South Shetland Islands, as well as tuffs, volcanic breccias, and basaltic intrusions (Machado et al. 2005). The fauna is composed of abundant petrels, terns, kelp gulls, and Weddell and fur seals.

The Chilean refuge Luis Risopatrón, built on the Coppermine Peninsula (Fig. 1b) in 1957, is seasonally used to support scientific activities. The refuge consists of four building blocks, two of which are badly conserved and present a large accumulation of debris and waste materials (wood pieces, plastics, PVC pipes, litter) deposited inside them and on the surroundings. Soil samples ($n = 40$) were collected from 21 sampling sites (Fig. 1c) in 2014 during the 32nd Brazilian Antarctic Expedition. Additional information about the sampling sites are shown in Table 1. After sampling, all soil samples were stored in Ziplock® bags, which were kept refrigerated until laboratory processing. At the laboratory, all samples were dried at 50 °C until constant weight, powdered in an agate mortar, and sieved to obtain particle sizes smaller than 210 μm.

2.2 Chemical Analyses

Aqua regia extraction was performed following the procedure described by the German Norm, DIN 38414-S7, as a way to evaluate the presence of the potentially toxic elements Cd, Cr, Cu, Mn, Ni, Pb, V, and Zn. An alkaline fusion was performed as described by Guerra et al. (2013) for Zr quantification. The elemental determination was performed by inductively coupled plasma optical emission spectrometry (ICP OES) using an instrument with dual-view configuration (Optima 7300 DV, Perkin Elmer, Shelton, CT, USA). A PEEK Mira Mist® nebulizer was connected to the cyclonic spray chamber. The following operating conditions were selected for the ICP OES measurements: generator frequency (40 MHz); RF applied power (1.3 kW); sampling flow rate (1.5 mL/min); and argon flow rates: plasma (15 L/min), auxiliary (1.5 L/min), and nebulizer (0.8 L/min). The monitored emission lines were the following: Cd I 228.802 nm, Cr II 267.716 nm, Cu I 327.396 nm, Mn II 257.610 nm, Ni II 231.604 nm, Pb II 220.353 nm, V II 290.882 nm, Zn II 206.200 nm, and Zr II 343.823 nm. The Certified Reference Material Montana II Soil (NIST SRM 2711a) was used to check the trueness of the method. All reagents used in this study were of analytical grade quality.

2.3 Geochemical Enrichment

Two indices based on geochemical enrichment ratios were calculated to evaluate the soil contamination degree. The enrichment factor (EF) was calculated following the proposal of Lee et al. (1997), using Zr as the reference element. This index is helpful as it reduces the influence of the grain size and mineralogy and it indicates anthropogenic contamination patterns. The EF was calculated according to the following equation: $EF = (Me/Zr)_{sample}/(Me/Zr)_{control\ soil\ sample}$, where Me/Zr is the ratio between the element under investigation and the reference element (Zr) mass fractions.

Table 1 Description of the sampling sites

Sampling sites[a]	Depth sampled (cm)	Remarks
P1–P3	0–10 and 10–20	No vegetation cover. High gravel-pebble content in the soil profile. Presence of orange paint chips on the soil
P4–P6	0–10 and 10–20	No vegetation cover
P7	0–10	Sparse mosses covering. Flooded soil layer (10–20 cm)
P8	0–10 and 10–20	No vegetation cover. Presence of orange paint chips on the soil
P9	0–10 and 10–20	No vegetation cover. Presence of orange paint chips on the soil
P10	0–10 and 10–20	Moss-covered field
P11	0–10 and 10–20	No vegetation cover
P12	0–10 and 10–20	Dense moss-covered field
P13	0–10 and 10–20	Moss-covered field presenting wood scraps. Near a metallic building
P14	0–10 and 10–20	Sparse mosses and lichens covering. Presence of orange paint chips on the soil
P15	0–10 and 10–20	Control point, visually undisturbed
P16–P17	0–10 and 10–20	Sampling sites near a high-pebble beach. Close to seals and elephant seals colonies
P18–P20	0–10 and 10–20	Sites close to a waste pill presenting wood, metal, and plastic scraps. Presence of orange paint chips on the soil
P21	0–10	Orange paint chips on the soil and presence of metal, wood, and plastic scraps. Flooded soil layer (10–20 cm)

[a] See locations in Fig. 1

According to Sutherland (2000), there are five degrees of environmental disturbance based on the EF data: EF <2—minimal or no pollution; 2 <EF <5—moderate pollution; 5 <EF <20—significant pollution signal; 20 <EF <40—very strong pollution signal; and EF >40—extreme pollution signal. The control point (P15, Fig. 1c) used for calculating the EF was chosen based on visual inspection since it is an undisturbed site and has the same geological context of the remaining sampling points. The reference values used for the geochemical enrichment calculation were the elemental mass fractions obtained from the analysis of the sample collected in the 0–10 cm depth in the P15 sampling site (control point, see Fig. 1c, and Table 3).

