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SOIL SCIENCE

Anthropogenic effect on the pedochemical variability of potentially toxic elements at the vicinity of an Antarctic research station

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Abstract: Antarctica represents an isolated continent devoted to conservation and scientific research, although it accumulates records of increasing anthropic contamination. The historical continued use of fuel for power generation in Antarctic settlements is a potential source of toxic elements to the soil. We investigate Cd, Cr, Cu, Mn, Ni, Pb, V and Zn levels in surface soils in the vicinity of the Henryk Arctowski Antarctic Station, aiming to identify anthropic effects on their local pedochemical variability. Pollution indices were used and compared to evaluate possible cumulative anthropic impacts, whereas correlation analyzes were explored to identify potential sources of contamination. High concentrations of Pb and Zn were locally observed near fuel tanks and machinery facilities. Correlation and principal component analysis suggest that old fuel tanks, vehicle traffic and machinery disturbance are key, and contrasting, sources of contamination. Among the eight indices we compared, Enrichment Factor and Modified Degree of Contamination were chosen, showing very high enrichment for Pb and moderate for Zn. All other elements presented minimal or null enrichment. The evidence of potentially toxic elements enrichment on Antarctic soils associated with the long-term occupation of Antarctic research stations highlights the need for further monitoring and mitigation measures, especially in energy-generating systems.

Key words: heavy metals, pollution indices, soil contamination, Admiralty Bay.

INTRODUCTION

Antarctica is a key continent to understand the planet's behavior and transformations through time, playing an essential role in our global climate system and to the primary production of marine ecosystems. Long seen as a pristine environment, Antarctica keeps records of human influence since the first expeditions in the 19th century, by whale and seal hunters (Villagran et al. 2013). Nowadays only tourism and scientific activities are permitted by the Antarctic Treaty, and most of these activities are developed in ice-free areas, which represent less than 0.5% of the continent's total area, representing terrestrial ecosystem biodiversity hotspots (Aislabie et al. 2004). The increase in human activity on the Antarctic continent in recent years has drawn attention to potential anthropogenic impacts and changes in the stability of the Antarctic ecosystem and its functions (Kennicutt et al. 2010, Lo Giudice et al. 2019, Palmer et al. 2022).

Environmental anthropic impacts in Antarctica are frequently related to old buildings and structures, sewage disposal systems, waste disposal sites and fuel spills (Tin et al. 2009). Fuels derived from crude oil have been used over the last 50 years to generate energy for settlements in Antarctica (Aislabie et al. 2004). Hence, it is essential to monitor the local environment occupied and shared by humans and the surrounding ecosystem, according to the Protocol on Environmental Protection to the Antarctic Treaty (CEP 1991), in order to understand potential human-caused changes in the Antarctic environment. Specific indicators, such as polycyclic aromatic hydrocarbons (PAHs) and spheroidal carbonaceous particles (SCPs), are often used to identify this type of contamination (Martins et al. 2010), but high concentrations of potentially toxic elements (PTEs) have also been related to contamination by fuel and oil spills (Lu et al. 2012).

PTEs occur naturally in the earth's surface and some of them are essential micronutrients for maintenance of biological processes in living organisms, but the exposure to high concentrations of these elements can confer toxicity (Hooda 2010). In contamination assessments, it is important to differentiate human influence on PTE levels from their natural levels in the environment (Alekseev & Abakumov 2020, Lu et al. 2012, Reimann & De Caritat 2005). Pollution indices have been successfully used over the years for this purpose (Hakanson 1980, Kowalska et al. 2018, Lee et al. 1997). The basic principle of pollution indices is to compare the levels of PTEs in environmental samples with their geochemical background in the environment (Kowalska et al. 2018). However, the comparison between the indices and their considerations has been little explored.

Anthropic contamination in Antarctica is usually recorded in different environmental matrices, as soil, air, water and life organisms (Amaro et al. 2015, Celis et al. 2015, Lima Neto et al. 2017, Espejo et al. 2014, Nydahl et al. 2015, Santos et al. 2005, Webster et al. 2003). Soil, acting as a reservoir, has a special relation with the ecosystem and plays an important role controlling the chemical transport of these contaminants to the atmosphere, hydrosphere and biosphere (Kabata-Pendias & Pendias 1999). Therefore, introduction of high PTEs loads into the environment related to human occupation in Antarctica are of special concern, as they tend to accumulate in the soil and thus, potentially interact with local fauna and flora (Fabri-Jr et al. 2018, Jerez et al. 2013).

The King George Island (South Shetlands Archipelago), historically concentrates human occupation, encouraging many studies to investigate potential anthropic contamination by PTEs in soils (Amaro et al. 2015, Dalfior et al. 2016, Fabri-Jr et al. 2018, Lu et al. 2012, Padeiro et al. 2016). The vicinity of Antarctic facilities (i.e. research stations, refuges) are known to be susceptible to this type of contamination (Lima Neto et al. 2017, Guerra et al. 2011a, 2013). However, some sites still have their soil contamination levels unknown, like the vicinity of the Polish Antarctic Station, Henryk Arctowski, the oldest research station located at Admiralty Bay. As part of the environmental assessments of King George Island, this study aimed to quantify potentially toxic elements (Cd, Cr, Cu, Mn, Ni, Pb, V and Zn) levels in surface soil samples collected around the Henryk Arctowski Antarctic Station and identify contamination trends by correlation analysis. The pollution indices were assessed and compared to verify possible anthropogenic effects on the pedochemistry variability of the area.

MATERIALS AND METHODS

Study area and soil sampling

The Arctowski Station, established in 1977, is located at Admiralty Bay (21S 423239 3107153; Figure 1) and works year-round. Arctowski is one of the most visited research stations in the Maritime Antarctic region by tourists, and concentrates scientific activities mainly in the austral summer, when the snow cover is minimal and the breeding seasons of native species occur (Chwedorzewska & Korczak 2010).

Mean annual temperature is -2.7 °C, and the precipitation is 510 mm (Lachasz et al. 2018). Soils of the area are mainly formed by uplift marine terraces, moraines and solifluction deposits, and derived from volcanic rocks (i.e. andesite, basalts, and pyroclastics) (Bölter et al. 1997, Bölter 2011). Cambisols and Regosols are dominant in the area, but Podzols, Gleysols, Umbrisols, Stagnosols and Leptosols (WRB taxonomy) were also described at the vicinity of the station by Bölter et al. (1997). The organic carbon content rarely exceeds 1% in soils not covered by vegetation or affected by ornithogenesis, and the clay mineralogy is mainly composed of feldspars and smecites (Blume et al. 2002, 2004). The vegetation cover is dominated by grass (*Deschampsia antarctica)*, lichens (mainly *Usnea antarctica*) and mosses (*Polytrichum sp.*). At least eight species of birds (mainly penguins, skuas and petrels) and three species of pinnipeds are regularly found near the station, and the increase of human activities over the years has affected local biome and the population of native species in the area (Chwedorzewska & Korczak 2010).

