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Influence of marine vertebrates on organic matter, phosphorus and other chemical element levels in Antarctic soils

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Abstract

The presence of marine vertebrates in dense reproductive colonies and other aggregations contributes to the input of organic matter and nutrients into the local environment and it is believed that chemical elements are subsequently remobilized from the excreta of these animals. In this study, we investigated 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), nutrient (total phosphorus) and soil organic matter (SOM) content from five locations with and without the presence of seabirds and marine mammals in Admiralty Bay, King George Island, South Shetland Islands, Antarctica. Soils were acid digested using a microwave digestion system, 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 the trace elements assessed, however, we observed a significant increase in SOM and P that was positively correlated with the concentrations of As, Cd, Se, Sr and Zn. Although marine vertebrates did not appear to significantly increase the elemental concentrations in the soils examined here, there is a clear evidence of selective enrichment indicating a zoogenic influence. Comparing our results with other studies, we conclude that soil elemental levels are result from an interplay between local geology, vertebrate diet and colony size. Further studies with increased sample size are required to obtain a better understanding of the influence of marine vertebrates on chemical element levels in Antarctic soils.

Keywords Soil contamination · Ornithogenic soils · Metals · Polar regions

Introduction

King George Island, the largest island in the South Shetland Islands archipelago north-west of the Antarctic Peninsula, hosts important breeding areas and other aggregation 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).

Whilst these marine vertebrates in detail occupy different positions in the trophic chain, they generally represent higher

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trophic levels, where they are susceptible to high levels of contaminant accumulation (Hazen et al. 2019). The main route by which chemical elements enter these organisms is through feeding (Burger and Gochfeld 2004; Bargagli 2008; Ramos and González-Solís 2012; Hazen et al. 2019). Once ingested, they can be absorbed by the gastrointestinal tract, transferred to the blood stream and stored in internal tissues, whilst any that are not absorbed are eliminated through the excreta (Yin et al. 2008; Pacyna et al. 2019). Absorbed elements 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 and pinniped colonies, the accumulation and local dispersal of guano leads to the formation of ornithogenic soils, representing an abundant source of organic matter, nutrients and other elements to the Antarctic terrestrial ecosystem (Michel et al. 2006; Yin et al. 2008; Bokhorst et al. 2019a; Castro et al. 2021; Convey and Hughes 2022). 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 behaviour 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 (Bargagli 2005; Bokhorst et al. 2007, 2019a, b; Zwolicki et al. 2015; Bokhorst and Convey 2016) with evidence that the input of organic matter and nutrients (e.g. nitrogen and phosphorus) increases the rate of local productivity creating a biological hotspot for plants and other organisms (Liu et al. 2013; Qin et al. 2014; Sparaventi et al. 2021).

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). Therefore, the current study set out to investigate the role of marine vertebrates in the input or remobilization of organic matter, nutrient and chemical elements to terrestrial ecosystems in Admiralty Bay, King George Island, Antarctica. For this purpose, soils from marine vertebrate colonies and non-influenced areas were collected to quantify organic matter content, phosphorus level and other 20 chemical elements (As, Cd, Co, Cu, Fe, Li, Lu, Mg, Mn, Ni, Pb, Sb, Sc, Se, Sm, Sn, Sr, Tb, U and Zn). We assume that different marine vertebrate species may differentially impact on elemental concentrations in soils at their breeding sites.