The geoaccumulation index (I_{geo}) had widely been used in trace metal studies of sediments and soils (Chandrasekaran et al. 2015; Ghrefat et al. 2011; Hasan et al. 2013). To assess the degree of toxic metal pollution of soils collected in the vicinity of the Antarctic refuge, I_{geo} was calculated following the Müller (1979) proposition. The formula is given following: $I_{geo} = \log_2(Cn/1.5\ Bn)$, where Cn is the concentration of the target element in the soil sample, Bn is the geochemical background value (basaltic rocks) of the target element (n) (Turekian and Wedepohl 1961), and $k = 1.5$ is used due to possible variations of the background values related to lithological effects. The geoaccumulation index consists of seven grades or classes: class 0 (unpolluted): $I_{geo} \leq 0$; class 1 (unpolluted to moderately polluted): $0 < I_{geo} < 1$; class 2 (moderately polluted): $1 < I_{geo} < 2$; class 3 (moderately to heavily polluted): $2 < I_{geo} < 3$; class 4 (heavily polluted): $3 < I_{geo} < 4$; class 5 (heavily to extremely polluted): $4 < I_{geo} < 5$; and class 6 (extremely polluted): $I_{geo} \geq 5$.

3 Results and Discussion

3.1 Determination of Cd, Cr, Cu, Mn, Ni, Pb, V, and Zn Mass Fractions

The Cd, Cr, Cu, Mn, Ni, Pb, V, and Zn mass fractions determined after the aqua regia extraction of the CRM NIST 2711a (Montana II soil) followed by ICP OES measurements were compared with the certified leachable fractions for these elements. No significant differences were observed between the certified and determined values after applying the Student's t test at 95% confidence level. The analytical figures of merit of the ICP OES measurements can be seen in Table 2.

The pseudototal concentrations (leachable fraction) of Cd, Cr, Cu, Mn, Ni, Pb, V, and Zn were compared with the prevention values recommended by the Brazilian National Council for the Environment (CONAMA).

Table 2 Analytical figures of merit for the quantitative determination of Cd, Cr, Cu, Mn, Ni, Pb, V, and Zn in the aqua regia extracts by ICP OES

Parameters	Elements							
	Cd	Cr	Cu	Mn	Ni	Pb	V	Zn
Limit of detection[a] (μg L^{-1})	2.0	0.32	13	1.0	2.2	11	4.0	13
Limit of quantification[b] (μg L^{-1})	6.0	0.96	39	3.0	6.6	33	12	39
Linear correlation coefficient (r)	0.9993	0.9997	0.9995	0.9998	0.9997	0.9973	0.9999	0.9997
Calibration range (mg L^{-1})	0.01–1	0.01–1	0.05–5	0.05–5	0.01–1	0.05–1	0.05–5	0.05–5
Measurement precision[c] (%)	7.2	7.6	4.3	6.3	7.1	3.3	6.9	5.1

[a] $LOD = [(3.3 \times BEC \times RSD_{blank}/100), n = 10]$

[b] $LOQ = 3 \times LOD$

[c] Coefficient of variation obtained from $n = 6$ random measurements of the following standard solution: [Cd] = 0.8 mg/L; [Cr] = 0.8 mg/L; [Cu] = 4 mg/L; [Mn] = 4 mg/L; [Ni] = 0.8 mg/L; [Pb] = 0.8 mg/L; [V] = 4 mg/L; and [Zn] = 4 mg/L

Prevention values are the threshold levels established for specific group of substances in the soil as a way to ensure its quality and vital role in the environment. For comparative purposes, Table 3 also shows an overview of potentially toxic metal mass fractions in soil samples collected in the neighborhood of several Antarctic scientific stations.