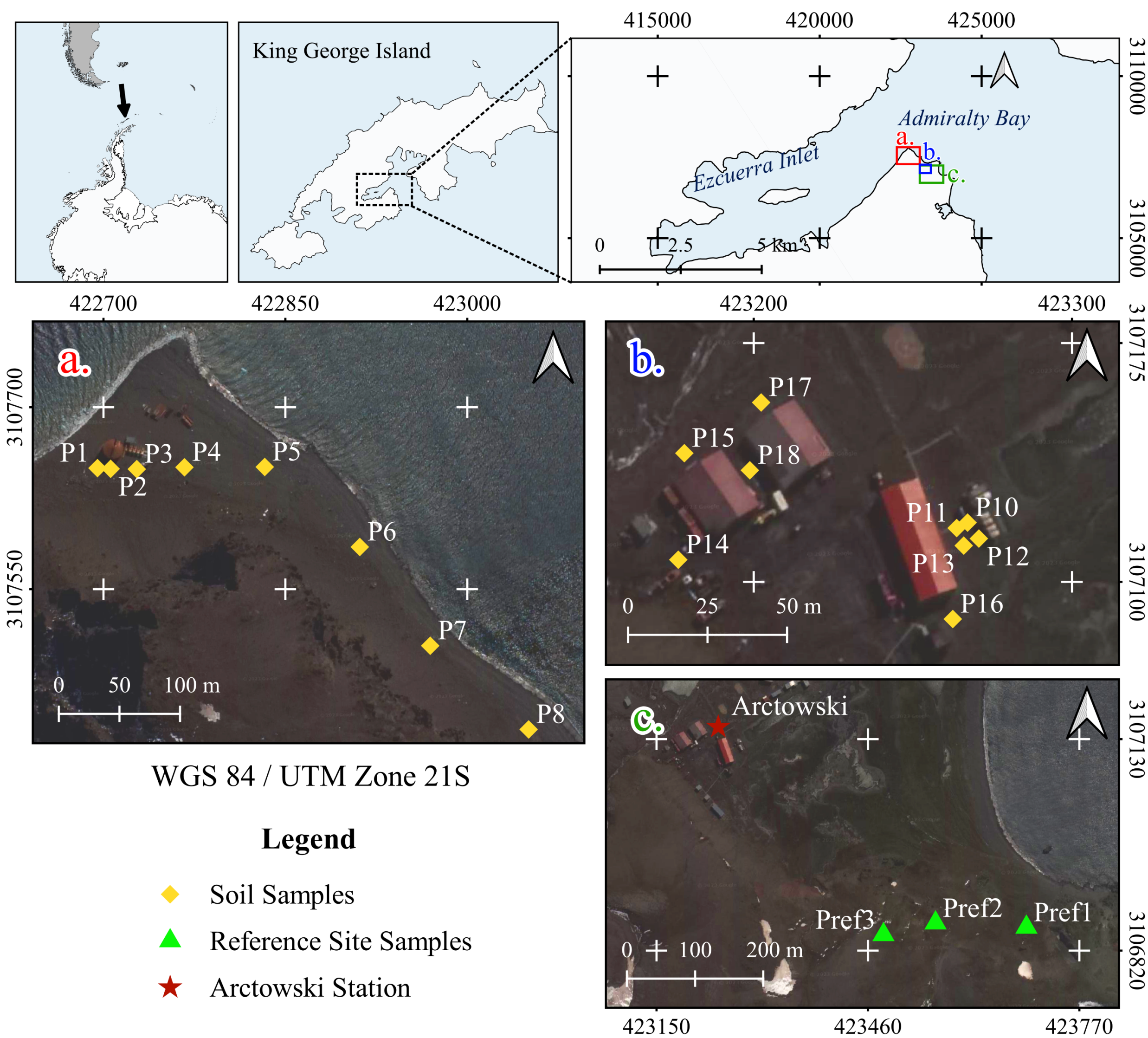

Figure 1. Sampling site locations.

Surface bare soil (0-10 cm) was sampled, in triplicate, in 17 selected sites at the vicinity of the station buildings on a recent raised beach geoenvironment (Figure 1) and packed in plastic bags. Areas with potential of PTEs contamination near roads, fuel and oil tanks, deposits, old structures and garages were sampled (Table I). A composite sample (Pref) was obtained from soil sampled in three undisturbed areas (Figure 1), with the same geological context as the others sampling points, for comparative use and to calculate the pollution indices.

Soil processing and laboratory procedures to PTEs analyzes

All soil samples were dried at 50 °C, until constant mass, grounded in an agate mortar, and sieved to obtain particle sizes smaller than 0.074 mm. All reagents (HNO_3, HCl and lithium metaborate) used in this study were of analytical grade quality (Sigma-Aldrich, Germany). All flasks and glassware were washed with detergent, immersed in a HNO_3 10% v v^{-1} solution during 16 h, and finally washed with fresh water and ultrapure water (Milli-Q, 18 Ω) before use.

Determination of Cd, Cr, Cu, Mn, Ni, Pb, V and Zn levels

The acid digestion was performed to determine the pseudototal concentrations of potentially toxic elements (Cd, Cr, Cu, Mn, Ni, Pb, V and Zn). Following the procedure described by the German Normative DIN 38414-S7, 0.3 g of dried soil sample was weighted, in triplicate, and transferred to closed digestion tubes, in which was added 3 mL of recently prepared aqua regia ($1HNO_3$:3HCl). After the addition of the solution, the material was left in repose for 12 h in exhaustion chapel, and then heated for 3 h

Table I. Sample sites characteristics and descriptions. UTM coordinates (WGS 84).

Sample	Coordinates (starting point)	Elevation (m)	Description
P1-P5	21E 422695 3107649	6	Vicinity of an old fuel tank. After the first sample (P1), the samples were collected at 10, 30, 70 and 140 m from the starting point.
P6-P8	21E 422911 3107584		240 m from P1. From this point were collected two more samples (P7; P8), distanced by 100 m from each other. The transect follows the road that borders the beach
P10-P13	21E 423267 3107118	3	Vicinity of fuel storage tanks. The area presents soil revolving by vehicles and fine metallic residues. Signs of fuel spill.
P14	21E 423176 3107106		Vicinity of an electric generator and metallic residues. Present signs of machinery transit and presence of defrost water.
P15	21E 423178 3107140	0	Behind a machinery deposit.
P16	21E 423262 3107088	6	Behind the generator building.
P17	21E 423202 3107156	7	Behind a garage, near containers and abandoned metal structures.
P18	21E 423198 3107135	8	Between two garages. Presence of residues (wood, fine metallic and incinerated residues).
Pref	-	8	Composite sample from preserved reference areas Pref1, Pref2 and Pref3 (Figure 1).

at 120 °C in a DigiPREP digestion block (SCP Science, Canada). The extract was centrifuged for 5 min at 3000 rpm, and the supernatant was transferred to another 50 mL centrifuge tube and the volume was completed with deionized water.

