Influence of marine vertebrates on organic matter and trace element levels in Antarctic soils

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Abstract

The presence of marine vertebrates in reproductive colonies contributes to the input of organic matter into the local environment and it is believed that trace elements are subsequently remobilized from the excreta of these animals. In this study, we investigate the influence of marine vertebrates on trace elements levels (As, Cd, Co, Cu, Fe, Li, Lu, Mg, Mn, Ni, Pb, Sb, Sc, Se, Sm, Sn, Sr, Tb, U and Zn) and soil organic matter (SOM) content from five locations with and without marine vertebrate influence in Admiralty Bay, King George Island, South Shetland Islands. Soils were acid digested using microwave, elements were quantified using inductively coupled plasma mass spectrometry and SOM was calculated by loss-on-ignition. The non-influenced and vertebrate-influenced soils had similar concentrations of most of trace elements assessed, however we observed a significant increase in SOM that was positively correlated with the concentrations of As, Cd, Se, Sr and Zn. Although marine vertebrates do not appear to significantly influence trace element concentrations in the soils examined here, this conclusion is based on a limited overall sample size and there is evident input of organic matter linked with increased concentrations of elements correlated with SOM, indicating a possible ornithogenic influence. Contrasting our results with other studies, we conclude that soil elemental levels are an interplay between local geology, vertebrate diet and colony size. Further studies with increased sample size are required to obtain a better understanding of marine vertebrate influence on trace element levels in Antarctic soils.

1. Introduction

King George Island, the largest island in the South Shetland Islands archipelago north-west of the Antarctic Peninsula, hosts important breeding areas for seabirds and marine mammals, such as penguins (*Pygoscelis antarcticus*, *P. papua* and *P. adeliae*), imperial shag (*Leucocarbo atriceps*), southern giant petrel (*Macronectes giganteus*), skuas (*Stercorarius maccormicki* and *S. antarcticus*) and southern elephant seal (*Mirounga leonina*) with colonies of different sizes and population densities (Salwicka and Sierakowski 1998; Shirihai 2008).

While these marine vertebrates in detail occupy different positions in the trophic chain, they generally represent higher trophic levels, where they are susceptible to high levels of contaminant accumulation (Hazen et al. 2019). The main route by which contaminants enter these organisms is through feeding (Burger and Gochfeld 2004; Bargagli 2008; Ramos and González-Solís 2012; Hazen et al. 2019). Once ingested, contaminants can be absorbed by the gastrointestinal tract, transferred to the blood stream and stored in internal tissues, while any that are not absorbed are eliminated through the excreta (Yin et al. 2008; Pacyna et al. 2019). Absorbed contaminants may also eventually be released into the environment through moulted fur and feathers, egg shells and the decay of carcasses. In and near dense bird colonies, the accumulation and local dispersal of guano leads to the formation of ornithogenic soils, representing an abundant source of organic matter, nutrients and contaminants to the Antarctic terrestrial ecosystem (Michel et al. 2006; Yin et al. 2008; Bokhorst et al. 2019a; Castro et al. 2021). Marine vertebrates can also act as vectors remobilizing nutrients, organic matter and contaminants in the terrestrial environment. They can eliminate trace elements thought faeces and feathers, effectively transporting these elements between regions, in this case from the marine to the terrestrial environment (Espejo et al. 2017). These contaminants and trace elements can accumulate in the soil (Cipro et al. 2018), where their behavior can be further affected by associated organic matter content (Alekseev and Abakumov 2020).

Various studies have reported contamination of Antarctic soils by anthropogenic pollution from both global (e.g. atmospheric currents) and local sources (e.g. research stations and logistic operations) (Santos et al. 2005; Amaro et al. 2015; Bueno et al. 2018; Potapowicz et al. 2019; Tapia et al. 2021). Previous studies have also confirmed the flow of marine-derived nutrients via marine vertebrates into the terrestrial food web in Antarctica, enriching plants and increasing invertebrate biomass (Bargagli 2005; Bokhorst et al. 2007, 2019a, b; Zwolicki et al. 2015; Bokhorst and Convey 2016). However, how the elemental concentration of soil ecosystems in Antarctica is shaped by marine vertebrates and how this process is controlled by different vertebrate species is still poorly recognised (Liu et al. 2013). The current study documents evidence of trace element and organic matter input or remobilization by marine vertebrates to soils in terrestrial ecosystems in Admiralty Bay, King George Island. We assume that different marine vertebrate species may differentially impact on elemental concentrations in soils at their breeding sites. For this purpose, soils from marine vertebrate colonies and non-influenced areas were collected and quantified to assess organic matter content and concentrations of 20 potentially toxic elements.