In this study, the pseudototal concentrations of the potentially toxic elements were determined in soils collected at two depths (0–10 and 10–20 cm). For Pb (Fig. 2b), a significant difference between the investigated profiles was observed (7.3 to 102 mg kg^{-1} for 0–10 cm and 5.4 to 25 mg kg^{-1} for 10–20 cm). However, only few samples ($n = 2$) presented Pb levels higher than the

Table 3 Potentially toxic metal mass fractions (mean values) in soil samples from the neighborhood of actual or former Antarctic scientific stations

Soil samples (sampling sites)	Cd mg kg^{-1}	Cr	Cu	Mn	Ni	Pb	V	Zn
Control soil (P15, 0–10 cm layer)[a]	<0.2	52 ± 1	47.8 ± 0.4	453 ± 3	40.4 ± 0.5	7.3 ± 0.5	109 ± 2	43.9 ± 0.2
Soil (P19, 0–10 cm layer)[a]	<0.2	72 ± 2	107 ± 1	545 ± 10	37.9 ± 0.5	102 ± 2	122 ± 2	148 ± 5
Soil from Trinity House Ruins[b]	<0.04	35	195	202	13	103	–	263
Soil from Fildes Bay near fuel tanks[c]	0.5	–	30	–	–	–	–	154
Soil from Great Wall Bay[c]	0.33	–	31	–	–	23	–	113
Soil from Ferraz station, after the fire[d]	<0.3	400	5000	1500	15.9	3000	62.5	15,000
Soil from Ferraz station, before the fire[e]	–	40	44	442	5.1	12	91	52
Gray soil from McMurdo station[f]	0.13	172	39	–	98	5.8	–	115
Soil from O'Higgins Base[g]	4.3	65	422	405	28	282	–	485
Prevention values[h]	1.3	75	60	–	30	72	–	300

[a] This study

[b] (Guerra et al. 2011c)

[c] (Amaro et al. 2015)

[d] (Guerra et al. 2013)

[e] (Santos et al. 2005)

[f] (Crockett 1998)

[g] (Celis et al. 2015)

[h] (CONAMA 2009)

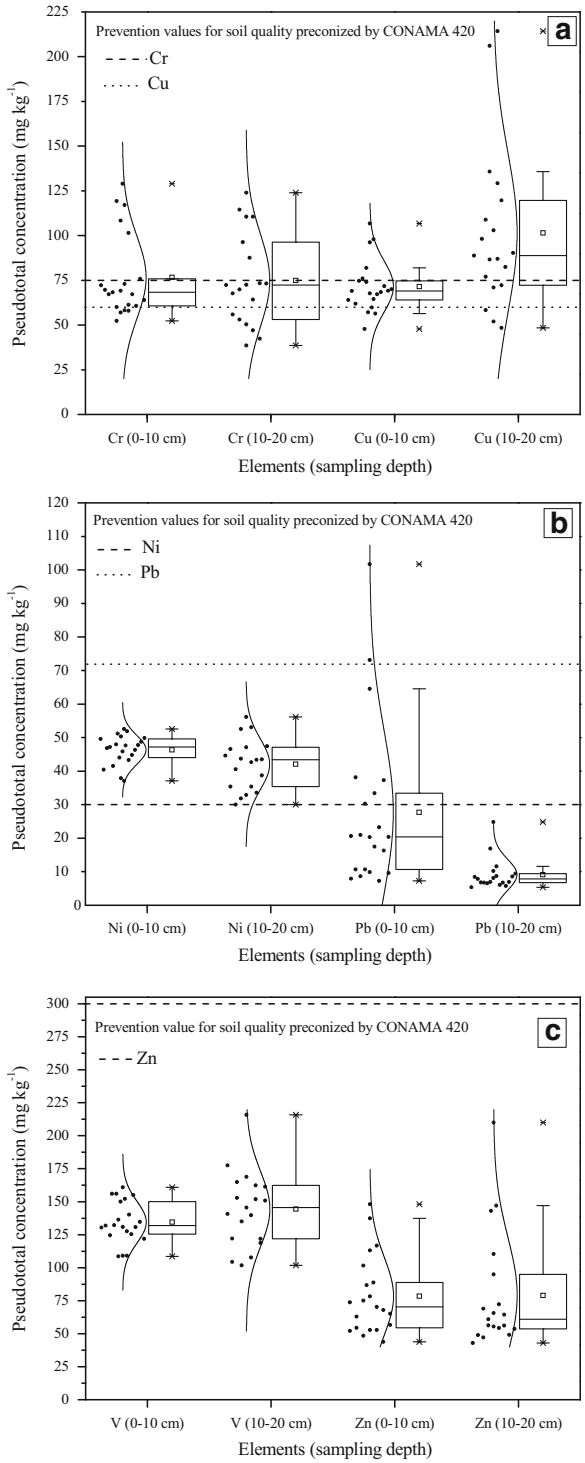

Fig. 2 Box plots highlighting the elemental distribution over the soil profile (0–10 and 10–20 cm) for Cr and Cu (**a**), Ni and Pb (**b**), and V and Zn (**c**)