A Certified Reference Material (CRM) Montana Soil II – NIST 2711a followed the same procedure to assess the reliability of the method. Before elemental quantification, all extracts were submitted to 2-fold dilution, being the acidity adjusted to 1% v v^{-1}, using nitric acid. Elemental quantification was performed by an inductively coupled plasma optical emission spectrometry (ICP-OES) Optima 7300 DV (Perkin Elmer, USA), monitoring the following emission lines: Cd 228.802 nm, Cr 267.716 nm, Cu 327.393 nm, Mn 257.610 nm, Ni 231.604 nm, Pb 220.353 nm, V 290.880 nm and Zn 206.200 nm.

Alkaline Fusion: Zr and Ti levels

To determine Zr and Ti concentrations, we performed the procedure described by Pansu & Gautheyrou (2006), using lithium metaborate as fusion reagent, as reproduced by Guerra et al. (2013). An aliquot of 60 mg of dried soil, in triplicate, was weighted into a graphite crucible, with 0.25 g of fusion reagent previously added. Then, 0.25 g lithium metaborate was added over the sample, forming a double-layer reagent. The material was placed in a muffle furnace with the following program stages: first, the samples were heated at 3 °C min^{-1} up to 450 °C, remaining in 450 °C for 1 h; second, the samples were heated at 10 °C min^{-1} up to 1000 °C, and kept in this temperature for 10 min. The muffle furnace was shut down and the samples were left inside the muffle furnace until the temperature reached 200 °C. The obtained melted beds were transferred to 50 mL centrifuge tubes, containing 25 mL of HNO_3 10% v v^1, and shaken in a horizontal shaker at 90 rpm for 4 h, to reach total dissolution. Finally, the volume was completed to 50 mL with deionized water.

Before elemental quantification, all extracts were submitted to 10-fold dilution, being the acidity adjusted to 1% v v^{-1}, using nitric acid. Elemental quantification was performed by an inductively coupled plasma optical emission spectrometry (ICP-OES) Optima 7300 DV (Perkin Elmer, USA), monitoring the emission line Zr 343.823 nm and Ti 337.279 nm.

Principal component analysis and Pearson correlation matrix

The principal component analysis (PCA) was performed as an exploratory approach to assess relationships between variables (PTEs) and between individuals (sampled points). For this, all input data has been scaled. Next, the individuals were grouped into clusters and plotted together. A Pearson correlation matrix was also made relating the contents of PTEs. In both Pearson correlation and PCA analyses, PTEs were additionally related to the ratio of stable soil constituents TiO_2/ZrO_2 to suggest the variability addressed to soil parent material (Chapman & Horn 1968, Daher et al. 2022). These elements are considered resistant to weathering when present in stable and insoluble mineral phases – e.g., rutile and zircon (Daher et al. 2022, Anda et al. 2009), and here it was considered that total contents of Ti and Zr are referred exclusively to their respective oxides.

Analyzes and graphs were performed in the R i386 v4.2.2 software. PCA was carried out using the *PCA* function from the FactoMineR package. The optimal number of clusters was determined with the *fviz_nbclust* function of the factoextra package, and the clusters were separated by the *kmeans* function using 50 different initial conformations. Libraries dplyr, ggplot2 and ggforce were used to plot graphs. Pearson correlation (r) was tested at 0.05 significance level.

Pollution indices

To investigate anthropic influence on PTEs levels and quantify pollution degrees, indices based on geochemical enrichment were calculated and compared. The geoaccumulation index (I_{geo}) was calculated following Muller (1979) proposition. The I_{geo} index calculation follow the equation:

$$I_{geo} = \log_2\left(\frac{C_n}{1{,}5.\,B_n}\right),$$

where C_n is the concentration of the element under investigation (n) in the soil sample and B_n is the geochemical background value for basaltic rocks for the target element (n) (Turekian et al. 1961). The constant (k = 1,5) was used to minimize possible variations of the background values related to lithological effects (Alekseev & Abakumov 2020, Lima Neto et al. 2017).

Indices considering the reference control area (unpolluted) sample as background were also calculated. Contamination Factor (CF) relates the ratio of the contents of each metal to its concentration in a reference area (background), and was calculated according to the equation proposed by Muller (1979):

$$CF_n = \frac{C_n}{B_n},$$

where C_n is the concentration of the element under investigation (n) in the soil sample and B_n is the concentration of the element (n) in the reference area sample.

The Enrichment Factor was calculated, following the proposal of Lee et al. (1997), using Zr as reference and conservative element. The EF equation was used:

$$EF = \frac{(Me/Zr)_{sample}}{(Me/Zr)_{control\ site\ sample}},$$

where Me/Zr was the ratio between the concentration of the element under investigation and the reference element (Zr) mass fraction.

Ecological Risk Index evaluates ecological risk based on toxicity response of each PTE and were proposed by Hakanson (1980) following the equation:

$$ER_n = CF_n \times T_n,$$

where T is referred to the toxicity response of the PTEs and CF is the Contamination Factor to each correspondent element. Toxicity responses for the eight assessed PTEs evaluated were Zn = V = Mn = 1; Cr = 2; Cu = Pb = Ni = 5; Cd = 30 (Hakanson 1980).

Aggregative indices, which consider all PTEs together, were also calculated. Degree of Contamination (C_{degree}) is an index resulting from the sum of CF from all PTEs considered, proposed by Hakanson (1980). The Modified Degree of Contamination (mC_{degree}) evaluates the average contamination by the number of PTEs considered (i) (Alekseev & Abakumov 2020, Machender et al. 2011). Pollution Load Index (PLI), proposed by Tomlinson et al. (1980), also evaluates the contamination load for all PTEs from the CF values. These indices were calculated following the equations:

$$C_{degree} = \Sigma CF_n;\ mC_{degree} = \frac{C_{degree}}{i};\ PLI = (CF_1 \times CF_2 \times \ldots \times CF_i)^{1/i}.$$

Potential Ecological Risk Index (RI) is an aggregative index based on toxicity response resulting from the sum of ER, proposed by Hakanson (1980), and were calculated by the equation:

$$RI = \Sigma ER_n.$$

Nominal categorization of levels for each index is represented in Supplementary Material (Tables SI and SII).

RESULTS AND DISCUSSION

Pseudototal Cd, Cr, Cu, Mn, Ni, Pb, V and Zn concentrations

The concentration of elements analyzed in the reference sample, CRM – NIST 2711a, are within the expected range for acid digestion stipulated by NIST – Special Publication 260-172 (Mackey et al. 2010), and the analytical figures of merit ICP-OES measurements were presented (Table SIII). Levels of PTEs were compared with the control site sample and the Prevention Values (PV) recommended by the Brazilian National Council for the Environment (CONAMA) 420/2009 resolution (Figure 2, Table II). Prevention Values are defined by the limit concentration of some substance in the soil such that it can perform its main functions.