2. Materials And Methods

2.1. Study area and sample collection

Fieldwork took place during the austral summers of 2012/2013 and 2013/2014. In order to estimate how different vertebrates influence elemental concentrations of soils, we sampled in the vicinity of colonies of vertebrates that differ in behavior, diet and breeding sites (sea shore, inland rocks). Samples of vertebrate-influenced soil, each consisting of about 25 cm^3, were collected using a plastic spoon within breeding colonies of the following Antarctic species (Figs. 1, 2): imperial shag (*Leucocarbo atriceps*; n = 8; Shag Island, feeding mostly on fish and octopods), southern giant petrel (*Macronectes giganteus*; n = 9; Vauréal Peak, scavenger, feeding on penguins and seals carcasses), brown skua (*Stercorarius antarcticus*; n = 2; Keller Peninsula, Comandante Ferraz Station, Brazil, feeding on penguin chicks, eggs, fishes and molluscs), chinstrap penguin (*Pygoscelis antarcticus*; n = 8; Thomas Point, Henryk Arctowski Station, Poland, feeding on crustacean *Euphausia superba*), and southern elephant seal (*Mirounga leonina*; n = 3, Thomas Point, feeding on fish and squid) (Shirihai 2008). In addition, soils not under the direct influence of marine vertebrate concentrations were collected at Crepin Point (n = 3; Machu Picchu Scientific Base, Peru). Collected soils were immediately placed in *ziplock* plastic bags and kept frozen until analysis.

2.2. Trace element quantification

Before commencing analyses, soils were defrosted at room temperature for 12 h, dried at 50 ºC for 48 h and passed through a 0.75 mm mesh sieve to remove stones, gravel and other impurities. About 200 mg of each soil sample was extracted with 5 mL of HNO_3 (65%; Sigma-Aldrich, USA) using a microwave oven (Mars 6, CEM Corporation, Austria). Samples were made up with Milli-Q water (Direct-Q system, Millipore, Germany) to 10 mL and then one aliquot was diluted 25 times. Quantification of 20 elements (As, Cd, Co, Cu, Fe, Li, Lu, Mg, Mn, Ni, Sb, Sc, Sr, Sm, Tb, Pb, U, Zn) was performed using inductively coupled plasma mass spectrometry (ICP-MS, PlasmaQuant® MS Q, Analytik Jena, Germany). For multi-elemental determination the conditions used were: nebulizer gas flow 1.05 L min^{-1}, auxiliary gas flow 1.5 L min^{-1}, plasma gas flow 9.0 L min^{-1}, Radio Frequency (RF) power 1.35 kW; the signal was measured in 20 scans and 5 replicates. Mass interference was reduced using the integrated Collision Reaction Cell (iCRC) working sequentially in three modes, with hydrogen as reaction gas, helium as collision gas, and without gas addition.

2.3. Organic matter quantification

Soil organic matter (SOM) content was determined by loss-on-ignition. About 3 g of each dried sample was weighed and then heated in a muffle furnace at 550°C for 4 h. SOM content was calculated by the mass difference before and after ignition and expressed as percentage weight loss.

2.4 Quality assurance/quality control (QA/QC)

For quality control, analytical reagent blanks (n = 2) and certified reference materials (IAEA 405: estuarine sediments from the International Atomic Energy Agency, n = 2) were submitted to the same procedures as the collected soil samples. Germanium, rhodium, scandium and iridium were used as internal standards. Following accepted international QA/QC criteria, the analyses were considered valid when reference materials gave recovery values between 80 and 120%.

2.5. Statistical analyses

Statistical analyses were performed using the software GraphPad Prism 5.0 (GraphPad Software Inc®). Due to the low sample numbers available from some sampling locations, non-parametric tests were performed in these cases. In these cases, interspecific differences in the trace element concentrations in soils associated with different marine vertebrates were investigated using Kruskal-Wallis analysis of variance and, when significant, Dunn`s multiple comparison *post-hoc* test was used to compare the sum of ranks between groups. When groups with sample size > 7 (i.e., imperial shag, chinstrap penguin, southern giant petrel) conformed to a normal distribution in the Shapiro-Wilk test, a one-way analysis of variance (ANOVA) was performed to investigate interspecific differences between these three groups. A significance level of $p < 0.05$ was adopted for all tests.