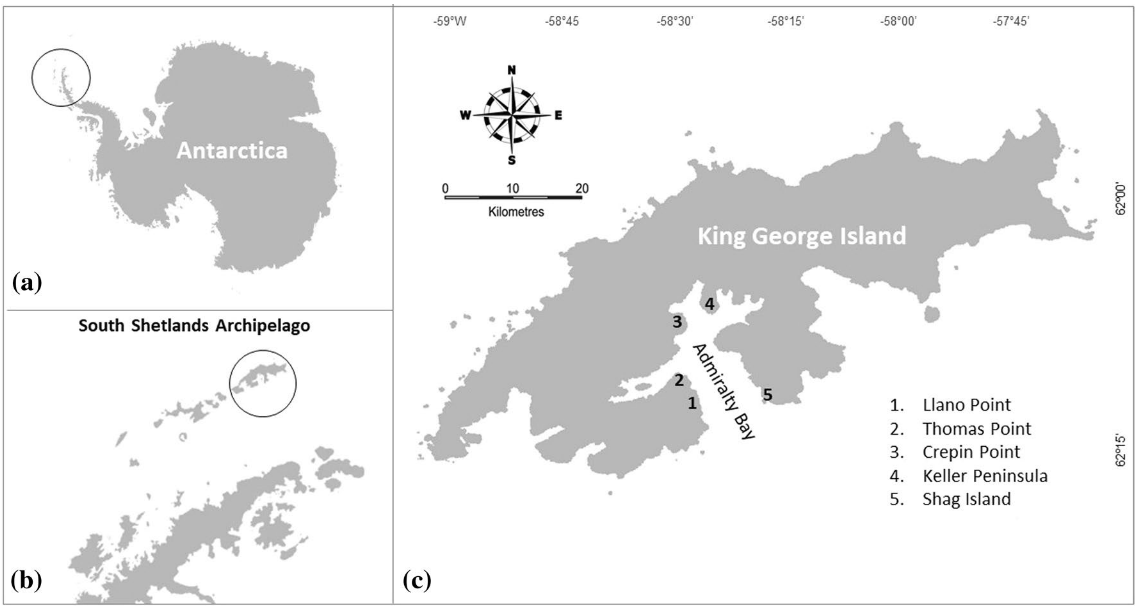


Fig. 1 Study area. **a** Antarctic continent with the northern Antarctic Peninsula shown in the circle; **b** Antarctic Peninsula and South Shetland Islands with King George Island shown in the circle; **c** King George Island. Sample collection points in Admiralty Bay at (1) Llano Point, (2) Thomas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

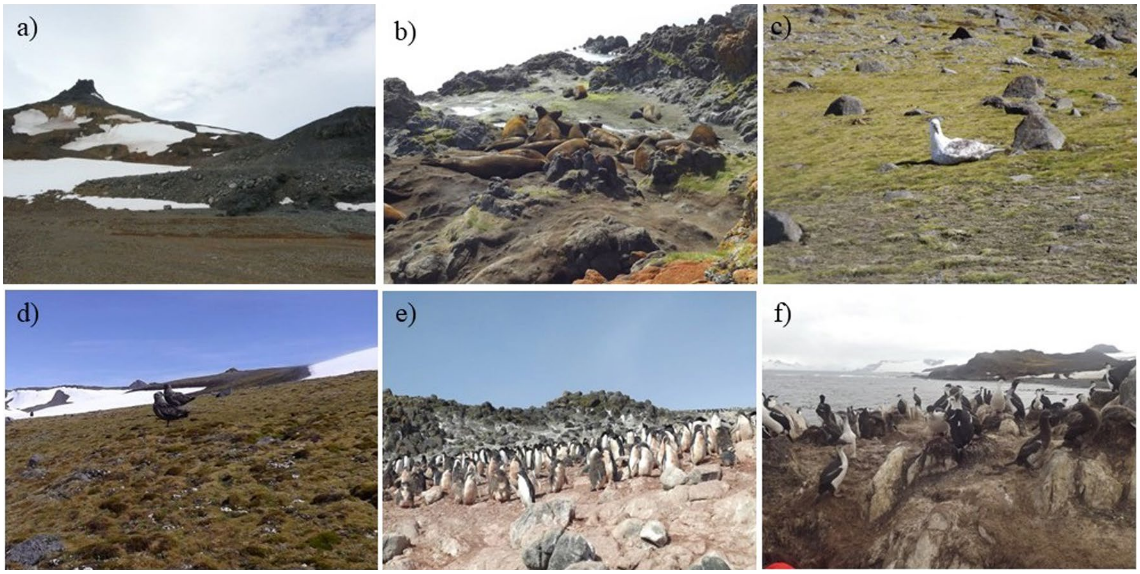


Fig. 2 Illustrations of sampling sites. **a** Non-influenced area; breeding colonies of **b** southern elephant seal, **c** southern giant petrel, **d** brown skua, **e** chinstrap penguin and **f** imperial shag

Materials and methods

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 behaviour, diet and breeding sites (sea shore and inland rocks). Samples of vertebrate-influenced topsoil were collected using a plastic spoon, consisting of an area of approximately 25 cm^3 with a depth of up to 5 cm. The samples were collected 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*; $n = 9$; Llano Point, scavenger, feeding on penguins and seals carcasses), brown skua (*Stercorarius antarcticus*; $n = 2$; Keller Peninsula, Comandante Ferraz Station, Brazil, feeding on penguin chicks, eggs, fish 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 soil samples were immediately placed in *ziplock* plastic bags and kept frozen until analysis.

