



Natural variability of major and trace elements in non-ornithogenic Gelisols at Edmonson Point, northern Victoria Land, Antarctica

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Abstract: Antarctica is perceived as one of the most pristine environments on Earth, though increasing human activities and global climate change raise concerns about preserving the continent's environmental quality. Limited in distribution, soils are particularly vulnerable to disturbances and pollution, yet lack of baseline studies limits our abilities to recognize and monitor adverse effects of environmental change. To improve the understanding of natural geochemical variability of soils, a survey was conducted in the fellfield environments of Edmonson Point (Victoria Land). Soil samples were analyzed for six major (Fe, Ca, Mg, Na, K and Ti) and 24 trace elements (As, Ba, Be, Bi, Cd, Co, Cr, Cs, Cu, Ga, Li, Mn, Mo, Ni, Pb, Rb, Sn, Sr, Tl, U, V, Y, Zn and Zr). Relationships among element concentrations in the samples and local bedrock were analyzed to identify their origin and similarities in geochemical cycles. Element concentrations in the soils were highly variable but generally within the lowest values reported elsewhere in Antarctica. Though values of Cd, Mn, Ni and Zn were relatively high, they are consistent with those in the local soil-forming rocks indicating an origin from natural sources rather than anthropogenic contamination. Chemical composition of soils vs. rocks pointed to alkali basalts as the lithogenic source of the soil matrix, but also indicated considerable alteration of elemental composition in the soil. Considering local environmental settings, the soil elemental content was likely affected by marine-derived inputs and very active hydrological processes which enhanced leaching and removal of mobilized elements. Both of these processes may be of particular importance

within the context of global climate change as the predicted increases in temperature, water availability and length of the summer season would favor mineral weathering and increase geochemical mobility of elements.

Key words: Antarctic, Victoria Land, soil, pedogenesis, weathering, geochemistry, natural background.

Introduction

Antarctica is generally perceived as one of the most pristine environments on Earth which provides a unique opportunity for investigating natural geochemical variation and cycling of elements. Nevertheless, Antarctica's environments are not immune to impacts from human activities occurring both globally and locally within the region, or climate change affecting ecosystem structure and processes elsewhere (Bargagli 2005, 2008; O'Neill *et al.* 2015). In fact, despite limited human presence and exploration beginning only ~100 years ago, some areas have been substantially altered already by human activities. The impacts are especially high in regions such as King George Island (Lu *et al.* 2012; Padeiro *et al.* 2016) and Hut Point, Ross Island (Sheppard *et al.* 2000; Kennicutt *et al.* 2010), where high concentrations of multinational activities and stations were established at a time when little attention was paid to environmental protection. The implementation of the 1991 Madrid Protocol on Environmental Protection to the Antarctic Treaty, ratified in 1998, has helped to significantly reduce further impacts as well as mitigate existing impacts. However, as the intensity and diversity of human activities in Antarctica expands, there are increasing concerns about the risk of disturbances over broader areas and their cumulative effects on the Antarctic flora, fauna and landscapes (O'Neill *et al.* 2015).

One of the effects of human impacts is a change in the concentrations of trace elements. In recent years numerous studies on trace metals and Persistent Organic Pollutants (POPs) in Antarctica have documented contamination in both biotic and abiotic components of terrestrial, freshwater and marine environments (see reviews by Bargagli 2005, 2008). However, the Pb is probably the only contaminant that has been significantly influenced over large regions of Antarctica from anthropogenic inputs. Levels of contamination of other pollutants from anthropogenic sources remain small and clearly restricted to a few local point-source inputs from ship, aircraft and research operations. In fact, available data indicate that concentrations of trace metals and POPs in soils and cryptogams throughout Victoria Land range among the lowest yet reported, even for remote areas (Bargagli *et al.* 1998; Bargagli 2005, 2008; Borghini *et al.* 2005).

In this context, Antarctica continues to be one of the least polluted regions on Earth. However, evidence of enhanced Hg accumulation in soils and biota at sites facing coastal polynyas raise concerns about the possible impacts of changes in

climate and sea ice coverage on global cycles of pollutants and their influx into terrestrial coastal ecosystems in Antarctica (Bargagli *et al.* 2005, 2007; Barrett *et al.* 2006). Therefore, investigating temporal variation in element concentrations could be of great value to assess local and global changes in geochemical cycles. For this approach to be effective, it is crucial to establish the natural variability in element concentrations and determine variation in their depositional fluxes. These topics only recently have been investigated in Antarctica focusing on the variety of different abiotic and biotic components, including glaciers (Fortner *et al.* 2011), terrestrial waters (Abollino *et al.* 2004; Nędzarek *et al.* 2014), lacustrine sediments (Malandrino *et al.* 2009), soils (Crockett 1998; Cannone *et al.* 2008), and vegetation (Bargagli *et al.* 1998, 2005; Culicov *et al.* 2017), as well as marine sediments (Giordano *et al.* 1999; Santos *et al.* 2005) and biota (Santos *et al.* 2006; Grotti *et al.* 2008).

Soils are particularly interesting since in Antarctic they have a crucial role in natural cycling of elements (Bargagli 2005; Barrett *et al.* 2006) and provide baseline environments for endemic biota (Wall 2005; Convey *et al.* 2014). Due to their physical properties and naturally slow pedological processes (Campbell and Claridge 1987), soils are also vulnerable to disturbances and pollution and are, therefore, regarded as reliable indicators of environmental change and human impacts (Ugolini and Bockheim 2008; O'Neill *et al.* 2015). However, soil geochemical studies in Antarctica are limited and focused mostly on those in the maritime Antarctic (Lee *et al.* 2004; Navas *et al.* 2008; Bölter 2011), coastal areas of Wilkes and Dronning Maud Lands (Beyer and Bölter 2002), and on the continental deserts of the Dry Valleys in southern Victoria Land (Bockheim and McLeod 2015a). Until now, relatively few studies have been conducted at other Victoria Land localities (Barrett *et al.* 2006; Cannone *et al.* 2008; Bockheim 2015).

We completed a large-scale survey and sampling of soils throughout ice-free areas of coastal Victoria Land. The major goal of this study was to characterize the variability in soil geochemistry (Smykla *et al.* 2015) and biotic diversity (Smykla *et al.* 2010, 2011, 2012, 2018; Iakovenko *et al.* 2015) across multiple habitats and environmental gradients. Here, we present analysis of soil elemental composition from Edmonson Point, northern Victoria Land (74°20'S, 165°08'E; Fig. 1). As indicated previously (Smykla *et al.* 2015, 2018), we selected this specific site for a separate treatment because it is one of the best examples of coastal ice-free ecosystems in northern Victoria Land and is, therefore, considered a model site for investigating environmental processes and changes of coastal ice-free ecosystems in this region (Bargagli *et al.* 1997; Harris and Grant 2003). The outstanding nature of the Edmonson Point terrestrial ecosystems has already resulted in numerous studies on soil properties and elemental biogeochemistry (Bargagli *et al.* 1998, 1999, 2007; Cannone *et al.* 2008; Malandrino *et al.* 2009; Smykla *et al.* 2015). Experimental sites also have been established for long-term research to monitor impacts of climate and environmental changes on

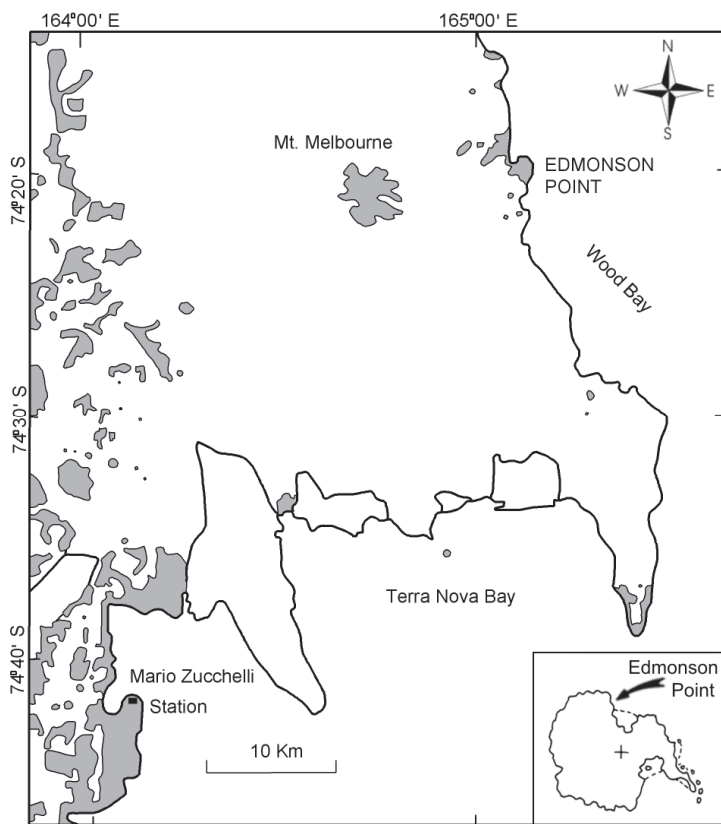


Fig. 1. Location of Edmonson Point in northern Victoria Land, Antarctica. Insert map shows the position of Edmonson Point in the Ross Sea region. Gray color indicates ice-free areas.

ecosystem processes and their potential implications for the region (Bargagli *et al.* 1997; Abollino *et al.* 2004; Borghini and Bargagli 2004; Cannone *et al.* 2008). However, this previous research focused mostly on cryptogamic communities and lacustrine environments with soil data usually limited to general pedological characteristics and major bio-elements.