3. Results

Table 1 and Fig. 3 summarize the trace element concentrations measured in marine vertebrate-influenced and non-influenced soils sampled on King George Island. Non-influenced soils had similar trace element concentrations when compared with vertebrate-influenced soils ones for the majority of elements analysed. Statistically significant differences in concentrations were only observed for Sn, lower than non-influenced soils in southern giant petrel colonies, and Li, Lu, Mb and Tb, higher in soils from imperial shag colonies than in non-influenced soils. Soils collected in the imperial shag breeding colony recorded lower Co, Fe, Lu and Sc concentrations than those from both southern elephant seal and southern giant petrel colonies (Dunn's Test, all $p < 0.05$), lower levels of Mn, Li and Sm than the southern elephant seal colony soils (Dunn's Test, both $p < 0.05$), lower levels of Ni, Cu, Sr, U than southern giant petrel colony soils (Dunn's Test, all $p < 0.05$) and lower levels of Cu, Mn and Sc when compared to chinstrap penguin colony soil (Dunn's Test, $p < 0.05$). In contrast, imperial shag colony soil had higher levels of As compared to brown skua colony soil and Zn compared southern giant petrel colony soil (Dunn's Test, all $p < 0.05$).

Table 1

Trace element concentrations and organic matter contents of marine vertebrate-influenced and non-influenced soils sampled in Admiralty Bay, King G

Soils	n	SOM		As	Cd	Co	Cu	Fe	Li	Lu	Mg	Mn	Ni	Pb	Sb	Sc	Se
Non-influenced (control samples)	3	8	**Mean**	3.39	0.70	10.7	114	24191	9.26	0.63	9035	488	8.86	3.44	1.57	15.2	18.3
			SD	3.26	0.63	1.42	95.2	3430	1.52	0.04	1345	80.5	3.27	0.56	0.02	1.6	24.7
			Median	1.90	0.38	9.91	66.7	23632	9.38	0.62	8879	530	7.09	3.53	1.56	15.6	18.3
			Min	1.15	0.30	9.80	51.6	21075	7.68	0.60	7775	395	6.87	2.83	1.55	13.5	0.86
			Max	7.13	1.43	12.3	223	27866	10.7	0.67	10451	539	12.64	3.95	1.58	16.5	35.7
Brown skua (Stercorarius antarcticus)	2	17	**Mean**	1.47	1.20	10.3	79.5	32106	2.61	0.60	9574	207	5.24	1.06	1.59	11.2	14.6
			SD	0.54	0.64	0.56	11.7	2079	0.66	0.03	1006	6.30	0.25	0.25	0.04	0.53	5.40
			Median	1.47	1.20	10.3	79.5	32106	2.61	0.60	9574	207	5.24	1.06	1.59	11.2	14.6
			Min	1.09	0.75	9.94	71.3	30635	2.14	0.58	8863	202	5.06	0.88	1.56	10.9	10.8
			Max	1.86	1.65	10.7	87.8	33576	3.08	0.63	10286	211	5.42	1.23	1.62	11.6	18.4
Imperial shag (Leucocarbo atriceps)	7	36	**Mean**	9.13	1.46	0.96	44.5	3379	2.93	0.50	14354	100	3.04	1.16	1.76	8.36	36.3
			SD	4.58	0.55	0.82	23.0	1241	1.19	0.01	8364	47	2.62	3.03	0.49	0.37	8.39
			Median	10.1	1.44	1.28	47.3	3803	3.21	0.50	15373	111	4.18	0.15	1.58	8.52	35.3
			Min	7.46	1.34	0.44	30.7	2930	2.37	0.49	4972	77.8	2.20	0.04	1.56	7.94	27.5
			Max	14.2	2.15	1.93	77.2	4600	4.19	0.51	26402	162	5.26	8.66	2.98	8.85	49.1
Chinstrap penguin (*Pygoscelis antarcticus)*	8	28	**Mean**	5.41	2.33	6.07	204	15649	5.20	0.56	17487	345	7.98	1.88	1.63	14.3	68.0
			SD	3.33	1.59	3.97	104	9369	1.52	0.07	12926	178	3.47	1.50	0.04	5.48	53.7
			Median	4.64	2.28	9.19	206	23654	5.91	0.56	16050	376	8.37	2.64	1.60	14.1	47.7
			Min	2.16	0.34	1.84	52.2	6075	2.96	0.50	4731	171	3.88	0.38	1.56	9.51	3.48
			Max	17.8	4.00	24.1	331	45988	18.0	0.65	37205	901	14.87	6.55	1.69	24.8	135
Southern giant-petrel (*Macronectes giganteus*	9	14	**Mean**	3.93	1.43	9.83	96.8	25135	5.43	0.59	8473	311	14.50	3.05	1.59	15.1	15.4
			SD	2.86	1.18	1.57	12.1	4217	1.33	0.02	1651	51.5	8.97	0.46	0.04	3.09	5.45
			Median	3.14	0.92	10.3	100	24029	5.25	0.58	8327	306	11.9	2.91	1.58	13.6	15.8
			Min	1.31	0.56	7.81	72.7	20485	3.63	0.56	6410	246	5.35	2.52	1.54	12.8	6.5
			Max	10.5	3.91	12.4	114	34765	7.99	0.62	11006	417	30.1	3.91	1.66	22.4	21.6
Southern elephant seal (*Mirounga leonine*)	3	16	**Mean**	4.11	0.57	14.4	84.1	29814	11.8	0.69	9828	1012	4.15	3.88	1.56	21.8	6.11*
			SD	2.25	0.28	3.78	17.3	5930	6.79	0.07	2771	390	4.56	0.64	0.01	0.76	
			Median	3.60	0.42	14.0	87.3	27445	8.28	0.70	9198	1221	2.86	3.74	1.55	21.6	
			Min	2.16	0.40	10.8	65.4	25435	7.48	0.61	7426	562	0.37	3.33	1.55	21.1	
			Max	6.57	0.89	18.3	99.5	36562	19.6	0.75	12860	1252	9.22	4.57	1.57	22.6	