Trace element quantification

Before commencing the analyses, soils were defrosted at room temperature for 12 h, dried at 50 °C 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) in closed Teflon vessels in a microwave digestion system (Mars 6 Xpress, CEM Corporation, Austria). Samples were made up to 10 mL with Milli-Q water (Direct-Q system, Millipore, Germany) 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 and 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.

Organic matter quantification

Soil organic matter (SOM) content was determined by loss-on-ignition (Andersen and Krysell 2005). 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.

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. The detection limit ranged between 0.06 (Pb) and 517 (Mg) mg kg^{-1} and the recovery of certified material was between 71 (Fe) and 115% (Tb), more details are available in the supplementary material (Tables S1, Table S2).

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. A significance level of $p < 0.05$ was adopted for all tests.

Results

Figure 3 shows the SOM content and P levels and Fig. 4 shows the mean element concentrations in the marine vertebrate-influenced and non-influenced soils from King George Island. A detailed summary of the elemental concentrations measured is available in the supplementary materials (Table S3).

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 giant petrel > southern elephant seal > non-influenced soils (Fig. 3). Significant positive correlations were detected between SOM and levels of As, Cd, P, Se, Sr and Zn and negative correlations with levels of Co, Fe, Li, Mn, Pb, Sc, Sm and Tb (Fig. 5). Similarly, the highest *P* levels was also found in the shag colony with concentrations decreasing in slightly different rank order imperial shag > chinstrap penguin > brown skua > non-influenced > southern giant petrel > southern elephant seal (Fig. 3). Significant positive correlations were detected between P and As, Cd, Se, Sr and Zn and negative correlations with levels of Co, Fe, Li, Lu, Mg, Mn, Pb, Sc, Sm and Tb (Fig. 6).

Regarding, the elemental concentrations non-influenced soils had similar levels when compared with vertebrate-influenced soils for the majority of elements analysed. Statistically, significant differences in concentrations were only observed for Sn, lower than non-influenced soils than in southern giant petrel colonies, and Li, Lu, Mg 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 the 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 $p < 0.05$).

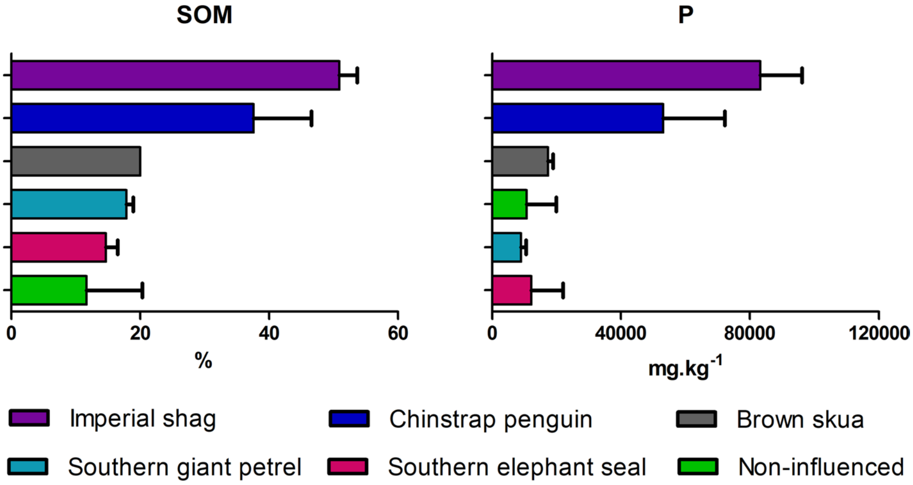


Fig. 3 Soil organic matter (SOM %) and phosphorus levels (P mg kg^{-1}) in marine vertebrate-influenced and non-influenced soils from Admiralty Bay, King George Island, South Shetland Islands