Results revealed low variation in Cu, Ni, Mn and V levels, with values below those preconized by Brazilian Normative CONAMA 420/2009, except for Cu. On the other hand, high variability occurs for Zn, Pb and Cr levels, nonetheless remains under PV and control site levels for Cr. All samples presented Pb levels above the control site (5.1 mg kg^{-1} to 165.9 mg kg^{-1}), and six samples (P1, P2, P10, P14, P17 and P18) presented Pb levels higher than PV (72.2 mg kg^{-1} Pb). Three samples presented Zn levels above PV (P15, P17 and P18), and ten samples (P2, P10 to P18) presented the concentration above the control site level. For Cu, the concentration in soil samples was within the range of the control area samples, but above PV (60 mg kg^{-1}). The high Cu content in the control samples may be due to the mineralogy of soil's parent material in the region, represented by volcanic rocks, mainly basalts and andesites, with Cu-sulfides (Guerra et al. 2011b). All Cd levels were below the limit of detection, except for P10 (1.3 mg kg^{1} Cd) that presented the Cd concentration according to the prevention value and, therefore, Cd levels are not shown from now on.

Highest Pb levels, similar to highest Zn levels, were found near old fuel and oil tanks, and garages, with abandoned containers and metal structures (Table SIV), where visual signs of fuel spill, fine fragments of metallic residues and paint particles were detected in the soil surface. Several authors highlighted that fuel spill, fuel power generation systems and abandoned sites are the mainly anthropic source of PTEs pollution in Antarctica (Abakumov et al. 2017, Alekseev & Abakumov 2020, Ribeiro et al. 2011, Tin et al. 2009), and the variability of Pb and Zn in distinction to other PTEs can be suggestive of non-natural processes (Xu et al. 2020). Lead was historically used as a fuel additive while zinc may be related to tires (Mielke et al. 2010), probably the reason for the highest Zn levels near a garage. Furthermore, continuous abrasion of metallic structures and paints produces small particles which can act as punctual sources of Pb in the vicinity of Antarctic facilities (Xu et al. 2020).

The results reported here are comparable to high levels of PTEs in soils sampled near Antarctic scientific facilities, most related to oil and fuel spills (Table II). High Pb concentrations near fuel and oil tanks (62 mg kg^{-1} to 1101 mg kg^{-1}) were reported by Amaro et al. (2015) in samples from Fildes Peninsula (Table II). Guerra et al. (2011a) found high concentrations of Ni (89 mg kg^{-1}), Pb (438 mg kg^{-1}) and Zn (3484 mg kg^{-1}) in soil samples with evident and discreet oil contamination at Hope Bay, at

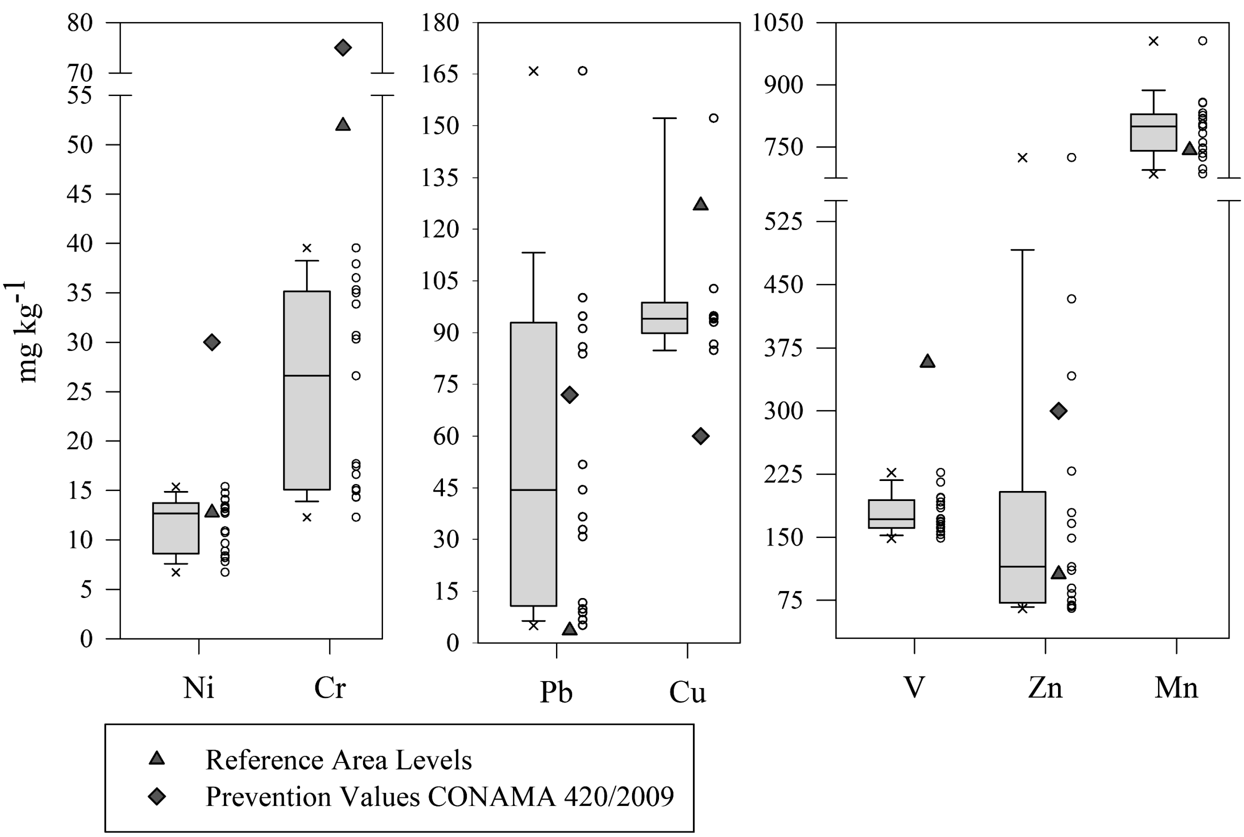

Figure 2. Plots of Ni, Cr, Mn, Ni, Pb, V, Zn, and Cu pseudototal levels for all samples, Prevention Values defined by CONAMA 420/2009 and reference area levels.

Table II. Comparative table with PTEs levels in soils sampled near Antarctic scientific facilities.