When comparing imperial shag, southern giant petrel and chinstrap penguin soils using ANOVA, the first species showed lower concentrations of the elements Co, Mn, Cu, Fe and Sm (Tukey's Test, all $p < 0.05$), with the southern giant petrel and the chinstrap penguin soils not presenting significantly different concentrations of these elements. Imperial shag soil had lower levels of Ni than southern giant petrel and Li than chinstrap penguin soils (Tukey's Test, both $p < 0.05$). Southern giant petrel soil had higher levels of Sr than the imperial shag and chinstrap penguin soils (Tukey's Test, both $p < 0.05$).

The highest SOM content was recorded in the shag colony soil samples, with content decreasing in the rank order imperial shag > chinstrap penguin > brown skua > southern elephant seal > southern giant petrel > non-influenced soils (Table 1). Significant positive correlations were detected between SOM and levels of As, Cd, Mg, Se, Sr and Zn and negative correlations with levels of Co, Cu, Fe, Li, Mn, Ni, Pb, Sc, Sm and Tb (Fig. 4).

4. Discussion

A number of studies have previously confirmed the transfer of organic matter, nutrients and trace elements into terrestrial ecosystems by marine vertebrates, especially seabirds, through their faeces in different parts of Antarctica (Santamans et al. 2017; Castro et al. 2022). These faecal inputs result in deposition and accumulation of potentially toxic elements such as As, Cd, Cu, Se and Zn in soils on the Antarctic Peninsula, which could lead to negative impacts on organisms and the environment. Although this study identified few statistically significant differences between non-influenced soils when compared with vertebrate-influenced soils, this may in part be a function of the different climates, geological heterogeneity of the areas, size colonies or even. relatively low sample sizes available, as visual inspection of the data obtained (Fig. 3) did suggest differences in the distribution of elements in the different soils.

Some studies have confirmed the transfer of elements from the sea to terrestrial ecosystems by marine vertebrates, whilst others have shown no or opposite trends. For example, Cipro et al. (2018) confirmed that seabirds input Cd, Hg and probably As, Se and Zn to their colonies. Sparaventi et al. (2021) highlighted that the high density of penguins in colonies and, consequently, the large amount of faeces released may contribute considerable amounts of trace elements. However, studies also identify no consistent pattern of change in concentrations of trace elements as a result of marine vertebrate influence (Nie et al. 2014; Abakumov et al. 2017; Santamans et al. 2017; Espejo et al. 2017; Abakumov 2018; Cipro et al. 2018; Bokhorst et al. 2019b, a; Alekseev and Abakumov 2020, 2021; Sparaventi et al. 2021; Castro et al. 2021, 2022). Our data are consistent with interpretations of Liu et al. (2013) and Cipro et al. (2018), who suggested that there may be selective enrichment of elements such as As, Cd, Cu, P, S, Se and Zn associated with the presence of seabirds. Soils from imperial shag and chinstrap penguin colonies had the highest concentrations of As, Se, Mg, Sr and Zn which are the elements positively correlated with SOM, as well as appearing to be directly proportional to colony size and density.

The data obtained in the present study indicate that soils obtained from a location not under the direct influence of marine vertebrates had trace element concentrations that were generally quite similar to those of soils obtained from many of the marine vertebrate colonies sampled. However, it is important to emphasize that the general lack of significance may be a consequence of the relatively small sample sizes for most groups. But also should be considered that the abundance of species in the breeding colonies is also an important factor, since the greater the number of individuals, the greater the collective potential to influence elemental concentrations.

In a few cases, the non-influenced soils recorded higher contents of some trace elements than did vertebrate-influenced soils, as was the case with Mn, Li and Tb contents being higher than in shag colony soils. Similarly, Castro et al. (2021) reported higher amounts of Mn, Ba, Co, Cr, Ni, and Sr in non-influenced soils when compared with ornithogenic soils, linking the dynamics of these elements to the parent material. Cipro et al. (2018) also reported higher levels of Co, Cr, Ni and Pb in control sites, hypothesizing that these elements are likely to be derived from sources other than colonies. It is also appropriate to note that wind can help to disperse elements from ornithogenic soils to other areas (Schmale et al. 2013), including to locations where there is no presence of marine vertebrates.