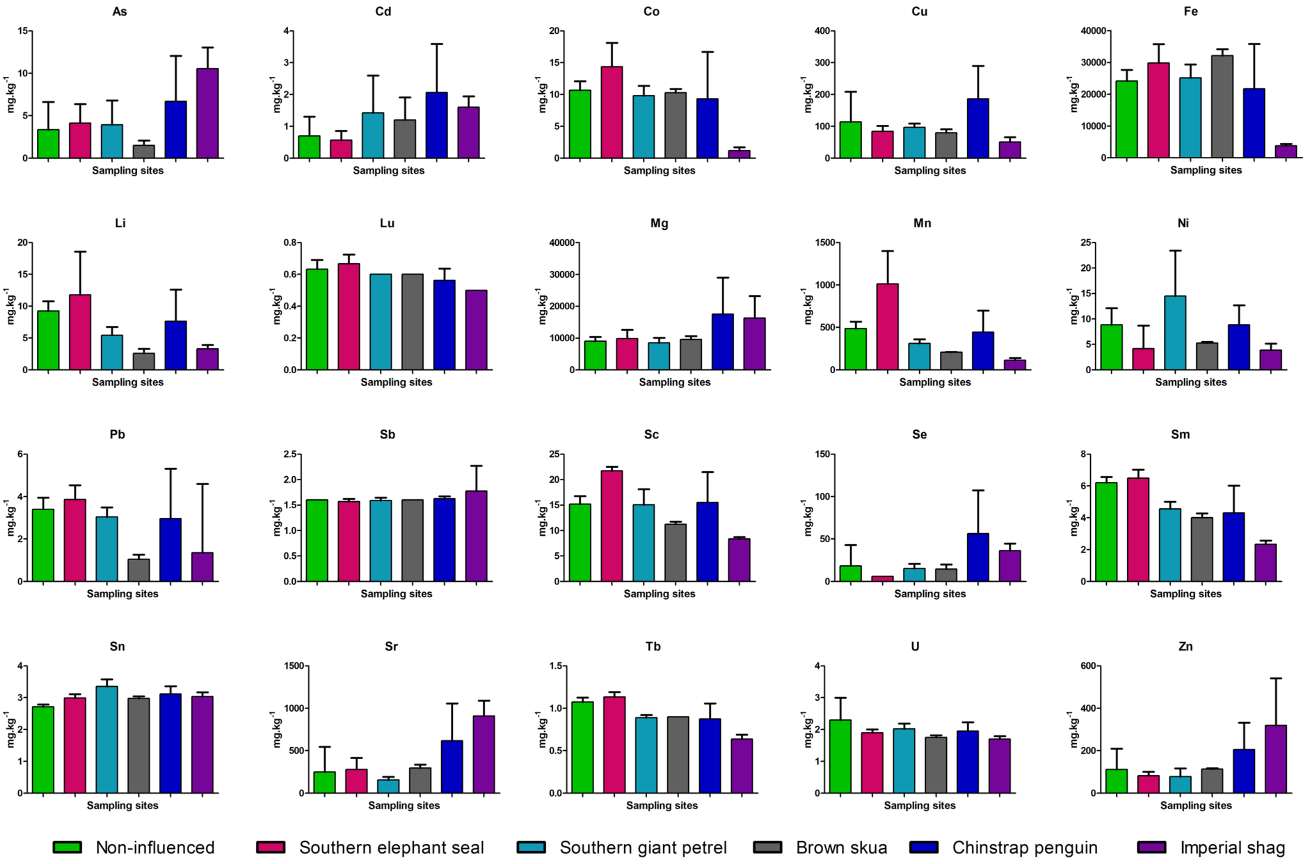


Fig. 4 Mean element concentrations (mg kg^{-1}) with standard deviation of marine vertebrate-influenced and non-influenced soils from Admiralty Bay, King George Island, South Shetland Islands