Sample	Cr	Cu	Mn	Ni	Pb	V	Zn
	mg kg^{-1}						
P1-P5[a]	12.3-17.4	84.9-94.8	684.7-760.6	6.7-10.9	8.8-100.1	148.8-165.2	69.2-110.5
P10-P13[a]	30.3-35.3	-	746.2-804.6	12.8-15.4	32.9-94.7	167.8-197.2	114.8-166.1
P17[a]	36.5	-	818.0	14.1	165.9	184.7	724.5
Soil sample with evident oil contamination, in Hope Bay[b]	225	159	326	89	438	-	3484
Soil sampled near fuel tanks, in Fildes Peninsula[c]	-	135	-	-	1101	-	557
Soil sampled near an Antarctic refuge[d]	72	107	545	37.9	102	122	148
Soil sampled near Gentoo penguin colonies, at O'Higgins Base[e]	64.8	421.9	404.8	28.1	281.5	-	485.0
Baseline values (mean) in soils at Fildes Peninsula[f]	32.0	122.3	923.0	14.3	15.9	-	58.7
Pref[a]	51.9	126.9	742.1	12.8	3.6	357.4	106.1
Prevention values[g]	75	60	-	30	72	-	300

[a]This study; [b](Guerra et al. 2011a); [c](Amaro et al. 2015); [d](Lima Neto et al. 2017); [e](Celis et al. 2015); [f](Lu et al. 2012); [g](CONAMA 420/2009).

a former scientific base that was burned by a fire event in 1948. These observations reinforce that management and storage of fuel is an imminent source of Pb pollution in Antarctic soils, and its related impacts can already be assessed on biota (Celis et al. 2015, Chu et al. 2019b) and vegetation (Chu et al. 2019a, Tapia et al. 2021). However, high concentrations of PTEs do not guarantee negative impacts on the ecosystem, since it also depends on the mobility of these elements in soil and water, on the interaction among the PTEs available in the environment and, consequently, on their availability to living organisms (Koppel et al. 2019). Even so, high levels of PTEs related to anthropic occupation in Antarctica highlights the need to rethink the use of fossil fuels as the main source of power by scientific facilities.

PCA and PTEs correlation

The variability of PTEs levels in soils is a result of combinations and interactions of different sources with the geochemical matrix present in the area (Alekseev & Abakumov 2020). Correlations between PTEs are frequently used to indicate anthropic pollution in Antarctica, while the PCA is usually explored to look for indications of potential sources of contamination (Alekseev & Abakumov 2020, Lima Neto et al. 2017, Lu et al. 2012). Significant correlation among elements suggests that they have similar geochemical behaviors or, alternatively, similar source of contamination (Lu et al. 2012). Three variables (PC1, PC2 and PC3) presented eigenvalues higher than 1, and they cumulatively explain 87% of the data variance. PC1 contains Ni (0.89), Cr (0.94), Zn (0.73) and ZrTi (0.66) positively correlated (Figure 3). Variations of Ni, Cr and Cu – here highly correlated (Table III) – are usually attributed to geochemical factors in soils derived from basalts (Lu et al. 2012, Siegel 2002), and their significant correlation with the Zr/Ti ratio suggest that the variability of these PTEs is associated with specific geochemical factors of the samples.

PC2 contains only negatively correlated Pb (0.71) and ZrTi (-0.64) (Figure 3), and its variation is likely attributed to anthropic factors, since Pb was the PTE that presented the highest levels in areas with visual signs of contamination. Although not contained in PC2, zinc is the only PTE high correlated with lead (Table III), suggesting that its higher levels may be attributed to the same source of Pb contamination. Strong correlations between Pb and Zn can be assigned to vehicle traffic disturb (Mielke et al. 2010), and have already been reported in Antarctica polluted sites (Alekseev & Abakumov 2020, Lima Neto et al. 2017). Here, higher concomitant concentrations of Pb and Zn were identified in samples near garages (P17, P18).

The plot of individuals was grouped in five clusters (Figure 3) and provides interesting interpretations. Group 4 (except for P16) contains only the samples collected in the P1-P5 transect, gradually distanced from old fuel tanks. Group 5 refers to samples from transect P6-P8, on the road that connects the old fuel tanks with the station area. Group 1 contains only samples collected in areas near the research station buildings, and Group 2 and 3 are exclusively composed by highly contrasting samples – the most contaminated sample (P17) and the reference site sample (Pref). From the clustering analysis of individuals, PC1 seems to distinguish the type of contamination and the sources are contrasting, with individuals subject to direct contamination by old fuel tanks showing negative values, and those subject to heterogeneous contamination (e.g. traffic disturbance, paint and metallic debris) close to the station buildings showing positive values. Otherwise, PC2

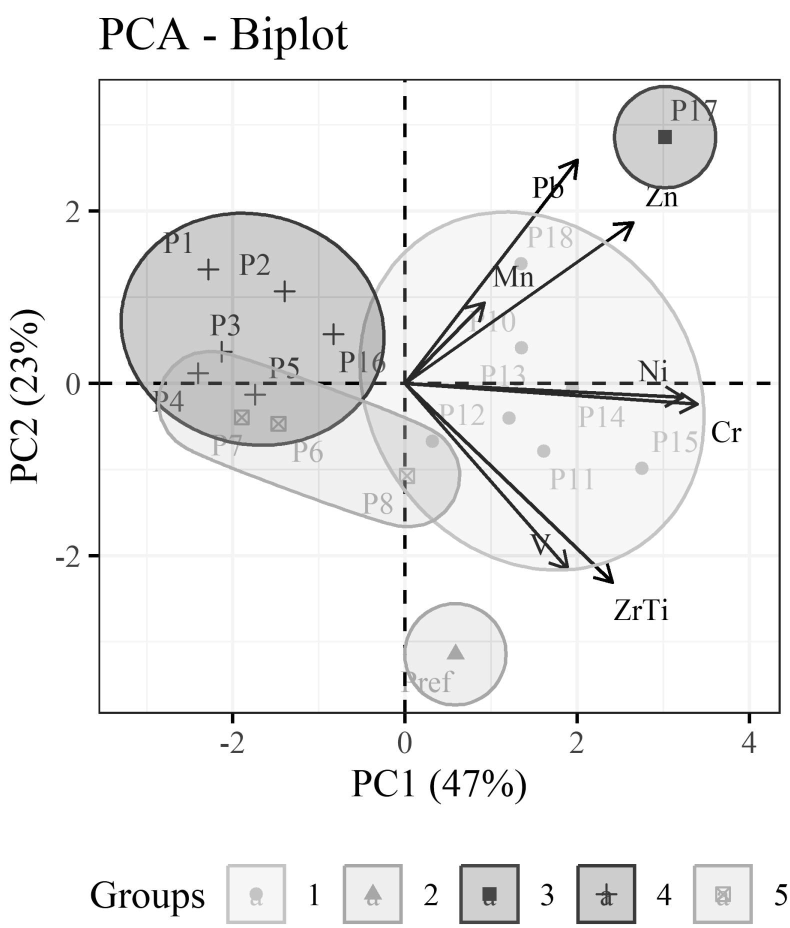

Figure 3. Biplot (variables and individuals) of Principal Component Analysis for the levels of Pb, Zn, Mn, Ni, Cr, V and Zr/Ti ratio.