Comparing the influence of different vertebrate species on colony soils, there is a suggestion in our data of different processes taking place in the soils of imperial shag colonies, influencing the concentrations of some trace elements. The shag colony soils had the highest percentage SOM content and consequently higher concentrations of some elements that are positively related to SOM (i.e. As, Sr and Zn). However, soils of this species also had lower concentrations of several trace elements in comparison with soils from colonies of other marine vertebrate species. This may suggest that the form or properties of shag colony locations may differ from the other species, with consequential influences on trace element concentrations. Breeding colonies of this species characteristically have a thick layer of guano, indicating the scale of contribution to input of organic matter (Cipro et al. 2018). However, no studies have yet attempted to compare rates at which different trace elements may be leached away from colonies of different vertebrate species. For instance, it is plausible that the presence of guano changes the pH of the soil (making it more acidic), in turn leading to release of elements from adjacent rocks which are then leached from the soils to the marine ecosystem. Moreover, the differences in the diet of specific marine vertebrate species and potential of prey and predator species to bioaccumulate trace elements cannot be ruled out, since dietary differences between these species can lead to different absorption and consequent elimination of trace elements to the environment.

Studies of Antarctic soils have previously reported correlations between trace element levels and organic matter content (e.g., Espejo et al., 2017), supporting that organic matter may play a role in either remobilization or retention of specific elements in soils. Here, we observed positive correlations between SOM and As, Cd, Mg, Se, Sr and Zn. Alekseev and Abakumov (2020) reported positive correlations between total organic carbon and As and Hg content while Castro et al. (2021) reported positive correlations between carbon and Zn, Cu and Pb contents, indicating the enrichment of these trace elements due to the presence of seabirds. Alternatively, negative correlations may be due to a dilution effect as suggested by Nie et al. (2014) for rare earth elements in ornithogenic sediments. Furthermore, SOM modifies soil characteristics, which could increase leaching of some trace elements over time (Castro et al. 2021).

Conclusions

The data obtained in the current study indicate that, despite contributing considerable input of organic matter to soils around their breeding colonies in Admiralty Bay, marine vertebrates do not generally significantly increase the concentrations of a range of trace elements in these soils. However, the positive relationships identified between SOM and As, Cd, Se, Sr and Zn may be indicative of ornithogenic influence. Soils not influenced by marine vertebrate colonies had a lower organic matter content but broadly similar concentrations of most trace elements to those under vertebrate influence. Species that typically breed in dense and large colonies (shags and penguins) were associated with the highest concentrations of SOM and, consequently, higher concentrations of elements associated with SOM. We did not identify any evidence of consistent relationships between marine vertebrate diet and the concentration of elements in the soils of their breeding areas. However, some of the food sources (e.g. crustaceans, fish, penguins) may themselves be characterised by different patterns of bioaccumulation of trace elements which could, in turn, become visible in differences between specific elements in colonies and vertebrate species. Both significant positive and negative correlations were found between SOM content and different trace elements, indicative of both vertebrate enrichment and differential leaching occurring. These are indicative that the concentrations of trace elements and organic matter in Antarctic soils are an interplay between local geology, vertebrate diet and colony size. Further studies of interactions between trace elements and organic matter are clearly required in the Antarctic region.