guideline value prescribed by CONAMA (72 mg kg^{-1} Pb). These Pb-enriched samples (P19 and P20, see Table 1 and Fig. 1c) were detected in the 0- to 10-cm layer in sites affected by the deposition of orange paint chips as well as by metal and plastic scraps. On the other hand, for some elements, such as Cu (Fig. 2a), Cr (Fig. 2a), and Ni (Fig. 2b), for several samples in both investigated soil profiles, the found mass fractions were higher than the prevention values. In the case of Ni, all analyzed samples presented pseudototal concentrations higher than the prevention value (30 mg kg^{-1}). Anomalous levels of Cr, Cu, and Ni are expected for soils derived from basalt rocks (Guerra et al. 2011d; Malandrino et al. 2009). In Antarctica, the influence of the parent rock material exerts prominent importance in the soil composition, given the inherent low rates of chemical weathering under the cold climate (Simas et al. 2006).

3.2 Enrichment Factor, Geoaccumulation Index, and Pearson Correlation Matrix

The enrichment factor (EF) and geoaccumulation index (I_{geo}) were calculated for the potentially toxic elements present in the most superficial soil layer (0–10 cm). The linear correlation coefficients (r) were calculated for the data provided by both indexes. The following values were found: $r = 0.94$ (Cr), 0.87 (Cu), 0.87 (Mn), 0.37 (Ni), 0.92 (Pb), 0.53 (V), and 0.96 (Zn).

The highest EF values were observed for Pb and Zn (Fig. 3). About 20% of all analyzed samples (P2, P3, P5,

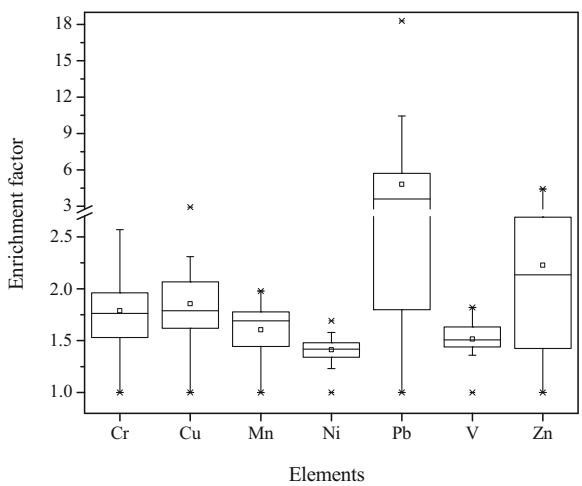

Fig. 3 Box plots showing the enrichment factors for Cr, Cu, Mn, Ni, Pb, V, and Zn, based on the pseudototal levels for soil samples collected in the superficial layer (0–10 cm depth)

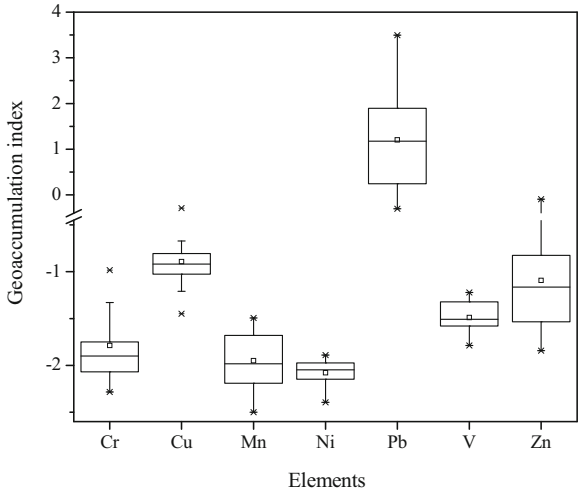

Fig. 4 Box plots showing the geoaccumulation index for Cr, Cu, Mn, Ni, Pb, V, and Zn, based on the pseudototal levels for soil samples collected in the superficial layer (0–10 cm depth)

P8, P16, P19, and P20) presented significant Pb enrichment, with mass fractions ranging from 30 to 102 mg kg^{-1} Pb. The same samples (including P11) presented a moderate pollution by Zn, ranging from the 68 to 148 mg kg^{-1} Zn. For the remaining investigated elements, the pollution was minimal or absent. The calculated EF and I_{geo} values also demonstrated that the soils presented low pollution degree or are unpolluted (Fig. 4). However, some samples (P8, P16, P19, and P20) were classified as moderately polluted to heavily polluted, regarding Pb.