To increase our knowledge on natural variation in soil geochemistry, we determined concentration levels for 30 elements in soils at Edmonson Point (Table 1). The most immature soils from fellfield environments were selected to provide baseline concentrations of soil elements, which could then be used as a reference for future monitoring activities and the assessment of geochemical variability in different soil environments. Taking into account the lack of significant differences in elemental concentrations (Smykla *et al.* 2015), soils from sites with limited moss growth were also included in the current analysis to provide a more representative data set. To our knowledge this is the first time

Table 1

Summary statistics (mean \pm SD, minimum, maximum, CV, median, skewness and kurtosis) and enrichment factor of elemental concentrations in soils from Edmonson Point, northern Victoria Land, Antarctica. Abbreviations indicate: min – minimum concentration, max – maximum concentration, CV – coefficient of variation, EF – enrichment factor based on Zr as the reference element and local alkali basalts (Wörner *et al.* 1989) as reference material.

element	mean	SD	min	max	CV (%)	median	skewness	kurtosis	EF
Major and minor elements (mg g ⁻¹)									
Fe	10.2	2.1	6.4	13.1	20	10.2	-0.2	-1.0	1.4
Ca	2.9	0.9	1.5	4.3	29	2.7	0.2	-1.0	0.6
Mg	2.4	0.7	1.1	4.4	31	2.3	1.1	2.0	0.9
Na	1.4	0.5	0.9	2.9	33	1.3	1.6	3.4	0.8
K	0.78	0.23	0.44	1.17	30	0.71	0.04	-1.5	1.0
Ti	0.71	0.25	0.41	1.15	34	0.73	0.1	-1.6	0.4
Mn	0.38	0.15	0.17	0.75	39	0.37	1.1	1.0	3.2
Trace elements (µg g ⁻¹)									
Zn	42.9	17.5	21.0	69.6	41	42.3	0.3	-1.5	4.6
Ba	32.9	17.8	14.5	88.4	54	28.1	1.7	3.5	0.8
Ni	33.6	9.3	20.3	53.0	28	31.5	0.6	-0.3	7.3
Sr	24.2	8.2	12.0	45.5	34	24.0	0.8	0.7	0.4
Zr	19.3	6.6	6.2	30.6	34	19.6	-0.4	-0.4	–
V	11.2	5.2	2.2	21.0	46	11.0	0.1	-0.9	0.7
Cr	7.8	6.8	nd	29.3	87	7.8	2.1	6.2	0.8
Y	6.3	2.2	4.5	15.2	35	5.9	3.6	14.4	3.6
Rb	4.6	1.2	2.6	7.8	27	4.7	0.6	1.1	2.2
Cu	3.9	1.2	1.9	6.3	32	3.5	0.6	-0.4	1.2
Li	3.9	1.1	2.0	5.8	28	3.9	0.2	-1.0	2.4*
Co	3.0	0.9	1.4	5.0	30	3.0	0.3	-0.5	0.8
Ga	1.9	0.5	1.0	3.3	27	1.9	1.1	2.5	1.1*
Pb	1.7	0.7	1.0	4.0	43	1.5	2.1	5.0	2.5*
Sn	0.91	0.84	0.09	2.70	93	0.45	0.9	-0.5	9.0*
Mo	0.84	0.31	0.45	1.62	37	0.77	1.2	1.4	7.8*
U	0.46	0.15	0.27	0.89	32	0.42	1.4	2.1	6.0*
As	0.45	0.35	nd	1.37	78	0.36	1.6	2.3	3.0*
Be	0.34	0.14	0.19	0.77	42	0.29	1.7	3.1	4.6*
Cd	0.21	0.19	0.05	0.91	91	0.15	2.7	9.2	12.5*
Bi	0.05	0.03	0.03	0.18	65	0.04	3.2	10.9	4.3*
Tl	0.07	0.05	nd	0.16	77	0.06	0.8	-0.6	2.2*
Cs	0.02	0.01	nd	0.03	45	0.01	0.4	-0.4	0.1*

* Indicate EF calculated based on alkaline magmatic rocks (global maximum values) taken from Kabata-Pendias and Pendias (1999).

that such a comprehensive study on elemental composition has been conducted in Victoria Land. Besides determining baseline concentrations of soil elements, which could be used as a reference for future monitoring activities, we also assess relationships among the soil elements as well as their levels with those in the local soil-forming rocks to provide insights into the origin and geochemical behavior of soil elements. Considering the relatively high abundance of water and active hydrological processes at Edmonson Point (Smykla *et al.* 2015, 2018) we expected the soils to show significant alterations in their elemental composition, with differences driven by element mobility, despite being geologically young and their properties strongly related to the parent material.

Materials and methods

Study area. — Edmonson Point (74°20'S, 165°08'E) is located in Wood Bay on the west coast of the Ross Sea, northern Victoria Land, continental Antarctica (Fig. 1). It is an ice-free coastal spur of Mount Melbourne, a dormant volcano showing evidence of very recent activity. The area encompasses ~6 km² and is one of the largest non-mountainous, coastal ice-free areas in Victoria Land. The landscape has been considerably modified by glacial and periglacial activity, resulting in a mosaic of hills, knolls and moraines separated by small valleys.

The ground is dark colored and consists of volcanic materials (basaltic lavas, scoria, pumice and tuff) which originated from the past volcanic activity of Mount Melbourne. Due to the presence of permafrost and active cryogenic processes, soils can be classified as Gelisols or Cryosols. They are generally immature and coarse textured with characteristics strongly related to the parent materials. Only a few exposed ridge crests, hills and mounds, occupied by active or relict penguin colonies, are characterized by the presence of ornithogenic soils that are distinctly different from the underlying parent materials. However, redistribution of penguin guano also influences chemical composition of soils near the active colonies, in particular soils in wet depressions and lacustrine environments can be considerably altered by accumulation of penguin-derived elements.

The climate is typical of coastal areas in the continental Antarctic, with low temperature, humidity and precipitation. However, Edmonson Point is well sheltered from local katabatic winds, and its climate is milder than in the neighboring ice-free areas. As a consequence, snow tends to melt rather than sublimate providing high abundance of water. After the spring snowmelt ephemeral melt-water streams and ponds are common, and soils become saturated with groundwater. By the onset of summer, water quickly drains and most of the area become extremely dry. Thus, the landscape is dominated by typical fellfield environments, where low temperatures and aridity are the main limiting factors for life and ecosystem developmental processes.

Owing to its environmental characteristics Edmonson Point is considered as one of the best examples of coastal ice-free ecosystems in northern Victoria Land. It has been, therefore, the subject of an increasing number of studies and efforts to protect its ecological and scientific values, such that the entire ice-free area is now designated as the Antarctic Specially Protected Area (ASP) No. 165. Detailed descriptions of Edmonson Point, and processes affecting development and diversity of its environments, have already been presented in several publications (*e.g.*, Baroni and Orombelli 1994; Bargagli *et al.* 1997; Harris and Grant 2003; Borghini and Bargagli 2004; Malandrino *et al.* 2009; Smykla *et al.* 2015, 2018).

Field survey and sampling. — The field survey and soil sampling follows the methods of Smykla *et al.* (2015). Briefly, during the Antarctic summers of 2003/04 and 2004/05, soil samples were collected within the Edmonson Point area as part of an investigation on soil biogeochemistry and biotic diversity. The samples were collected from the upper soil layer (0–10 cm deep) using a sterile scoop, then placed into sterile polyethylene bags (Whirl-Pak®). To obtain homogeneous material for different analyses, each sample was gently mixed immediately after collecting and split into separate bags. Gravel larger than ~5 mm diameter was removed from the samples in the field. This approach was adopted both to correspond with previous investigations on soil biotic diversity and to accommodate limited time in the field due to logistic constraints (see Smykla *et al.* 2015, 2018). Quantities sampled were limited to achieve the best possible compromise between avoiding disturbance of the surface while still obtaining enough soil for adequate analyses.

Within a few hours after collection, all samples were transported to the Italian Station *Mario Zucchelli* at Terra Nova Bay and frozen by reducing the temperature over a 48-h period from 1° to -20°C. The samples were then shipped and stored in a frozen state for processing and analyses.

Soil processing and laboratory analyses. — In the laboratory, samples were thawed by increasing the temperature over a 24-h period from -20°C to 3°C, and then sub-sampled using sterile techniques for analyses of biota and soil geochemical characteristics. All analytical techniques and procedures of these analyses were described in detailed by Smykla *et al.* (2015).

Inductivity Coupled Plasma Mass Spectrometry (ICP-MS, Elan 6100, Perkin Elmer) was used to determine “total” concentration of six major (Fe, Ca, Mg, Na, K and Ti) and 24 trace elements (As, Ba, Be, Bi, Cd, Co, Cr, Cs, Cu, Ga, Li, Mn, Mo, Ni, Pb, Rb, Sn, Sr, Tl, U, V, Y, Zn and Zr). The analysis was performed on the soil fine fraction (<2 mm) oven dried at 105°C for 48 h. Prior to the analysis ~0.5 g of each dry sub-sample was precisely weighed and digested in Teflon tubes with a mixture of nitric (HNO₃) and hydrochloric (HCl) acids

(4:1) using microwave Speed Wave, Berghof. The accuracy of digestion and analytical procedures was verified for each batch of samples through analysis of reagent blanks and determination of elemental concentrations in Standard Reference Material (NCS DC 73308). All measurements were conducted at a constant solution volume. The final concentrations of elements in samples were obtained after subtraction of their appropriate blanks. The recovery rates ranged from 64 to 116% when compared to certified concentrations, and replicates were generally within 2–12% of each other (with the exception of Cr which had a lower precision of 25%). The overall blank levels were below 0.6% relative to the samples, which can be considered satisfactory for the methodology employed in the chemical analysis. Sample preparation and digestion were done at the laboratory of Institute of Nature Conservation Polish Academy of Sciences and the analytical determinations of elements was completed at the hydrogeochemical laboratory of University of Science and Technology (AGH) in Kraków (Poland).