Discussion

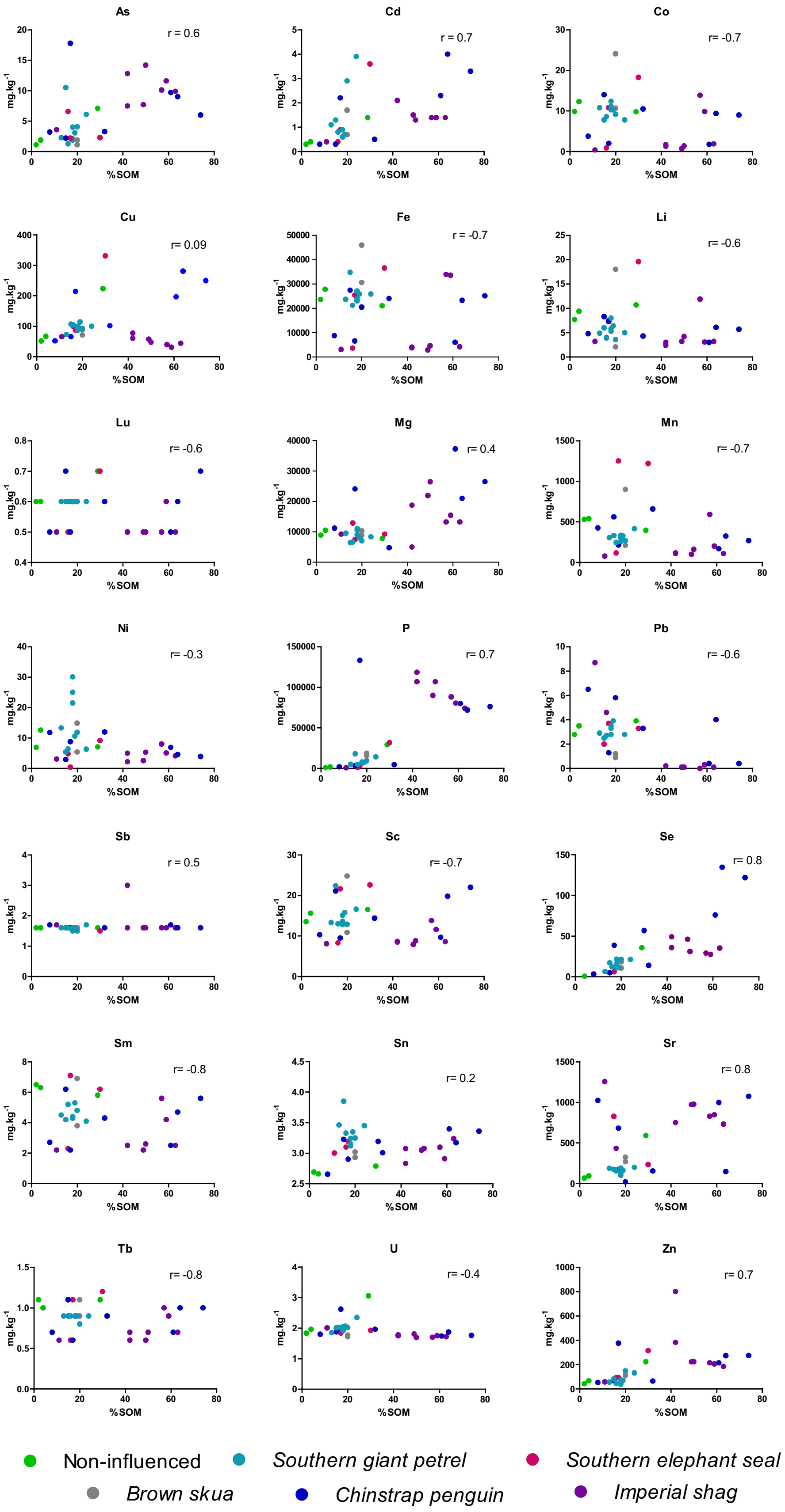
This study identified only a few statistically significant differences between non-influenced soils when compared with vertebrate-influenced soils. However this may in part be a function of the different climates, geological heterogeneity of the areas, size of colonies or because of the relatively low sample sizes available, as visual inspection of the data obtained (Fig. 3) did suggest differences in the distribution of elements in the different soils.

Our data are consistent with the interpretations of other authors who suggested that there may be selective enrichment of some elements associated with the presence of marine vertebrates. Such studies have previously confirmed the transfer of organic matter and nutrients (e.g. phosphorus) into terrestrial ecosystems through their faeces in different parts of Antarctica (Santamans et al. 2017; Alekseev and Abakumov 2020; Rodrigues et al. 2021; Castro et al. 2022). These inputs result in the deposition and accumulation of elements, including several potentially toxic in soils, which could lead to negative impacts on organisms and the environment.