Declarations

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Figures

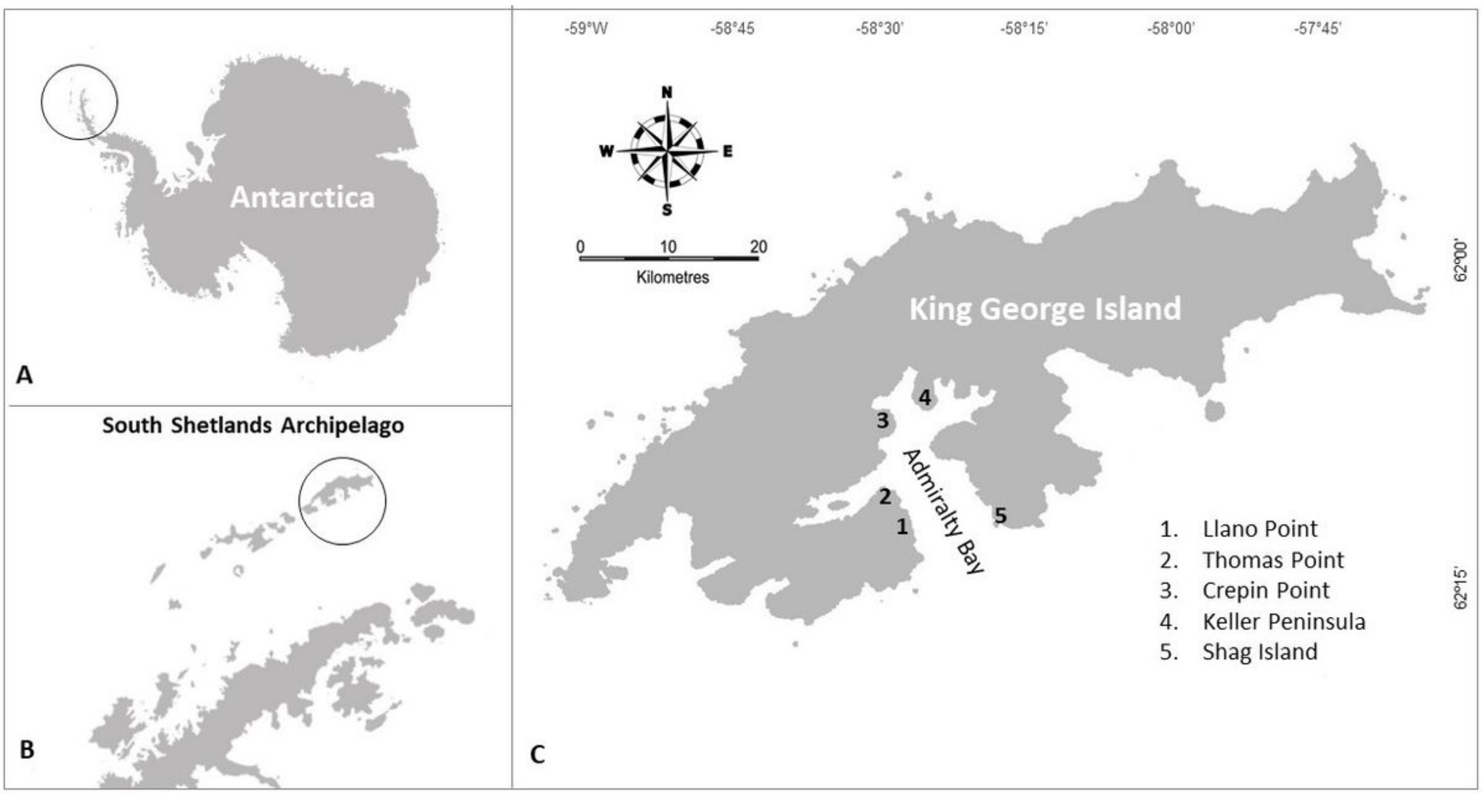

Figure 1

Study area. A) Antarctic continent with the northern Antarctic Peninsula shown in the circle; B) Antarctic Peninsula with South Shetland Islands and King George Island shown in the circle; C) King George Island. Sample collection points in Admiralty Bay at 1) Llano Point, 2) Thomas Point, 3) Crepin Point, 4) Keller Peninsula and 5) Shag Island