Data analyses. — A number of descriptive statistics were calculated to characterize the soil elemental composition and determine variability in their concentrations, including the arithmetical mean concentration, standard deviation (SD), coefficient of variation (CV), median, skewness and kurtosis. Principal Component Analysis (PCA) and Pearson's correlation coefficients (r) were used to determine relationships among the concentration of elements in the soils, and investigate similarity in their origin and biogeochemical cycles. The PCA, with the type of substrate as categorical predictor, was also used to examine the relationship between the soils and local bedrocks. A variety of local rocks was used in the analysis, including alkali basalt (AB), hawaiite (HAW), mugeaerite (MUG), trachyandesite (TRAND), benmoerite (BEN) and trachyte (TRA), with data on their elemental composition taken from Wörner *et al.* (1989). For all PCA the data were $\log(n+1)$ -transformed to satisfy assumptions of normality and uniformity of variance, variables were standardized and centered, and the sample standardization was centered and normal.

The Enrichment Factor (EF) was also applied to assess changes in soil element concentrations in relation to the local bedrocks and calculated using the following formula (Zoller *et al.* 1974):

$$EF = (C_n/C_{ref})/(B_n/B_{ref})$$

where C_n is an element concentration in the sample, C_{ref} is the reference element concentration in the sample, B_n is an element concentration in the reference material, and B_{ref} is the reference element concentration in the reference material. For reasons discussed below, Zr was chosen as the reference element and the elemental composition of the local alkali basalts reported by Wörner *et al.* (1989) as the reference system. However, due to the lack of data on local bedrocks, the global elemental concentration (maximum values) in the alkaline

magmatic rocks reported by Kabata-Pendias and Pendias (1999) were adopted as the reference system for As, Be, Bi, Cd, Cs, Ga, Li, Mo, Pb, Sn, Tl and U.

The statistical characteristics and Pearson's correlation coefficients (r) were computed with the software package PAST 3.06 (Hammer *et al.* 2001) and the PCA using CANOCO 5.0 (ter Braak and Šmilauer 2012).

Results and discussion

Soil elemental composition and variability. — Analytical results for the 30 elements investigated in our study include the arithmetical mean concentration, standard deviation (SD), coefficient of variation (CV), median, skewness and kurtosis (Table 1). For comparative purposes, elemental concentrations for soils developed on similar bedrock from several Antarctic localities were obtained from available literature (Table 2).

Among the studied elements Fe was the most abundant across all samples, with concentration ranges (6.4–13.1 mg g⁻¹) at 1–2 order of magnitude greater than other major and minor elements, such as: Ca (1.5–4.3 mg g⁻¹), Mg (1.1–4.4 mg g⁻¹), Na (0.9–2.9 mg g⁻¹), K (0.44–1.17 mg g⁻¹), Ti (0.41–1.15 mg g⁻¹) and Mn (0.17–0.75 mg g⁻¹). With regard to the mean concentration values, trace elements could be divided into three groups. The first group included elements with the highest concentrations of 10–100 µg g⁻¹, such as Zn, Ba, Ni, Sr, Zr, and V. The second group included elements with concentrations between 1–10 µg g⁻¹, such as Cr, Y, Rb, Cu, Li, Co, Ga, and Pb. Finally, the third group included elements characterized by the lowest concentrations below 1 µg g⁻¹: Sn, Mo, U, As, Be, Cd, Bi, Tl and Cs.

The statistical characteristics indicate considerable variation in elemental concentrations among the samples, with differences between the minimum and maximum values ranging from 2.1–4.3 times the minimum value (Table 1). The apparent fluctuations of individual elements are also underlined by CV values, which usually ranged from 20–39 for major and minor elements. For most trace elements the variation in concentration values was similar, though it was strikingly higher for As, Bi, Cd, Cr, Sn and Tl.

In general, the concentration levels obtained in our study had the same order of magnitude as, or were lower than, those reported previously in Victoria Land (Crockett 1998; Bargagli *et al.* 1999, 2004; Sheppard *et al.* 2000; Webster *et al.* 2003; Malandrino *et al.* 2009) and elsewhere in Antarctica (Lee *et al.* 2004; Santos *et al.* 2005; Lu *et al.* 2012; Zvěřina *et al.* 2012; Padeiro *et al.* 2016). However, some of the elements, including Be, Bi, Ga, Li and Tl, were not investigated during earlier studies and comparisons were not possible. These lower values are not surprising because geologically young and poorly developed soils in the study area normally have low levels of extractable elements due to

Table 2
 Element concentration mean values \pm SD and ranges (expressed in soil dry weight) in soils from Edmonson Point compared with literature values from other studies in Antarctica for soils developed on similar bedrock, and with alkali basalts from Mt. Melbourne Volcanic Fields and global values for alkaline magmatic rocks.

Study site	Fe mg g ⁻¹	Ca mg g ⁻¹	Mg mg g ⁻¹	Na mg g ⁻¹	K mg g ⁻¹	Ti mg g ⁻¹	Mn mg g ⁻¹	References
Edmonson Point	10.2 \pm 2.1 6.4–13.1	2.9 \pm 0.9 1.5–4.3	2.4 \pm 0.7 1.1–4.4	1.4 \pm 0.5 0.9–2.9	0.78 \pm 0.23 0.44–1.17	0.71 \pm 0.25 0.41–1.15	0.38 \pm 0.15 0.17–0.75	Current study
Edmonson Point, lacustrine environments	60.4–62.3 60.9	20.4–28.6 33.39	4.9–9.5 12.67	37.1–37.8 32.86	27.2–32.1 23.61	5.7–7.3 8.39	1.4–1.6 1.31	Malandrino <i>et al.</i> (2009)
Victoria Land, Mt. Melbourne	44 \pm 9.0 32–56	5.3 \pm 1.0 4.1–6.5	3.6 \pm 1.4 2.2–5.6	4.5 \pm 3.2 1.9–9.0	3.8 \pm 0.5 3.1–4.3	–	1.1 \pm 0.4 0.7–1.7	Bargagli <i>et al.</i> (2004)
Victoria Land, Lake Vanda, control	8.9 \pm 2.5 6.4–12	–	–	–	–	–	0.11 \pm 0.03 0.07–0.15	Webster <i>et al.</i> (2003)
Victoria Land, Lake Vanda, station	8.0 \pm 1.2 2.2–4.2	–	–	–	–	–	0.08 \pm 0.02 0.06–0.12	Webster <i>et al.</i> (2003)
Ross Island, Scott Base, control	0.11 \pm 0.09 0.01–0.22	–	–	–	–	–	0.004 \pm 0.002 0.001–0.06	Sheppard <i>et al.</i> (2000)
Ross Island, Scott Base, station	0.12 \pm 0.11 0.01–0.43	–	–	–	–	–	0.01 \pm 0.01 0.01–0.14	Sheppard <i>et al.</i> (2000)
Ross Island, gray soils (extractable metals)	32.1 \pm 5.1 21.9–42.3	–	–	–	–	–	–	Crockett (1998)
Ross Island, gray soils (total metals)	86.7 \pm 63.1 74.6–98.9	–	–	–	–	–	–	Crockett (1998)
James Ross Island (2–10 cm)	35	3.6	8.2	–	2.2	–	0.59	Zvěřina <i>et al.</i> (2012)
King George Island, Fildes Peninsula	57.2 \pm 6.3 43.3–70.5 50.6	29.6 \pm 8.4 10.9–49.4 19.7	12.7 \pm 6.0 1.44–25.7 5.7	–	–	7.9 \pm 2.1 4.39–12.7 5.68	0.92 \pm 0.24 0.45–1.40 0.64	Lu <i>et al.</i> (2012)

King George Island, Barton Peninsula	mean±SD range	59.3±8.6 39.8–69.7	31.8±11.3 9.0–57.6	18.7±4.4 8.0–24.2	21.7±4.8 8.1–29.2	11.1±3.9 4.8–17.4	6.7±1.8 4.5–9.5	1.14±0.26 0.62–1.55	Lee <i>et al.</i> (2004)
King George Island, Admiralty Bay, Keller Peninsula	–	61.5	4.8	1.2	–	–	5.8	0.44	Santos <i>et al.</i> (2005)
Alkali basalts, Mt. Melbourne Volcanic Fields	mean±SD range	98.7±10.9 77.4–116.7	66.0±6.0 55.7–76.7	33.1±6.1 24.1–46.6	26.8±2.1 23.4–29.9	11.2±2.1 7.1–14.2	22.0±3.9 15.3–29.0	1.66±0.21 1.47–2.17	Wörner (1998)
Alkaline magmatic rocks (basalts, gabbros)	global range	70–80	67–76	40–43	18–23	7.5–120	7–14	1.2–2.0	Kabata-Pendias and Pendias (1999)

Table 2 – continued.