Table III. Pearson correlation matrix for PTEs levels of all samples.

	Ni	Pb	Cr	Cu	Mn	V	Zn
Ni	1.00						
Pb	0.36	1.00					
Cr	**0.85***	0.47*	1.00				
Cu	**0.85***	-0.42	0.55	1.00			
Mn	0.33	0.15	0.02	0.32	1.00		
V	0.38	-0.16	0.37	**0.90***	0.31	1.00	
Zn	0.51*	**0.71***	0.61*	-0.34	0.23	0.17	1.00
Ti/Zr	0.55*	0.03	**0.70***	0.54	-0.21	0.58*	0.14

*Significant correlation at 0.05 significance level. Bold values highlight strong correlation (> 0.70).

seems to refer to the intensity of contamination, with the extreme positive individual represented by the sample with the highest levels of Pb and Zn (P17), followed by others with a high level of contamination (P18, P1, P2), and the extreme negative individual represented by the reference site sample (Pref).

Pollution indices

Given the great influence of parental material in Antarctic soils due to low chemical weathering rates (Simas et al. 2006), pollution indices have been widely used in assessments of PTEs in Antarctica (Alekseev & Abakumov 2020, Guerra et al. 2011a, 2013, Lima Neto et al. 2017, Xu et al. 2020). These indices are useful to reduce the bias caused to grain size and mineralogy, and helps to search human-originated contamination (Lee et al. 1997). For all indices, highest Pb levels reach high to extreme pollution ratings [max. 29.5 (EF); 4.2 (I_{geo}); 46.2 (CF); 231.2 (ER)] (Figure 4; Tables SVI and SVII). The highest Zn levels presented wide variation in the nominal rating between the indices, ranging from low ecological risk (ER = 6.8) or moderate enrichment (EF = 4.8), to extreme pollution (CF = 6.8) (Figure 4). Except for Cu and Mn outliers, all other PTEs presented the lowest ratings for all indices (Figure 4), highlighting signs of non-contamination for these elements.

The highest indices for Pb (EF = 29.5; I_{geo} = 4.2) and Zn (EF = 4.8; I_{geo} = 2.2) found here are higher than those reported for Pb (EF = 18; I_{geo} = 3.5) and Zn (EF = 4; I_{geo} < 0) by Lima Neto et al. (2017) in soil sampled in the vicinity of an Antarctic refuge. Alekseev & Abakumov (2020) also found values lower than those reported in this study for Pb and Zn in I_{geo}, CF and ER indices, but found high index values for Cd in soils sampled under moss cover related to bioaccumulation and biotransport by Antarctic fauna in Ardley Island. However, some authors have reported even higher pollution indices in Antarctica. Also, in soil sampled near to fuel tanks, Amaro et al. (2015) reported an EF mean of 16 (± 23) for Pb, higher than the EF mean reported here for Pb [11.8 (± 9.5)]. Soils sampled by Guerra et al. (2013) under an Antarctic research station that suffered a fire event were extremely enriched, presenting maximum EF values of 1132 (Pb) and 1153 (Zn).

Four indices for each element were presented in Figure 4. The I_{geo} index is calculated from the global mean values of PTEs in the soil parent material as reference background (Kowalska et al. 2018). Using global mean values as background may be inappropriate for contamination assessment due to potential environmental singularities in different sampling areas (Kowalska et al. 2018, Reimann & De Caritat 2005). All other indices use reference area levels for the calculation with a local background approach, which is recommended when anthropogenic contamination is suspected (Kowalska et al. 2018). However, CF and, consequently, ER do not consider normalization by a conservative element, and can lack elements with low occurrence of variability (Kowalska et al. 2018). The main consideration in using an immobile and conservative reference element for the calculation, such as Zr (Chapman & Horn 1968), is that the unnatural proportion of it is expected to be negligible (Lee et al. 1997). Therefore, the EF index is more suitable to avoid variability addressed to natural composition of the sampled soil, avoiding potential under or overestimation. The ER index is an interesting approach by applying factors based on the toxicity response of each PTE. Toxicity response factors were determined based on abundance, environmental dynamics and toxic effects on bioproduction in limnological systems (Hakanson 1980), and may be useful in research in areas occupied by Antarctic