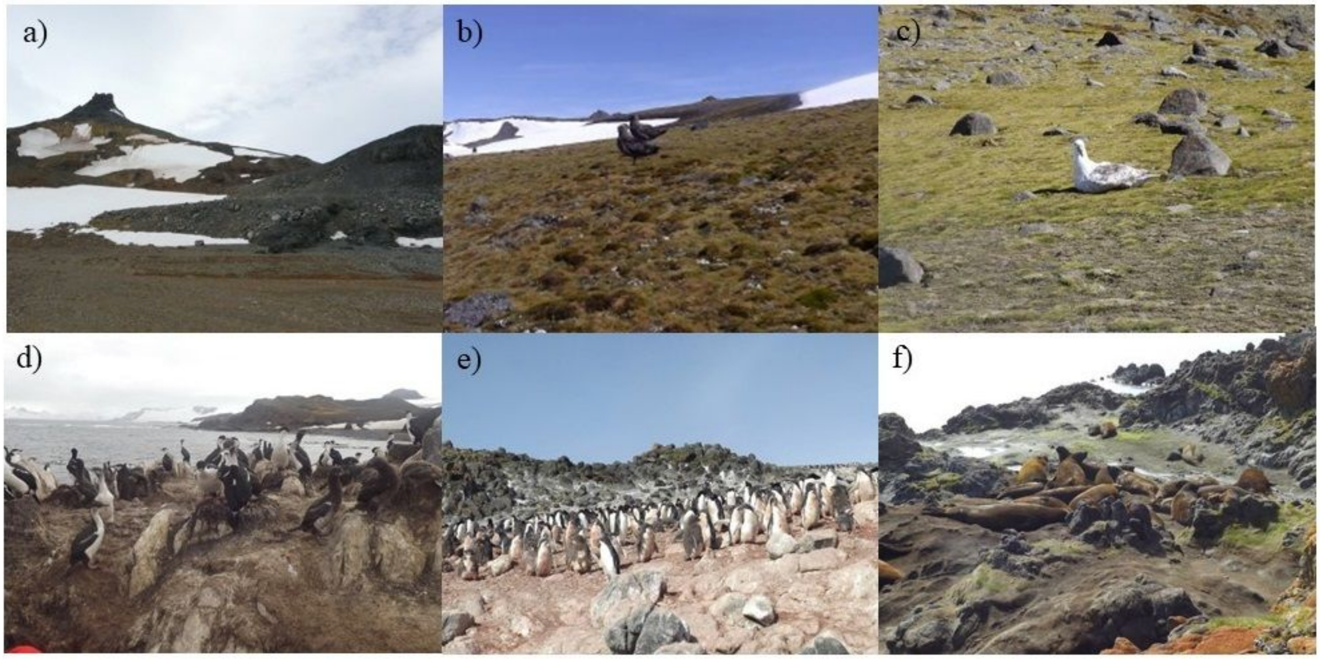

Figure 2

Areas not influenced and under the influence of marine vertebrates: a) non-influenced area; breeding colonies of b) brown skua; c) southern giant petrel; d) imperial shag; e) chinstrap penguin; f) southern elephant seal