Study site	As µg g ⁻¹	Cd µg g ⁻¹	Co µg g ⁻¹	Cr µg g ⁻¹	Cu µg g ⁻¹	Ni µg g ⁻¹	Pb µg g ⁻¹	Zn µg g ⁻¹	References
Edmonson Point	0.45±0.35 nd–1.37	0.21±0.19 0.05–0.91	3.0±0.9 1.4–5.0	7.8±6.8 nd–29.3	3.9±1.2 1.9–6.3	33.6±9.3 20.3–53.0	1.7±0.7 1.0–4.0	42.9±17.5 21.0–69.6	Current study
Edmonson Point, lacustrine environments	2.26–3.30 2.78	0.16–0.29 0.29	–	8.3–18.1 34.5	4.9–19.6 23	15.1–21.0 28.43	9.8–34.2 8.71	13.6–121 110	Malandrino <i>et al.</i> (2009)
Victoria Land, Mt. Melbourne	–	0.34±0.23 0.08–0.64	–	26.0±6.1 18–35	7.0±4.3 3.2–13	–	15.8±12.8 6.2–35	95.7±13.7 80–121	Bargagli <i>et al.</i> (2004)
Victoria Land, Lake Vanda, control	–	0.02±0.01 0.01–0.03	–	–	26.4±4.7 19–31	11.7±1.9 8.3–13	2.3±0.3 2.1–2.8	19.4±5.6 13–27	Webster <i>et al.</i> (2003)
Victoria Land, Lake Vanda, station	–	0.04±0.02 0.01–0.07	–	–	26.2±5.6 19–40	10.5±1.1 8–12	5.2±6.6 1.4–23	22.7±14.1 15–64	Webster <i>et al.</i> (2003)
Ross Island, Scott Base, control	0.06±0.04 0.02–0.12	0.007±0.009 0.002–0.024	–	0.7±0.5 0.01–0.11	0.15±0.10 0.04–0.31	0.14±0.06 0.06–0.21	0.09±0.14 0.01–0.38	0.75±0.38 0.33–1.11	Sheppard <i>et al.</i> (2000)
Ross Island, Scott Base, station	0.16±0.25 0.02–1.16	0.12±0.17 0.01–0.81	–	0.08±0.07 0.01–0.28	0.32±0.27 0.06–1.60	0.29±0.60 0.05–3.91	0.18±0.31 0.01–1.44	1.63±1.68 0.36–9.35	Sheppard <i>et al.</i> (2000)
Ross Island, gray soils (extractable metals)	1.1±0.33 0.4–1.8	<0.62	–	16±4.3 7.5–25	–	57±19 19–95	2.2±0.4 1.4–3.0	47±7.5 32–62	Crockett (1998)

Table 2 – *continued.*

Study site	As μg g ⁻¹	Cd μg g ⁻¹	Co μg g ⁻¹	Cr μg g ⁻¹	Cu μg g ⁻¹	Ni μg g ⁻¹	Pb μg g ⁻¹	Zn μg g ⁻¹	References
Ross Island, gray soils (total metals)	<2.6	0.13±0.02 0.08–0.17	–	172±38.6 95–249	39±6.2 27–52	98±26.4 45–150	5.8±2.4 1.0–10.6	115±2.2 111–119	Crockett (1998)
James Ross Island (2–10 cm)	5.4	0.07	13	12	17	23	–	56	Zvěřina <i>et al.</i> (2012)
King George Island, Fildes Peninsula	–	0.17±0.08 0.04–0.34 0.09	–	32±13.8 17.1–64.9 22.6	122.3±32.1 51.1–176.5 89.5	14.3±5.0 7.18–25.0 10.4	15.9±13.5 2.76–60.5 5.44	58.7±9.4 41.6–80.7 51.4	Lu <i>et al.</i> (2012)
King George Island, Fildes Peninsula	4±2 7.4–21	0.4±0.9 6.3–7.4	–	–	34±4 135–220	–	20±5 62–1101	115±13 557–612	Amaro <i>et al.</i> (2015)
King George Island, Fildes Peninsula, Ardley Cove	18±2 13–23	0.29±0.15 0.2–1.2	–	50±35 15–263	91±23 56–179	24±16 12–141	27±60 3–418	114±107 68–949	Padeiro <i>et al.</i> (2016)
King George Island, Fildes Peninsula, reference	16±2 12–18	0.3±0.22 0.1–0.5	–	33±4 28–38	61±8 49–70	16±2 12–18	6±1 5–7	75±14 56–87	Padeiro <i>et al.</i> (2016)
King George Island, Barton Peninsula	–	0.14±0.05 <0.06–0.26	22.9±6.6 11.1–31.0	23.7±9.5 6.4–39.0	133.1±49.2 66.7–266.5	13.3±5.0 5.7–21.9	–	82.3±14.2 48.3–103.8	Lee <i>et al.</i> (2004)
King George Island, Admiralty Bay, Keller Peninsula	–	118	–	40	44	5.1	11.5	118	Santos <i>et al.</i> (2005)
Alkali basalts, Mt. Melbourne Volcanic Fields	–	–	36.0±14.1 24–79	70.9±59.2 7–179	35.5±11.8 12–56	51.9±47.7 8–178	–	133.4±19.8 115–184	Wörner (1998)
Alkaline magmatic rocks (basalts, gabbros)	0.6–2	0.13–0.22	35–50	170–200	60–120	130–160	3–8	140–460	Kabata-Pendias and Pendias (1999)

Table 2 – continued.

Study site	Ba μg g ⁻¹	Be μg g ⁻¹	Bi μg g ⁻¹	Cs μg g ⁻¹	Ga μg g ⁻¹	Li μg g ⁻¹	Mo μg g ⁻¹	Rb μg g ⁻¹	References
Edmonson Point	32.9±17.8 14.5–88.4	0.34±0.14 0.19–0.77	0.05±0.03 0.03–0.18	0.02±0.01 nd–0.03	1.9±0.5 1.0–3.3	3.9±1.1 2.0–5.8	0.84±0.31 0.45–1.62	4.6±1.2 2.6–7.8	Current study
Ross Island, gray soils (extractable metals)	109±19 71–147	–	–	–	–	–	–	–	Crockett (1998)
Ross Island, gray soils (total metals)	–	–	–	–	–	–	–	–	Crockett (1998)
King George Island, Barton Peninsula	266±103 101–468	1.82±0.65 1.09–3.11	–	1.95±1.15 0.83–5.27	26.9±3.7 21.4–34.2	–	1.33±0.92 <0.05– 4.17	28.1±11.5 12.0–48.1	Lee <i>et al.</i> (2004)
King George Island, Keller Peninsula	–	–	–	–	–	–	2.1	–	Santos <i>et al.</i> (2005)
Alkali basalts, Mt. Mel- bourne Volcanic Fields	542.7±76.2 370–661	–	–	–	–	–	–	35.2±14.1 19–74	Wörner (1998)
Alkaline magmatic rocks (basalts, gabbros)	250–400	0.3–1	0.01–0.15	0.5–1.5	15–20	6–20	1–1.5	20–45	Kabata-Pendias and Pendias (1999)

Table 2 – continued.

Study site	Sn μg g ⁻¹	Sr μg g ⁻¹	Tl μg g ⁻¹	U μg g ⁻¹	V μg g ⁻¹	Y μg g ⁻¹	Zr μg g ⁻¹	References
Edmonson Point	0.91±0.84 0.09–2.70	24.2±8.2 12.0–45.5	0.07±0.05 nd–0.16	0.46±0.15 0.27–0.89	11.2±5.2 2.2–21.0	6.3±2.2 4.5–15.2	19.3±6.6 6.2–30.6	Current study
Ross Island, gray soils (extractable metals)	<14	–	–	–	–	–	–	Crockett (1998)
Ross Island, gray soils (total metals)	3.0±0.098 2.8–3.2	–	–	–	–	–	–	Crockett (1998)

Table 2 – *continued.*

Study site		Sn	Sr	Tl	U	V	Y	Zr	References
		$\mu\text{g g}^{-1}$	$\mu\text{g g}^{-1}$	$\mu\text{g g}^{-1}$	$\mu\text{g g}^{-1}$	$\mu\text{g g}^{-1}$	$\mu\text{g g}^{-1}$	$\mu\text{g g}^{-1}$	
King George Island, Barton Peninsula	mean \pm SD		366 \pm 74.5	–	1.10 \pm 0.34	184 \pm 55	21.4 \pm 6.8	102 \pm 56.5	Lee <i>et al.</i> (2004)
	range		237–529	–	0.46–1.82	56–278	11.2–36.5	40.2–194	
King George Island, Keller Peninsula	–	–	109	–	–	91	–	–	Santos <i>et al.</i> (2005)
Alkali basalts, Mt. Melbourne Volcanic Fields	mean \pm SD		785 \pm 62.9	–	–	217 \pm 41.7	30.6 \pm 4.8	247 \pm 65.9	Wörner (1998)
	range		684–889	–	–	149–279	23–41	155–394	
Alkaline magmatic rocks (basalts, gabbros)	global range	0.9–1.5	250–400	0.1–0.4	0.3–1	200–250	5–32	80–200	Kabata-Pendias and Pendias (1999)

the extremely coarse texture and very low organic matter content (Bargagli *et al.* 1998, 2004; Malandrino *et al.* 2009).