Most of the studies are focussed on the influence of seabirds on their reproductive colonies being studies with southern elephant seals and other marine mammals largely neglected (Bedernichek et al. 2020). For example, Cipro et al. (2018) confirmed that seabirds input Cd, Hg and probably As, Se and Zn to Antarctic terrestrial ecosystems, whilst Espejo et al. (2017) reported the input of Cd, Co, Cr, Cu, Mo, V and Zn from penguin colonies from Chile and the Antarctic Peninsula area. Brimble et al. (2009) found levels of As, Cd and Zn in ponds affected by seabirds that exceeded local environmental protection guidelines in Arctic Canada. Some authors have suggested marine-derived elements such as Cu, Pb and Zn (Castro et al. 2021), As, Cd, K, P and Zn (Brimble et al. 2009) or Cd, Co, Cr, Cu, Mo, V and Zn (Espejo et al. 2017). This variation may be due to differences in local geology or in the feeding habits of the species. In a study comparing avian bio-elements on a global scale, Liu et al. (2013) identified overlap of As, Cd, Cu, P, Se and Zn in ornithogenic sediments from Antarctica, the South China Sea and the Arctic.

However, studies also identify no consistent pattern of change in concentrations of most elements as a result of

Fig. 5 Correlation (Spearman *r*) between chemical 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



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. 2019a, b; Alekseev and Abakumov 2020, 2021; Castro et al. 2021, 2022; Sparaventi et al. 2021).

The present study indicated that soils obtained from a location not under the direct influence of marine vertebrates had trace element concentrations that were generally similar to those of soils obtained from many of the marine vertebrate colonies sampled. However, it is important to emphasise that the general lack of significance may be a consequence of the relatively small sample sizes for most groups.

In a few cases, the non-influenced soils recorded higher contents of some elements than in shag colony soils, in particular with Mn, Li and Tb levels (see discussion about low levels in shag colony soils below). 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, hypothesising 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. Furthermore, we cannot ignore the presence of scientific stations close to the reproductive colonies that can affect the concentration of elements associated with anthropogenic activities, such as Pb, Ni and Sn (Tin et al. 2009).

Comparing the different vertebrate species influences on colony soils, different processes seem to taking place in the soils of imperial shag and chinstrap penguin colonies, influencing the concentrations of some trace elements.

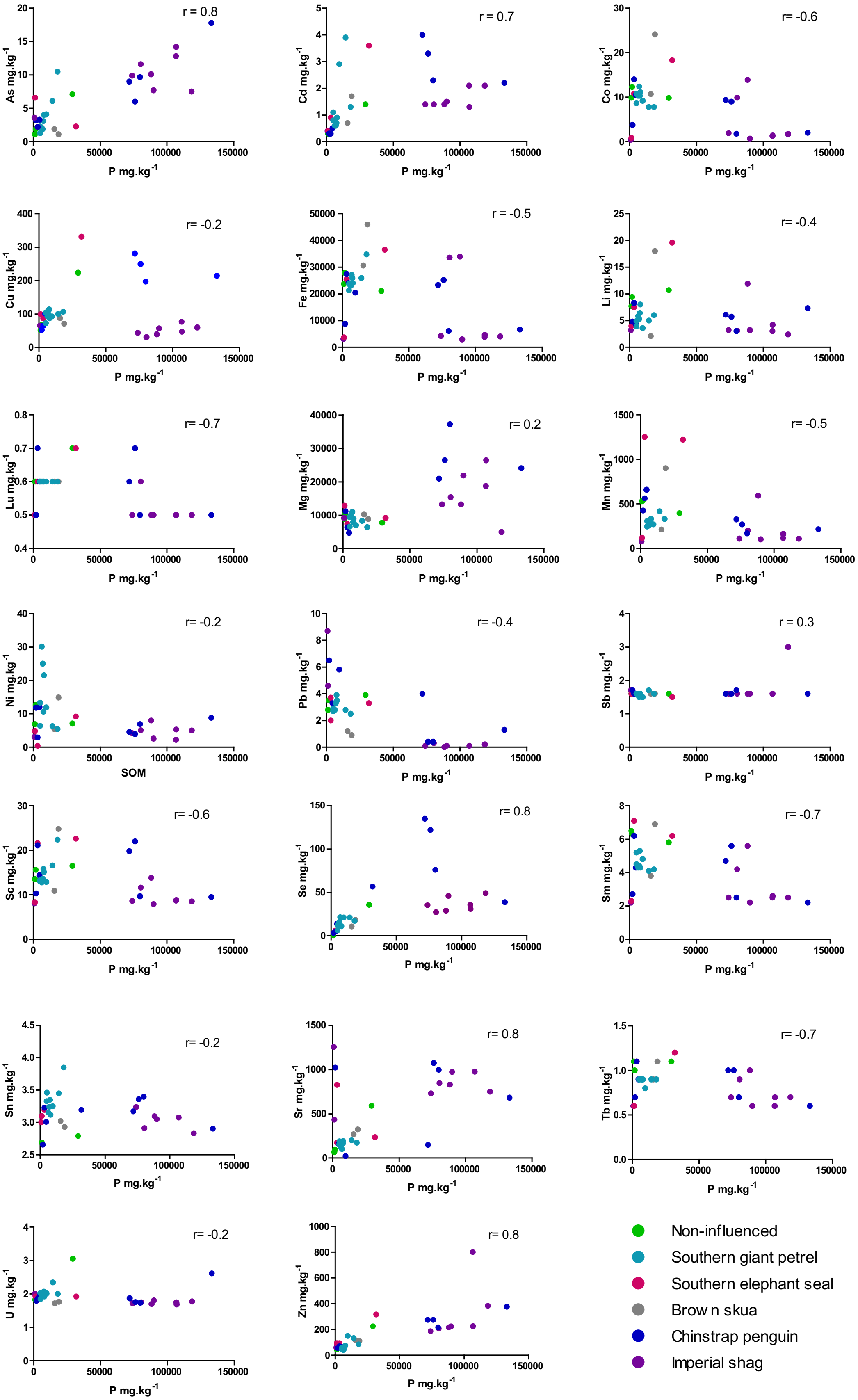
Furthermore, the abundance of species in breeding colonies is also an important factor, since the greater the number of individuals, the greater the collective potential to influence elemental concentrations. Consistent with this, soils from imperial shag and chinstrap penguin colonies had higher concentrations of SOM and P and, consequently, higher concentrations of the elements that are positively related to them (i.e. As, Se, Sr and Zn), indicating that there is a proportional relationship between the size and density of the colony and the relative influence of the species in these 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 chemical elements.