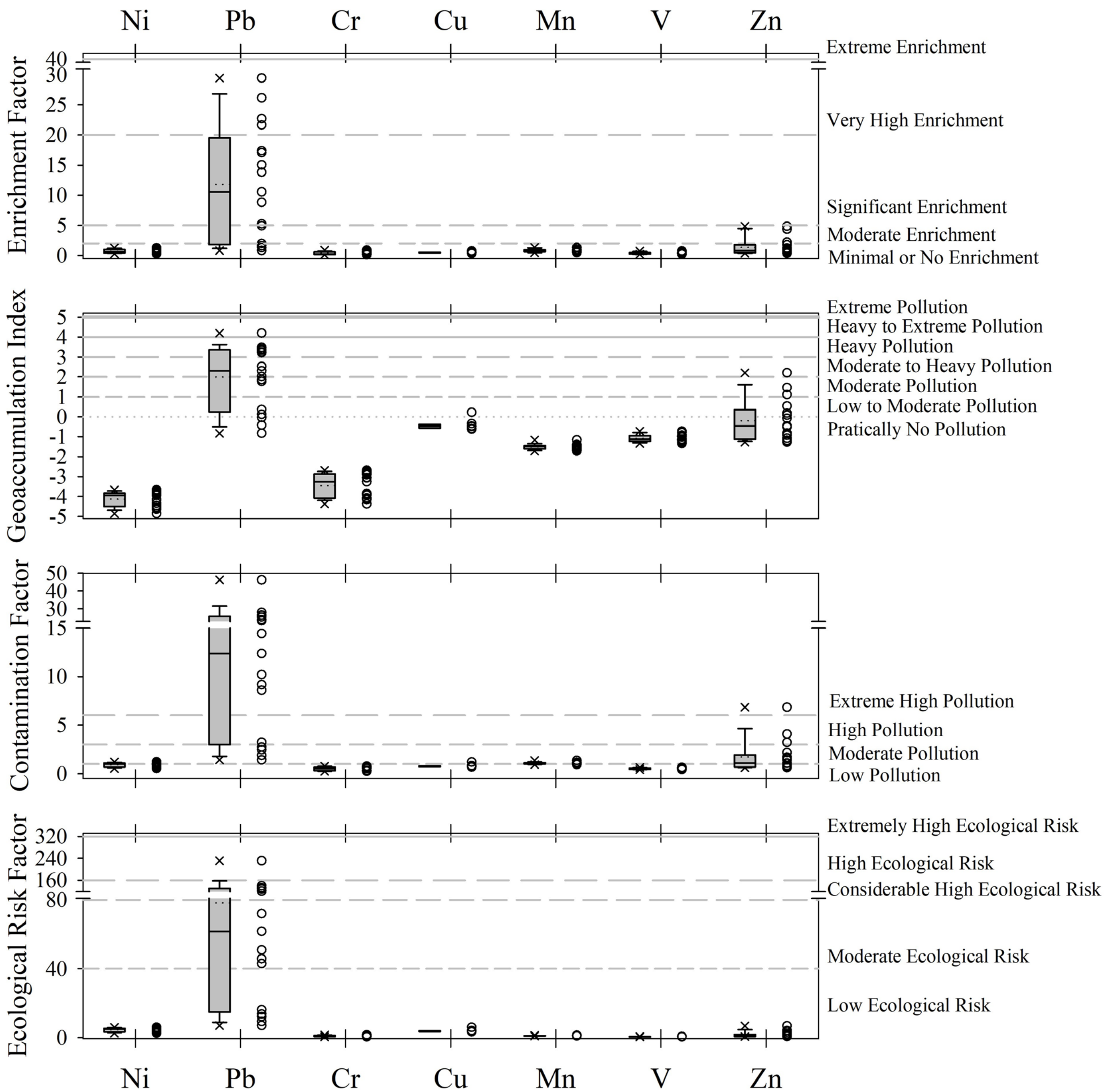

Figure 4. Enrichment factors (ER), geoaccumulation index (Igeo), contamination factors (CF) and ecological risk factors (ER) of Ni, Pb, Cr, Cu, Mn, V and Zn for all samples. Nominal ratings are displayed on the right of each index chart.

biota or vegetation. In addition to not normalizing the calculation with a conservative element, the CF index has the least number of classes and may seem more extremist. For example, the highest CF value of Zn is classified as extreme pollution, while for EF index this sample is moderately enriched, and, considering ecological issues, ER classifies the sample as of low ecological risk (Figure 4).

Aggregative indices allowed classifying the samples pollution considering all PTEs together (Figure 5; Table SV). For C_{degree}, 6 samples were classified as extremely very polluted, while for $mC_{dregree}$ only one sample achieved the rating of very high polluted. The values are higher than those reported by Alekseev & Abakumov (2020), which recommended the use of PLI for Antarctic soils due to geochemical and ornithogenic factors. The highest reported PLI value (2.3) for our samples classifies it as moderately contaminated, even though it has 165.9 mg kg^{-1} Pb and 724.5 mg kg^{-1} Zn (P17). Therefore, the use of the PLI index in Antarctic soils with visual or historical evidence of contamination may lead to underestimation.

The aggregative indices were also calculated based on EF instead of CF (ratings are not changed), in our view of better EF suitability, and the same could be done for ER. Normalization by the conservative element Zr helped to reduce the variability of outliers for all indexes (Figure 5). For mC_{degree} and RI indices, the most polluted sample (P17) went from very high to high pollution and from high to moderate ecological risk, respectively. The modified degree of contamination, based on EF values, was chosen and is recommended as a suitable aggregative pollution index for soil samples with signs of anthropic pollution in Antarctica. In this case, 29% (n = 5) of the soil samples collected in this study presented high pollution. The RI index does not show similarity with other aggregative indices (Kowalska et al. 2018), and can be a useful tool for considering a summary of the toxicological

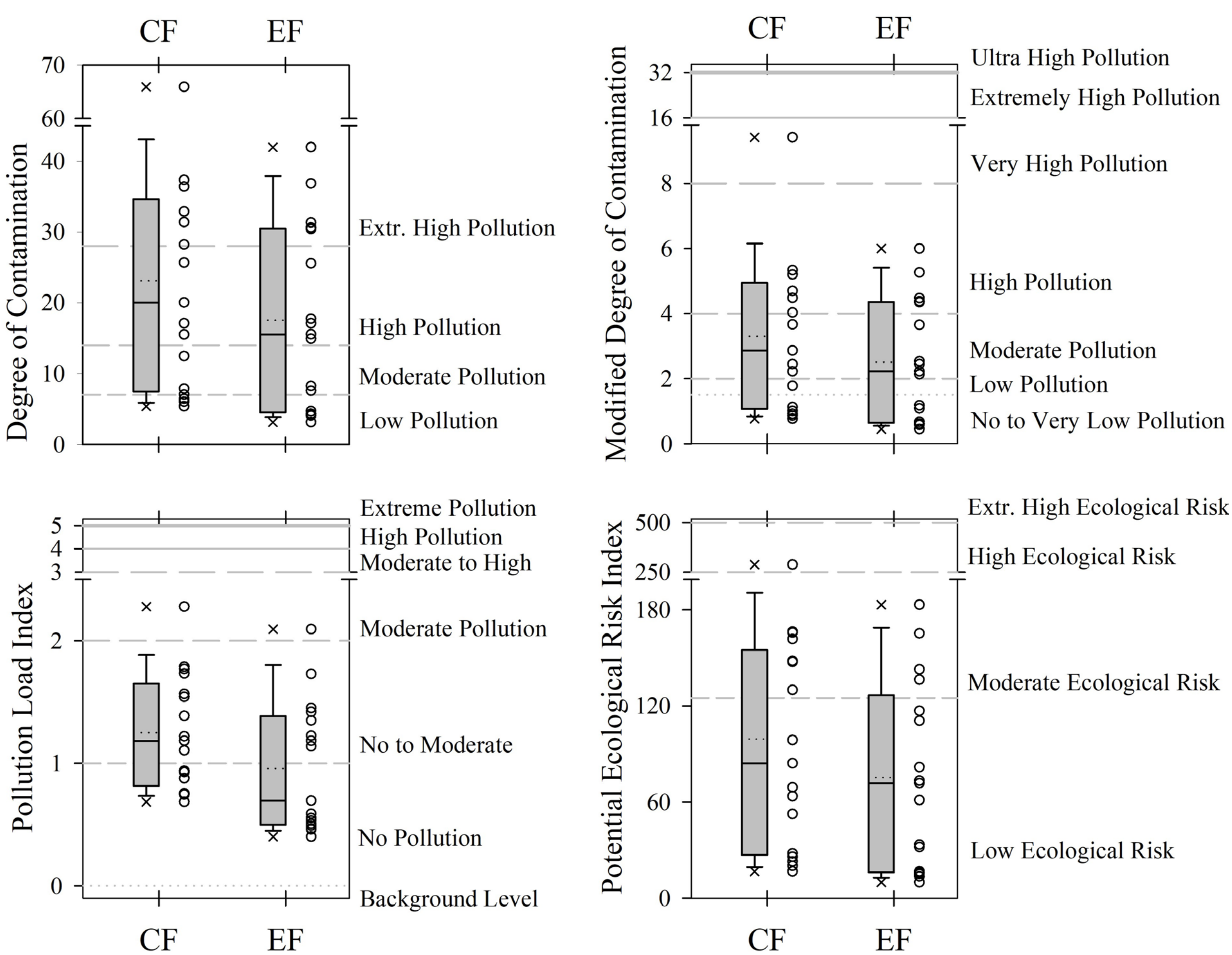

Figure 5. Degrees of contamination (Cdegree), modified degrees of contamination (mCdegree), pollution load index (PLI) and potential ecological risk index (RI) for all samples. Plotted values calculated with CF (left) and EF (right) values. Nominal ratings are displayed on the right of each index chart.

responses of the individual elements in research with ecological approach and influence of the Antarctic fauna and flora.