A number of elements (i.e., Fe, Ca, Mg, Na, K, Mn, Zn, Cr, Cu, Pb and Cd) in our study had considerably lower concentrations even when compared to values reported earlier from Edmonson Point by Malandrino *et al.* (2009; Table 2). However, these authors used the total mineralization method with application of an *aqua regia* and hydrofluoric acid mixture for sample digestion. Although this method allows for leaching higher amounts of elements from the sample (Crockett 1998), with such an aggressive technique it is difficult to distinguish between mobile or easily leachable fractions and those bound in mineral grains (Sheppard *et al.* 2000). Moreover, Malandrino *et al.* (2009) focused on soils and sediments from lacustrine environments. Due to their restricted drainage these environments collect snowmelt and melted groundwater with dissolved elements from the catchment area (Campbell and Claridge 1982; Abollino *et al.* 2004). Their elemental composition may also be strongly influenced by deposition of windblown materials from the surroundings, including sea-spray, weathered bedrock and eroded penguin guano (Abollino *et al.* 2004; Smykla *et al.* 2015). As a consequence they may accumulate high concentrations of numerous major and trace elements and can have very different characteristics than soils in the surrounding areas. Thus, the higher levels reported from Edmonson Point by Malandrino *et al.* (2009) are likely due to differences in both analytical procedures and geochemical settings of the sampling sites.

Higher concentrations of elements (including Fe, Ca, Na, K, Zn, Mn, Pb, Cr and Cd) were also found in “*geothermal soils*” from the slopes and summit of Mt. Melbourne and Mt. Rittmann (Bargagli *et al.* 2004), where only contents of Cu and Mg were similar (Table 2). Despite short distances between these study sites elemental levels varied significantly between the samples. Bargagli *et al.* (2004) attributed these differences mainly to variation in the local bedrocks, though some of the higher values may have been influenced by gaseous emissions, and, thus be the consequence of soil contamination from the active fumaroles.

Despite the general perception of Antarctica as a pristine continent, higher values and greater data variability recorded in some studies could also be attributed to contamination due to human activities. In Victoria Land, for example, elevated levels of Ag, As, Cd, Co, Cu, Pb and Zn were found in soils around *Scott Base* on Ross Island (Sheppard *et al.* 2000). Compared with reference sites, the maximum levels in these contaminated soils were three to four times higher for most of the elements, but nine times higher for As and up to 50 times higher for Ag. Similarly, human activity at the site of a former field camp on the shores of Lake Vanda in the Dry Valleys resulted in greater contents of Ag, Cd, Co, Cu, Ni, Pb and Zn (Webster *et al.* 2003). However, the values from the contaminated sites around Lake Vanda were not necessary greater than those reported in our study. In fact, levels of Ag, Cd, Ni, Pb and Zn were generally lower, whereas Co and Cu were higher even at the control sites (Table 2).

Considerable contamination of soil was also found at Fildes Peninsula on King George Island, where several countries, including Chile, Russia, Uruguay, Germany and China, have established permanent research stations and a number of field huts. With the intensive human activities dating back to the 1950s, soil contamination in this area is an important environmental issue (Peter *et al.* 2008). Several elements (As, Cd, Cu, Cr, Hg, Ni, Pb and Zn) have been associated with anthropogenic impacts on soils in this area (Lu *et al.* 2012; Amaro *et al.* 2015; Padeiro *et al.* 2016). However, the contaminated soils from Fildes Peninsula had levels of Ni considerably lower and levels of Cd and Zn within the ranges reported in our study. On the other hand the baseline values of Ca, Cu, Fe, Pb and Ti determined by Lu *et al.* (2012) for unpolluted soils were considerably greater in samples from Fildes Peninsula (Table 2).

From the data summarized in Table 2 it is quite apparent that other studies at King George Island (Lee *et al.* 2004; Santos *et al.* 2005) as well as James Ross Island (Zvěřina *et al.* 2012) also generally reported higher concentrations for majority of elements. Consistently, though, they found lower levels of Cd and Ni, and levels of Mn, Zn and U mostly within the range of our data. Comparable values were also reported for Ca, Cr and Mg, but this varied among the studies. While the higher values might to some extent be related to methodological differences among the studies, in particular the usage of *aqua regia* and hydrofluoric acid mixture (*e.g.*, Santos *et al.* 2005; Padeiro *et al.* 2016) or finer soil fraction (*i.e.*, <63 μm by Lee *et al.* (2004)), the high consistency in lower/similar values of Cd, Mn, Ni and Zn indicate significant differences in geochemical signatures of the soil-forming rocks despite their seemingly similar origin. These results also highlight a remarkably high natural variability in the soil matrix elemental contents which must be taken into account when interpreting results of environmental studies.

Variability of elemental composition in the Edmonson Point soils. — To better understand variability in elemental composition of the investigated soils, we investigated relationships among the elements using Principal Component Analyses (PCA). The PCA provides indirect information on the relationships between the analyzed parameters, with the length of the vectors indicating the importance and direction of a positive or negative relationship that can indicate similarity in origin and biogeochemical cycles of elements in the soils.

The first two principal components accounted for most of the variance (56.4 and 13.2%, respectively). The correlation coefficients (Table 3) indicated that the first component (PC 1) was positively correlated with all trace elements belonging to the group with the lowest concentrations (*i.e.*, Mo, U, Sn, Be, Cd, Bi, Tl and Cs) as well as Y, Cu, Li and Ga, and negatively correlated with K, Zn, Ba, V, Cr, Ca and Ti. The second component (PC 2), on the other hand, was positively correlated with Na, Ca, Sr, Pb, Sn and Mg, and negatively with

Table 3
 Principal component (PC) loadings of elemental concentrations for soil samples
 from Edmonson Point.

The most significant correlations for each element are indicated in bold.

Element	PC 1	PC 2	PC 3
Ca	-0.41	0.50	0.23
K	-0.53	-0.20	-0.34
Na	0.15	0.55	0.18
Mg	0.08	0.41	0.73
As	0.12	-0.15	-0.56
Ba	-0.66	-0.29	-0.43
Be	0.89	0.18	-0.24
Bi	0.90	-0.22	-0.16
Cd	0.53	0.07	-0.31
Co	0.09	-0.06	0.84
Cr	-0.96	0.21	-0.09
Cs	0.90	-0.31	-0.12
Cu	0.59	0.33	0.15
Fe	-0.10	-0.45	0.47
Ga	0.49	-0.16	-0.30
Li	0.77	-0.12	0.02
Mn	-0.38	-0.57	0.48
Mo	0.94	-0.10	-0.05
Ni	-0.28	-0.39	0.66
Pb	0.17	0.44	-0.50
Rb	0.14	0.04	-0.80
Sn	0.78	0.56	-0.02
Sr	-0.37	0.51	0.03
Ti	-0.43	-0.85	0.12
Tl	0.93	-0.19	-0.17
U	0.90	-0.01	-0.24
V	-0.68	0.37	0.46
Y	0.67	0.10	-0.20
Zn	-0.82	-0.25	-0.01
Zr	-0.32	-0.52	-0.01

Fe, Ti, Mn and Zr. Although the third component (PC 3) explained only an additional 7.8% of the variance, it indicated further relationships among the elements, in particular Co, Ni and Mg with the “Fe group of elements”, but also with As and Rb with Pb and Ba. The relationships among the elements are more evident in the ordination biplots of the PC 1 and 2, and the PC 1 and 3 (Fig. 2a and 2b, respectively). The remaining components did not provide any

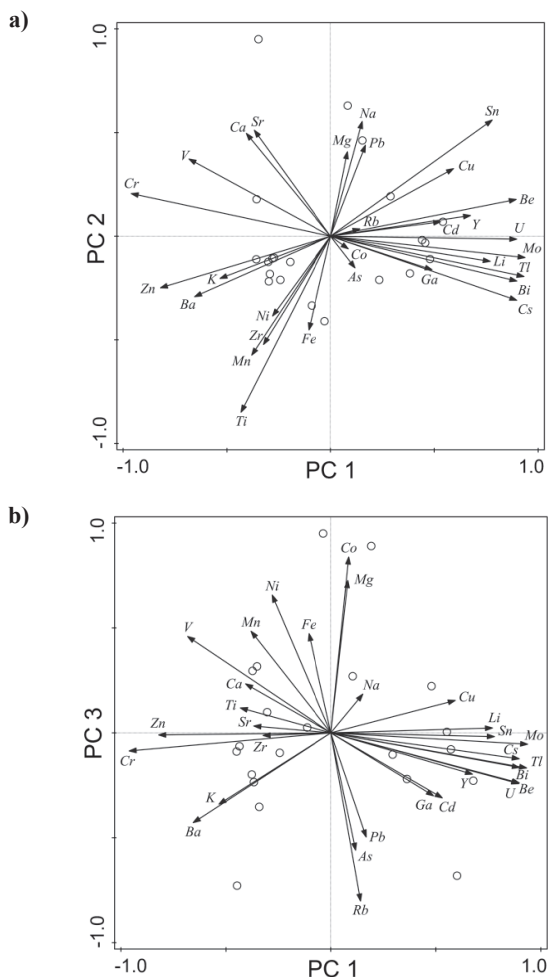


Fig. 2. The PCA ordination biplot of soil samples (open circles) showing relationships among elements; **a)** PC1 and PC2, **b)** PC1 and PC3.

additional information on relationships among the elements and, therefore, were not considered in data interpretation.