In Antarctica, the most severely impacted areas by anthropogenic activities are those situated in the vicinity of oil tanks, electricity generators, waste disposal sites, or those directly affected by fire incidents. Guerra et al. (2011c) found very high enrichment factors for Pb (EF = 768) and Zn (EF = 74) for soil samples collected at Hope Bay, Antarctic Peninsula, in sites contaminated by a fire event in 1948. Soil samples collected immediately after a fire that destroyed the Brazilian Antarctic Station in King George Island also exhibited a high degree of contamination by Pb (EF = 1320) and Zn (EF = 1153) (Guerra et al., 2013). Other potential sources of Pb and Zn contamination can be related to fossil fuel spills, sewage, and paint residues (Alam and Sadiq 1993; Santos et al. 2005; Webster et al. 2003).

A Pearson correlation matrix was calculated to assess the relationship between the mass fractions of the potentially toxic elements. According to the data obtained (Table 4), strong positive correlations were observed between the following pairs of elements: Ni and Mn ($r = 0.7953$), V and Cr ($r = 0.7787$), V and Mn ($r = 0.8212$), V and Ni ($r = 0.8161$), as well as Zn and Cu ($r = 0.8573$). The observed significant positive correlation between Cr, Ni, and V can be attributed to their common source, the mafic parent rock. Consistently, high levels of these associated elements were detected in marine sediments from the Penguin Island (South Shetland), where a similar olivine basalt occurs (Guerra et al. 2011d).

Although most studies related to soil pollution in Antarctica show that the contamination is mainly concentrated around the on-site buildings, environmental monitoring studies are extremely important for aiming at the preservation of the fragile endangered biological species of this continent. Refuges and seasonal stations require special attention regarding a detailed assessment program, as around these sites, metal wastes, paint scraps, and PVC pipes are more often observed.

Table 4 Pearson correlation matrix for the potentially toxic elements Cr, Cu, Mn, Ni, Pb, V, and Zn mass fractions

	Cr	Cu	Mn	Ni	Pb	V	Zn
Cr	1						
Cu	0.4855*	1					
Mn	0.6849*	0.3277	1				
Ni	0.6079*	0.0636	**0.7953***	1			
Pb	−0.0321	0.5649*	−0.1008	−0.3644	1		
V	**0.7787***	0.2769	**0.8212***	**0.8161***	−0.1340	1	
Zn	0.3499	**0.8573***	0.0925	−0.0353	0.6383*	0.0966	1

Bold values represent strong correlations between the potentially toxic elements mass fractions

* Significant correlation at 95% confidence interval

3.3 Conclusions and Outlook

Despite the occasional human occupation for over half a century, the results of this study permit to conclude that among the investigated elements, the environmental pollution of soils around the Luis Risopatrón refuge varies from low to moderate. However, attention must be paid to the Pb enrichment at the surface soil, which can lead to detrimental changes in the ecosystem. This finding also corroborates the need for the implementation of systematic environmental monitoring and assessment program for the Antarctic refuges. The combined use of both geochemical indices, EF and I_{geo}, appears to be a suitable and reliable environmental assessment tool for such systematic monitoring.

Future studies focusing on the chemical speciation analyses of the potentially toxic elements determined herein, especially Pb, should be subject to investigation in order to provide detailed information on the real menace of the anomalous levels found in the hotspot areas to the adjacent environment. Additional investigations dealing with the determination of the mobile fraction of the toxic metals can also be advantageous in order to give support to the environmental impact mitigation measures.

The results of the present study can alert researchers and environmental agencies towards the implementation of monitoring programs to Antarctic refuges, taking into account that similar constructive materials are used in these human settlements anywhere in Antarctica, and the strict rules imposed by the Madrid Protocol regarding impact mitigation.

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