Figure 6 spatially summarizes the levels of Pb – PTE that presented the highest enrichment – in addition to their EF values and the mC_{degree} of the soil samples – pollution indices chosen as suitable. It is worth noting the decrease trend in Pb levels and pollution indices with increasing distance from the old fuel tanks on the P1-P5 transect (Figure 6; Tables SIV to SVII), suggesting that these facilities act as a source of Pb contamination. However, the sources of contamination seem to be punctual, as an abrupt contrast (~20 m) is noted between very highly enriched (P10 and P11) and moderately enriched (P6) samples (Figure 6). It is also evident the functionality of the pollution indices in distinguishing natural and anthropic anomalies in the pedochemical variability of the samples. At P15, for example, weighing the EF index with the conservative element Zr reveals that the sample is significantly enriched even with Pb levels below the PV (Figure 6; Tables SIV and SVI).

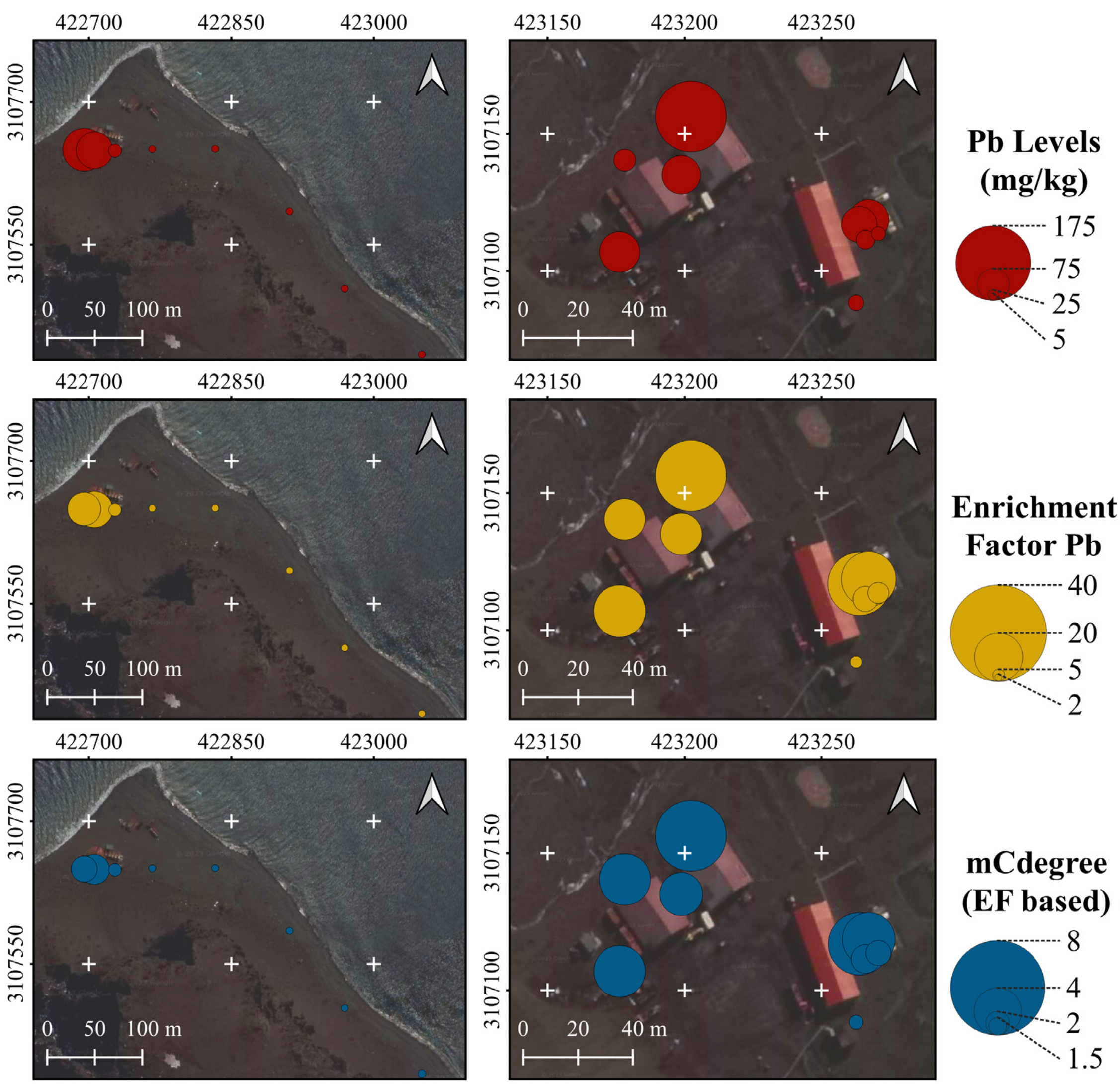

Figure 6. Spatialized size circle diagrams for Pb levels, EF for Pb and mCdegree of the samples.

CONCLUSIONS

This study shows that the long-time occupation at an Antarctic research station has affected the pedochemical variability of the vicinity soils due to anthropic activities. Pb levels were higher than the reference area for all samples, and 35% (n = 6) of them were higher than Prevention Value. Zinc levels were higher than the reference area in 53% (n = 9) of the samples, and higher than Prevention Value in 18% (n = 3). The high correlation between these two elements and PCA results suggests that old fuel tanks and vehicle traffic disturbances are the main, and contrasting, sources of pollution.

We compared pollution indices and suggested the use of Enrichment Factor and the Modified Degree of Contamination, based on EF, as suitable indices for research in Antarctic soils with signs of contamination. Significant or very high enrichment of Pb were detected for 65% (n = 11) samples, while for Zn the enrichment is moderate. All other PTEs showed minimal or no enrichment, but 59% (n = 10) of the samples were moderately to highly polluted by the aggregative index. Results of the pollution indices and their spatialization reinforce the evidence of point sources of contamination.

The results presented here reinforce that the long-term use of fossil fuels and the traffic of vehicles in the vicinity of old research stations are potential sources of pollution by PTEs. This study contributes to the environmental monitoring preconized by the Protocol on Environmental Protection to the Antarctic Treaty and highlights the need for rules with mitigation and monitoring practices to the Antarctic research stations, avoiding the use of fossil fuel as the main source of power, the excessive use of vehicles and opening specific tracking roads for personnel traffic.

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SUPPLEMENTARY MATERIAL

Table SI-SVII.

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