Pearson's correlation coefficients also were determined to examine the relationships among elements, which may give further insights into the major factors controlling elemental content of the investigated soils. The results (Table 4) confirm the general relationships demonstrated by PCA, though the Pearson's correlations also indicated a close relationship of the "K group of elements" with the "Na group", and high heterogeneity of the "Mo group". Accordingly, similarity in origin and geochemical behavior of elements could be inferred from both analyses. For instance, the correlations among elements of the "Fe group" are surely the result of

Table 4
 The Pearson's correlation matrix of elemental concentrations in soils from Edmonson Point. Statistically significant correlations (r) with $P \leq 0.05$ are indicated in bold. Different uppercase letters indicate $a P \leq 0.05$, $b P \leq 0.01$ and $c P \leq 0.001$. Lines indicate groups of related elements as defined by the PCA.

	K	Rb	Zn	Ba	As	Ca	Sr	V	Cr	Pb	Na	Mg	Fe	Ni	Mn	Ti	Co	Zr	Mo	Tl	U	Bi	Cs	Be	Sn	Li	Y	Cu	Cd	Ga			
K	1																																
Rb	0.72^c	1																															
Zn	0.67^c	0.57^b	1																														
Ba	0.62^b	0.76^c	0.74^c	1																													
As	0.61^b	0.70^c	0.45^a	0.60^b	1																												
Ca	0.55^b	0.56^b	0.59^b	0.50^b	0.41	1																											
Sr	0.55^b	0.69^b	0.54^a	0.68^c	0.59^b	0.91^c	1																										
V	0.53^b	0.50^a	0.70^c	0.53^b	0.30	0.93^c	0.84^c	1																									
Cr	0.58^b	0.60^b	0.77^c	0.48^b	0.36	0.65^b	0.53^a	0.74^c	1																								
Pb	0.51^a	0.64^b	0.47^a	0.41	0.32	0.59^b	0.55^b	0.64^b	0.81^c	1																							
Na	0.27	0.33	0.42	0.11	0.05	0.55^b	0.43^a	0.59^b	0.64^b	0.58^b	1																						
Mg	0.14	0.11	0.29	0.13	-0.10	0.70^c	0.62^b	0.73^c	0.34	0.30	0.63^b	1																					
Fe	0.55^b	0.17	0.62^b	0.32	0.17	0.47^a	0.35	0.55^b	0.48^a	0.24	0.23	0.46^a	1																				
Ni	0.45^a	0.14	0.70^c	0.23	0.10	0.49^a	0.27	0.63^b	0.52^a	0.25	0.31	0.41	0.81^c	1																			
Mn	0.44^a	0.07	0.63^b	0.21	0.12	0.24	0.08	0.36	0.28	0.00	0.10	0.16	0.72^c	0.92^c	1																		
Ti	0.67^c	0.27	0.70^c	0.54^b	0.25	0.28	0.22	0.37	0.28	0.02	-0.08	0.00	0.66^b	0.68^b	0.79^c	1																	
Co	0.32	0.10	0.42	0.23	0.06	0.73^c	0.61^b	0.80^c	0.30	0.16	0.30	0.74^c	0.58^b	0.70^c	0.54^a	0.44^a	1																
Zr	0.55^b	0.09	0.50^a	0.59^b	0.19	0.37	0.37	0.40	0.30	0.09	-0.06	0.09	0.38	0.34	0.34	0.70^c	0.34	1															
Mo	-0.46^a	-0.21	-0.56^b	-0.57^b	-0.25	-0.41^a	-0.45^a	-0.44^a	-0.38	-0.23	-0.06	-0.24	-0.57^b	-0.37	-0.33	-0.55^b	-0.33	-0.63^b	1														
Tl	-0.44^a	0.09	-0.48^a	-0.04	0.09	-0.13	0.12	-0.21	-0.37	-0.10	-0.18	-0.01	-0.62^b	-0.61^b	-0.62^b	-0.62^b	-0.22	-0.33	0.39	1													
U	0.00	0.34	0.05	-0.02	0.25	0.13	0.08	0.19	0.46^a	0.52^a	0.37	0.09	-0.11	-0.03	-0.24	-0.38	-0.12	-0.26	0.54^a	0.22	1												
Bi	0.14	0.46^a	0.38	0.25	0.05	0.40	0.37	0.47^a	0.73^c	0.83^c	0.59^b	0.29	0.11	0.16	-0.11	-0.26	-0.02	-0.13	-0.05	0.07	0.70^c	1											
Cs	0.04	0.47^a	-0.16	0.17	0.37	0.13	0.29	0.04	-0.08	0.14	0.00	-0.09	-0.49^a	-0.39	-0.39	-0.25	-0.10	-0.01	0.46^a	0.70^c	0.41	0.10	1										
Be	0.02	0.33	-0.04	-0.13	0.30	0.31	0.28	0.24	0.46^a	0.60^b	0.54^b	0.21	-0.17	-0.14	-0.35	-0.57^a	-0.09	-0.51^a	0.37	0.34	0.72^c	0.70^c	0.41	0.37	0.34	0.18	-0.25	0.42	0.01	0.30	1		
Sn	-0.42	-0.16	-0.40	-0.45^b	-0.29	0.13	0.06	0.10	0.07	0.28	0.40	0.36	-0.41	-0.30	-0.54^b	-0.77^c	0.00	-0.54^a	0.40	0.50^a	0.47^a	0.45^a	0.22	0.68^b	1								
Li	-0.43	-0.33	-0.59^b	-0.43	-0.47^a	-0.19	-0.24	-0.19	-0.35	-0.27	-0.16	0.01	-0.39	-0.38	-0.45^b	-0.38	-0.04	0.05	0.43	0.36	0.18	-0.25	0.42	0.01	0.30	0.42	0.36	0.18	-0.25	0.42	0.01	0.30	1
Y	-0.14	0.10	-0.13	-0.07	0.05	-0.14	-0.06	-0.05	0.08	0.08	0.00	-0.02	-0.15	-0.07	-0.12	-0.30	-0.07	-0.36	0.49^a	0.43	0.62^b	0.24	0.25	0.41	0.38	0.07	1						
Cu	0.09	0.36	0.04	0.13	0.45^a	0.54^a	0.61^b	0.42	0.11	0.20	0.31	0.47^a	0.03	-0.02	-0.17	-0.23	0.35	-0.14	0.27	0.39	0.36	0.30	0.55^b	0.50^b	0.31	0.06	0.12	1					
Cd	0.37	0.40	0.54^a	0.24	0.40	0.40	0.33	0.43	0.79^c	0.74^c	0.62^b	0.24	0.35	0.33	0.15	-0.04	0.00	-0.20	-0.22	-0.27	0.43^a	0.81^c	-0.20	0.64^b	0.20	-0.59^b	0.08	0.16	1				
Ga	0.35	0.61^b	0.38	0.79^c	0.34	0.56^b	0.74^c	0.56^b	0.24	0.33	0.13	0.37	0.06	0.05	-0.08	0.20	0.40	0.46^a	-0.08	0.31	0.07	0.20	0.40	-0.06	-0.05	0.00	0.06	0.34	-0.06	1			

the combination of effects related both to their common lithogenic origin and their chemical properties. Moreover, the close relationships between Fe and Mn (Figs 2 and 4, Table 4) can be linked to their tendency to form on minerals and fine soil particles Fe/Mn hydroxide coatings. These metallic hydroxides are well known as “scavengers” of trace elements in soils (Calmano *et al.* 2005). Thus, the lack of an Fe and Mn relationship with “Mo group of elements” in our study indicates low importance of the Fe and Mn compounds in the trace element binding. The importance of this process is probably limited because the investigated soils are very coarse-textured and therefore unable to absorb trace metals effectively.

Strong correlations among elements are often attributed to the mineralogical composition of the soil forming rocks (Liu *et al.* 2003; Lee *et al.* 2004; Navas *et al.* 2008; Lu *et al.* 2012). In particular in Antarctica, where the extreme environmental conditions render physical weathering as the major soil forming process, chemical weathering and the organic matter cycles have very little influence (Campbell and Claridge 1987; Navas *et al.* 2008; Simas *et al.* 2008). Therefore, PCA was further applied to assess the relationship of the soil elemental composition to a variety of local bedrocks. A broad range of different rocks representative for the area was used in the analyses, with data on their elemental composition taken from Wörner *et al.* (1989).

The PCA ordination biplot (Fig. 3a), with the type of substrate as supplementary variables, grouped the rock samples into a series of clusters arranged along a distinct geochemical gradient, ranging from alkali basalt (AB) to trachyte (TRA) and intermediate rock types represented in the following order by hawaiite (HAW), mugeaerite (MUG), trachyandesite (TRAND) and benmoerite (BEN). Although the biplot clearly discriminated soils from all types of rocks, the soil samples overlap with alkali basalt and hawaiite rocks along the first component and with trachyte rocks along the second component (Fig. 3a). However, while the PCA based on major elements provided virtually identical patterns to the above mentioned results (data not shown) the ordination restricted to trace elements (Fig. 3b) demonstrated close relationship of the soil chemical composition with alkali basalts (AB), which is the most abundant type of lava in the study area (Wörner and Viereck 1989).

Consequently, the other types of bedrock were removed from the dataset and PCA was further applied to investigate the relationships in elemental distributions between the soils and alkali basalts. The first principal component accounted for most of the variance (67.0%) and discrimination between soil and rock samples (Fig. 4). The relationships among element concentrations and PC 1 indicated clear alteration in soil chemical composition compared to alkali basalts. In particular, the soil samples are characterized by enrichment of Ni, Fe, Mn, Zn, Y, Rb and Cu, but decreased levels of Sr, Ca, Ti, Na, V and Ba. On the other hand the loadings of Co, Zr, K, Mg and Cr were low (Table 5) indicating that their levels remained relatively unchanged.