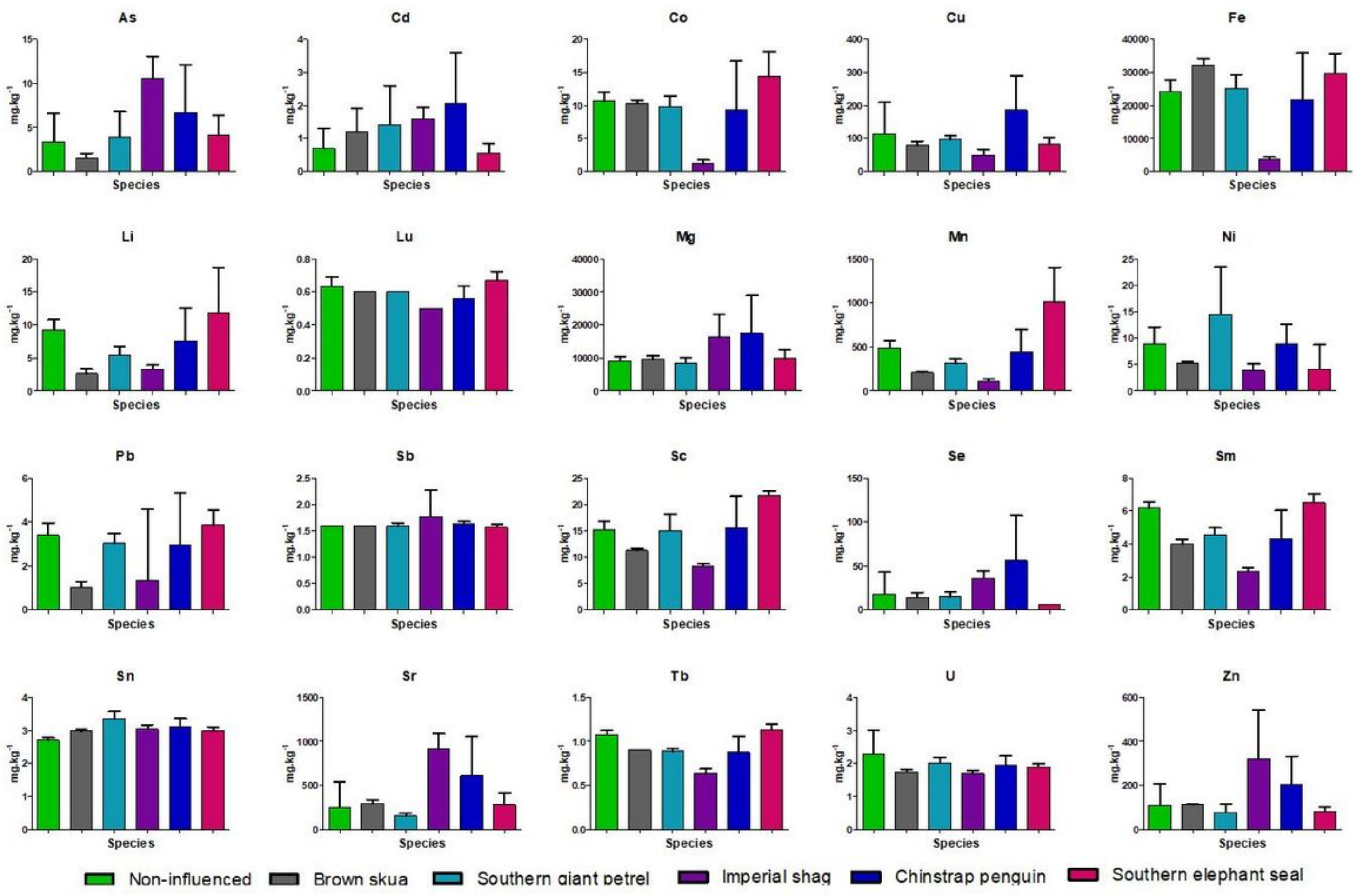

Figure 3

Mean element concentrations (mg.kg^{-1}) with standard deviation of marine vertebrate-influenced and non-influenced soils sampled in Admiralty Bay, King George Island, South Shetland Islands.

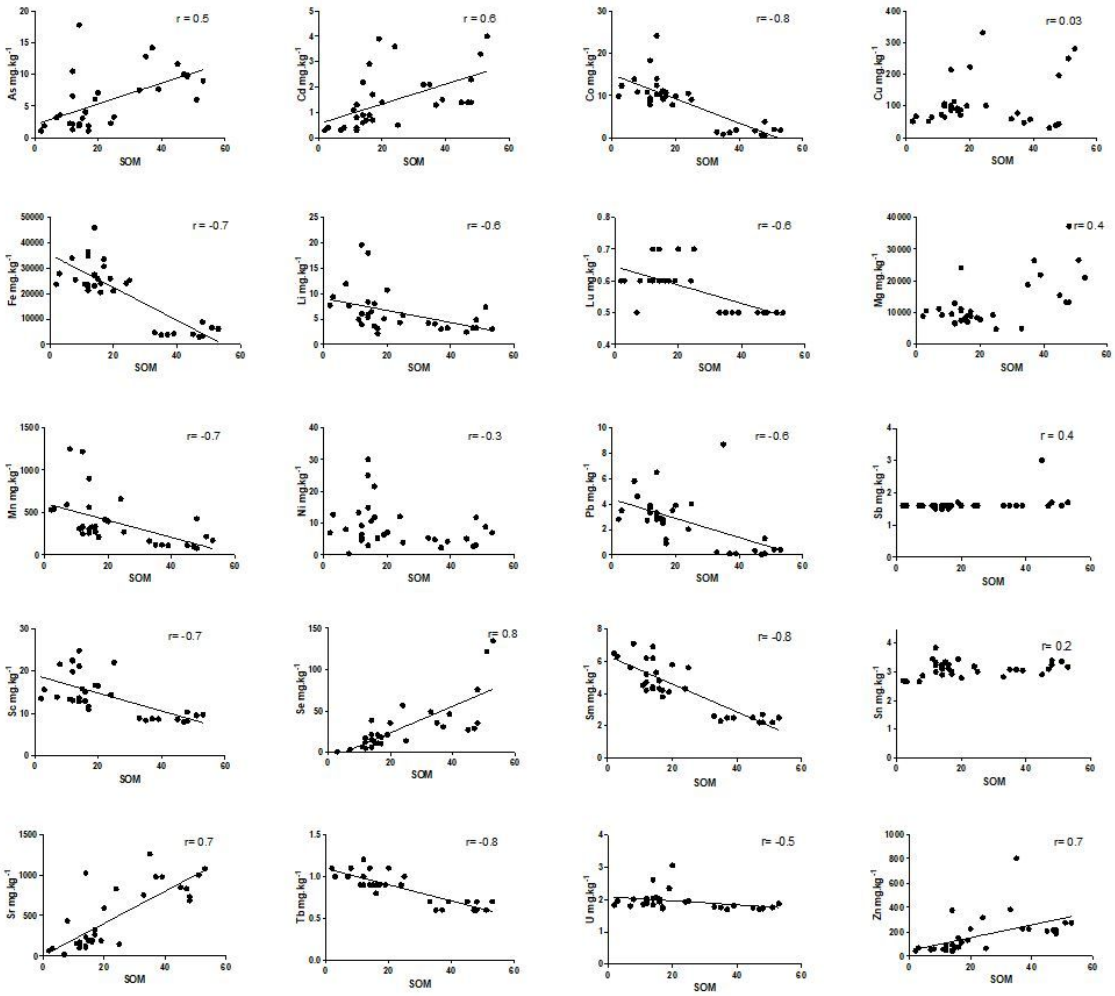

Figure 4

Relationships between trace element concentrations and soil organic matter (SOM) content in marine vertebrate-influenced and non-influenced soils from Admiralty Bay, King George Island, South Shetland Islands.