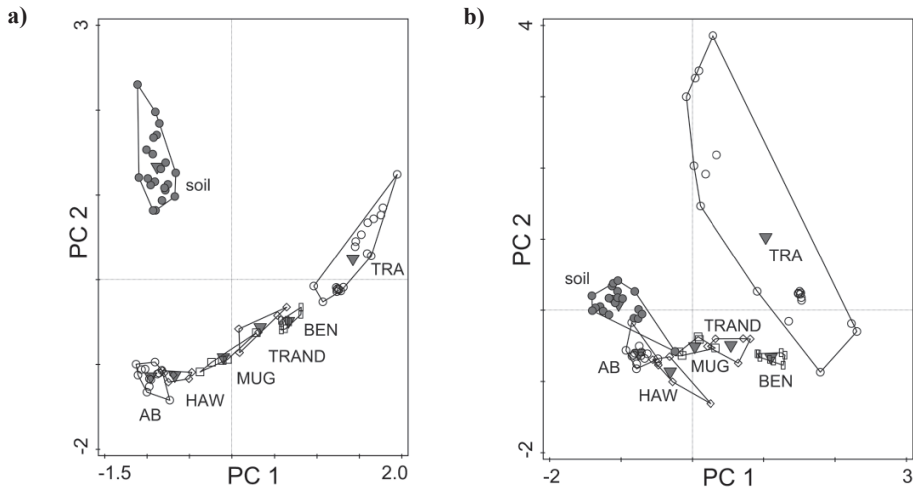


Fig. 3. The PCA ordination biplots (PC 1 and PC 2) of soil samples and local bedrocks, with the type of substrate as supplementary variables, based on concentrations of **a)** all major, minor and trace elements, **b)** trace elements only. AB – alkali basalts, HAW – hawaiite, MUG – mugeaerite, TRAND – trachyandesite, BEN – benmoerite and TRA – trachyte.

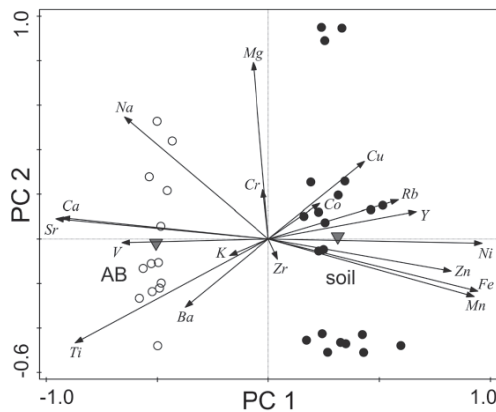


Fig. 4. The PCA ordination biplot (PC 1 and PC 2) of soil samples (filled circles) and local alkali basalts (AB, open circles) showing relationships among elements and the type of substrate.

Quantitative evaluation of alternations in soil element concentrations. — We used the enrichment factor (Zoller *et al.* 1974) to evaluate the relative enrichment or depletion of the soil element concentrations in relation to the bedrock (Table 1). The enrichment factor (EF) is broadly used for pollution assessment (Liu *et al.* 2003; Santos *et al.* 2005; Guerra *et al.* 2011; Lu *et al.* 2012; Padeiro *et al.* 2016). Due to its universal formula, it is a relatively simple tool that can be used for the

assessment of relative changes in element contents related to natural geochemical processes (Lee *et al.* 2004; Waller *et al.* 2008; Nie *et al.* 2012; Xu and Gao 2014; Culicov *et al.* 2017). The EF methodology requires the adoption of a reference material and a reference element, which may cause differences in data interpretation. It is also important to note that reference values are often based on literature data for total element concentrations, whereas data presented in environmental studies (including this study) are usually obtained by extractions of elements available for biological uptake, referred to as “total” or “pseudo-total” concentrations. Therefore, the results may be affected by differences in relative solubility of elements (Reimann and Caritat 2000; Gaudino *et al.* 2007). Despite these limitations, the data obtained by analyzing the “total” elements allow us to derive useful quantitative conclusions (Blaser *et al.* 2000; Guerra *et al.* 2011; Culicov *et al.* 2017).

Fe and Ti have been widely used as reference elements, though there is no consensus on their universal applicability (Liu *et al.* 2003; Santos *et al.* 2005; Padeiro *et al.* 2016). In our study concentrations of both Fe and Ti showed relatively small variation and skewness values in the samples (Table 1), suggesting that they are feasible candidates for the reference element (Lu *et al.* 2012). However, as demonstrated above, the PCA analyses (Fig. 4, Table 5) indicated considerable enrichment of Fe and depletion of Ti in the soil compared to their content in the bedrock. High concentration of Fe and lower levels of Ti in comparison with the reference values were also reported from the local soils and lacustrine sediments by Malandrino *et al.* (2009). This result might be surprising, because both Fe and Ti are generally considered as a fairly immobile lithological elements. However, Ti is susceptible to loss if present in the volcanic glass rather than in a more weather-resistant minerals (Lee *et al.* 2004). On the other hand Fe released by weathering of rocks may form coatings on surface of stones and on soil particles, often referred to as rock varnish (Campbell and Claridge 1987; Mergelov *et al.* 2012). This phenomenon is particularly pronounced in Antarctica and likely explains the strong enrichment of pedogenic iron in soils formed on basalts (Sheppard *et al.* 2000; Blume *et al.* 2002). Therefore, both Fe and Ti were excluded from being viable candidates for the reference element in our study. Instead, reference elements can be successfully determined by statistical analyses (Liu *et al.* 2003; Santos *et al.* 2005). Based on the loading distribution of element variables in the PCA (Fig. 4, Table 5), the content of Zr was the least altered relative to the bedrock. Its concentration also showed normal distribution and moderately low variation among the samples (Table 1). Zr, which is an ubiquitous element hosted mainly in the mineral zircon, is very resistant to chemical weathering and has no significant anthropogenic sources. It is, therefore, often used in geochemical studies as a conservative lithogenic element, against which relative enrichment or depletion of more reactive elements can be compared (Blaser *et al.* 2000). Accordingly, Zr was selected as the reference element for the EF calculation in our study.

Table 5

Loadings of elemental concentrations from the PCA of soil samples from Edmonson Point and local alkali basalts (AB). The most meaningful correlations are indicated in bold.

Element	PC 1	PC 2
Ca	-0.93	0.10
K	-0.18	-0.07
Na	-0.65	0.55
Mg	-0.07	0.79
Ba	-0.37	-0.31
Co	0.23	0.16
Cr	-0.03	0.22
Cu	0.43	0.35
Fe	0.94	-0.23
Mn	0.93	-0.26
Ni	0.96	-0.02
Rb	0.59	0.18
Sr	-0.96	0.09
Ti	-0.87	-0.47
V	-0.66	-0.02
Y	0.67	0.12
Zr	0.04	-0.09

In general the calculated EF values varied over a broad range of values, from 0.14 for Cs to 12.53 for Cd (Table 1). The EF values below one indicate depletion while higher values reflect element enrichment (Zoller *et al.* 1974; Blaser *et al.* 2000; Liu *et al.* 2003). Thus, our data suggest pronounced differences in element behavior in the soils. However, a clear discrepancy is noticeable between a calculated EF based on local alkali basalts and the generally very high EF values based on data taken from Kabata-Pendias and Pendias (1999) as reference materials (*i.e.*, Li, Pb, Mo, U, Sn, Be, As, Cd, Bi and Tl; see Table 1). This difference raises a question on applicability of global values as reference levels for estimation of EF. In fact, their usage has been criticized due to failure to function in many specific areas (Gibbs 1993; Reimann and Caritat

2000). Because these EF values may not reflect real behavior of the elements we refrain from further interpretation.

The EF values calculated based on local alkali basalts are generally in good agreement with patterns demonstrated by the PCA analyses (Fig 4, Table 5). However, considering the extent of element relative enrichment $> 100\%$ ($EF > 2$) as significant (Blaser *et al.* 2000) the data indicate considerable enrichment of Ni, Zn, Y, Mn and Rb ($EF = 7.3, 4.6, 3.6, 3.2$ and 2.2 , respectively), but only moderate enrichment of Fe and Cu ($EF = 1.4$ and 1.2 , respectively). On the other hand, the extent of the element depletion decreases in the order: $Sr > Ti > Ca > V > Ba > Na > Co > Cr > Mg$.

Considering, that an element enrichment or depletion in the soil is governed mainly by leaching and depends on a specific mobility of the element (Blaser *et al.* 2000), the behavior of elements is not in complete accordance with their known relative mobility. For instance, Ti is generally considered as an immobile element, but it is susceptible to loss if present in volcanic glass (Lee *et al.* 2004), which is common constituent of the bedrock in the study area (Wörner and Viereck 1989; Wörner *et al.* 1989). Thus, depletion of Ti suggests that the investigated soils have undergone some degree of chemical weathering. Similarly, simultaneous depletion of Ca, Sr, Na and Mg in soils formed from basalts suggest their leaching due to alteration of plagioclase (Lee *et al.* 2004). Accordingly, the apparent enrichment of Ni, Zn, Y, Mn, Rb and Fe might be the net result of their low mobility and loss of the highly mobile elements. However, it can also result from accumulation of weathered elements on the surface of soil particles in the form of rock varnish (Mergelov *et al.* 2012). As indicated above, this phenomenon can explain soil enrichment with Fe (Campbell and Claridge 1987; Sheppard *et al.* 2000), but it can also be related to accumulation of other elements with similar geochemical behavior, such as Mn, Ni and Zn (Mergelov *et al.* 2012).

While physical disintegration is surely the major soil-forming factor, these observations suggest that the degree of chemical weathering in the study area may not be as low as commonly assumed for Antarctic soils. In fact, this conclusion is consistent with some recent observations suggesting that chemical weathering can locally be an active process, especially in more favorable warmer and humid climatic conditions found in the maritime Antarctic (Simas *et al.* 2006, 2008; Haus *et al.* 2016; Wilhelm *et al.* 2016). Further studies are needed, including analyses of mineralogical species, to confirm this possibility and estimate intensity of these processes in the investigated area.

It is important to note that alteration in soil chemical composition might also be related to heterogeneity of the soil matrix. In fact, Wörner and Viereck (1989) pointed out that the surface layers of the basaltic rocks at Edmonson Point are mixed with variable amounts of trachyte pumice. This may explain the overlap of soil samples with trachyte rocks along the second axis demonstrated by the PCA (Fig. 3a–b). Similarly, Malandrino *et al.* (2009) indicated that the matrix of soils and

sediments from the local lacustrine environments was derived from two different types of magmatic flows that erupted from Mt. Melbourne at different times, with one eruption characterized by a greater content of rhyolite and the other of basalt, along with variable amounts of pumice. Lacustrine environments with restricted drainage are obvious sites for the accumulation of windblown materials (Campbell and Claridge 1982; Abollino *et al.* 2004; Malandrino *et al.* 2009; Smykla *et al.* 2015). For instance, Lee *et al.* (2004) estimated that soils in sheltered environments may comprise over 50% of allogenic materials due to eolian additions. Thus, the high mineral heterogeneity of the samples investigated by Malandrino *et al.* (2009) might be attributed to topographical features of the study sites that support deposition and accumulation of windblown materials from the surrounding landscape.

Implications of marine and climate influences. — In agreement with previous studies on the geochemistry of Victoria Land coastal environments (Claridge and Campbell 1987; Barrett *et al.* 2006; Cannone *et al.* 2008), accumulation and cycling of elements in the soils are likely to be affected by ions of marine origin. In particular, the marine environments can be the major source of Ca, Na, Mg and K (Weller *et al.* 2008; Xu and Gao 2014), but may also provide significant inputs of a number of trace elements, including Ba, Cu, Cd, Hg, Li, Se, Sr, Pb and Zn (Weller *et al.* 2008; Liu *et al.* 2013). These inputs can occur directly through the marine aerosols and/or snow blown off the sea ice (Bargagli *et al.* 1999; Malandrino *et al.* 2009). Presence of penguin colonies and breeding skuas, through deposition of guano, can also be a major source of marine-derived elements for the local terrestrial environments (Barrett *et al.* 2006; Cannone *et al.* 2008; Liu *et al.* 2013; Smykla *et al.* 2015).

Previous studies in the Edmonson Point area demonstrated that content of major ions in snow, melt water and lacustrine environments is indeed considerably affected by the marine inputs (Bargagli *et al.* 1998, 1999; Abollino *et al.* 2004; Borghini and Bargagli 2004; Malandrino *et al.* 2009). However, Bargagli *et al.* (1999) pointed out that Mg and Ca values, as well as the Na/Cl and Mg/Cl molar ratios, in stream and lake waters in Edmonson Point did not correspond to those of seawater. Similar results were also demonstrated for the K/Na and Ca/Na molar ratios (Borghini and Bargagli 2004), indicating the contribution of ions weathered from the substratum and their importance in local geochemical processes.

Low conductivity of the samples (Smykla *et al.* 2015) and the low EF values (Table 1) indicating lack of the soil enrichment with marine-derived elements are consistent with these observations. This conclusion, however, contrasts with some other studies from Victoria Land. In particular soils in the Dry Valleys, but also soils in the Transantarctic Mountains, are often characterized by high conductivity and elevated levels of salts (Bockheim and McLeod 2015a, b). These soils are highly saline due to long exposure ages and accumulation of inorganic ions (*i.e.*, Na, Cl, Ca, Mg, K) from atmospheric deposition, in the

absence of precipitation and leaching (Campbell and Claridge 1987). By contrast, the geologically young, weakly developed fellfield soils at Edmonson Point have had considerably less time to accumulate atmospheric deposition.

Moreover, at Edmonson Point, due to protection from the dry katabatic winds and relatively milder climatic conditions compared to other sites in Victoria Land, snow tends to melt rather than sublimate (Campbell and Claridge 1987; Barrett *et al.* 2006). Easterly winds and oceanic air masses with accompanying low clouds also bring additional moisture. Consequently ephemeral melt water ponds and streams are common and sub-surface soils are often saturated with water from snow- and ice-melt (Harris and Grant 2003). However, the coarse structure and high stone content of the soil provide only low water-holding capacity and water from the snowmelt percolates through the soil promoting significant leaching of soluble salts (Borghini and Bargagli 2004; Malandrino *et al.* 2009; Smykla *et al.* 2015). The mobilised ions may flow along the surface of the underlying permafrost and release into the streams they are “flushed” back to the sea (Ugolini and Anderson 1972; Borghini and Bargagli 2004). However, some ions may be deposited into lacustrine environments and depressions with restricted drainage. In contrast to the investigated soils, these environments can accumulate high levels of major and trace elements and have very different geochemical signatures (Campbell and Claridge 1982; Abollino *et al.* 2004; Malandrino *et al.* 2009; Smykla *et al.* 2015).

Because for most of the year there is little or no liquid water available (Malandrino *et al.* 2009; Smykla *et al.* 2015), these processes are only episodic and limited to brief period of snow- and ice-melt at the beginning of the summer season. It seems, however, that hydrology is an important driver of geochemical processes in the area and the abundance of water, promoting mineral weathering and leaching, is likely to account for alteration of elemental content in the investigated soils. Considering that current climate change in Antarctica is predicted to increase both the availability of water and the length of the summer season (Convey *et al.* 2009), it is reasonable to expect that the intensity of these hydrological processes will accelerate. This acceleration in turn will favour faster mineral weathering and an increase in geochemical mobility of the soil components. Changes in ice coverage in the Ross Sea may also intensify the marine-land geochemical cycles, including transfer and redistribution of bioavailable elements and pollution from local and global sources (Bargagli 2005; Bargagli *et al.* 2005; Barrett *et al.* 2006).

Our quantification of baseline elemental concentrations in the soil provides a starting point for future assessment and monitoring of environmental changes, but to predict specific outcomes of the changes requires further work. In particular, the effects of variation in microclimate encountered over local environmental gradients warrants further study to provide more detailed insights on the soil ecosystem processes and geochemical cycles with global climate change.

Conclusions. — In an attempt to improve the understanding of natural geochemical variability and soil formation processes, the geologically young and poorly developed soils from fellfield environments at Edmonson Point (northern Victoria Land, Antarctica) were characterized in reference to the “total” elemental content. Considering a large suite of elements, including six major (Fe, Ca, Mg, Na, K and Ti) and 24 trace elements (As, Ba, Be, Bi, Cd, Co, Cr, Cs, Cu, Ga, Li, Mn, Mo, Ni, Pb, Rb, Sn, Sr, Tl, U, V, Y, Zn and Zr), this is the first time that such a comprehensive study on soil geochemistry has been conducted in Victoria Land.

The elemental concentrations were generally similar or lower than values reported elsewhere in Antarctica, which reflects a very early developmental stage of the soils. Only concentrations of Cd, Mn, Ni and Zn were relatively high, but they were consistent with high levels in the local soil-forming rocks, indicating an origin from natural sources rather than anthropogenic contamination.

In general, physicochemical characteristics of the soils were strongly related to the parent material, indicating physical disintegration as the major contributor to the soil formation. Considerable alteration of elemental composition in the soils, with a pattern generally corresponding to the known mobility of elements, suggests that the degree of chemical weathering in the study area may not be as low as commonly assumed for Antarctic soils. Further studies are needed, including analyses of mineralogical species, to confirm this possibility and estimate intensity of these processes.

Considering local environmental settings, the soil elemental content was likely affected by marine-derived inputs and very active hydrological processes which enhanced leaching and removal of mobilized lithogenic elements and marine ions to the sea or into lacustrine environments with restricted drainage. Both of these processes may be of particular importance within the context of global climate change as the predicted increases in temperature, water availability and length of the summer season would favor mineral weathering and increase geochemical mobility of elements.

Due to diversity of terrestrial environments, and variability affected by hydrological processes and marine inputs, Edmonson Point is considered as one of the best examples of coastal ice-free ecosystems across the Ross Sea region. Its geologically young and poorly developed soils, therefore, provide an excellent model for studies on soil formation as well as the effects of climatic and environmental changes on soil geochemistry. The data presented here and in our previous work (Smykla *et al.* 2015) can thus be considered as benchmarks or background information on the soils’ physical and geochemical properties. It is important to note, however, that the data also highlight a remarkably high natural variability in geochemical signatures, both locally and among different ice-free areas, even among seemingly similar soil-forming rocks. These differences must be taken into account when interpreting results of environmental studies.

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