Intriguingly, soils in imperial shag colonies also had lower concentrations of several elements (e.g. Co, Cu, Fe, Li, Mn, Ni, Sc, Sm, U) 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 element concentrations. Breeding colonies of this species characteristically have a thick layer of guano, indicating the scale of contribution to the input of organic matter (Cipro et al. 2018). However, studies have no 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 organic matter 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, 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 elements to the environment.

Studies of Antarctic soils have previously reported correlations between element levels, phosphorus and organic matter content (e.g. Espejo et al. 2017) supporting hypotheses that both 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, and also P and As, Cd, Sr, Zn with overlapping elements being more likely to be influenced by marine vertebrates. Some studies reported positive correlations between carbon and As, Cu, Hg, Pb Zn contents (Alekseev and Abakumov 2020; Castro et al. 2021) and between P and Cd, Cr, Cu, Hg and Zn (Ziółek et al. 2017; Castro et al. 2021) 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, as outlined above, SOM modifies soil characteristics, changing pH and cation exchange capacity (Walsh and McDonnell 2012) which could increase the leaching of some elements over time. For instance, elements unrelated to SOM or P (such as Cu, Mg, Ni, Sn, U) likely originate from another sources, either natural or anthropogenic (Cipro et al. 2018).

Conclusion

Marine vertebrates have the potential to influence the organic matter content and the chemical element levels in soils around their colonies. Our results reinforce that Antarctic marine vertebrate species, in particular those that typically breed in dense and large colonies contribute to the input of organic matter, phosphorus and other selected elements to soils of the breeding colonies in King George Island. Soils not influenced by marine vertebrate had a lower organic matter content, intermediated phosphorus level and broadly similar concentrations of most chemical elements to those under vertebrate influence. We did not


As mg.kg⁻¹
r = 0.8
Cd mg.kg⁻¹
r = 0.7
Co mg.kg⁻¹
r= -0.6
Cu mg.kg⁻¹
r= -0.2
Fe mg.kg⁻¹
r = -0.5
Li mg.kg⁻¹
r= -0.4
Lu mg.kg⁻¹
r= -0.7
Mg mg.kg⁻¹
r= 0.2
Mn mg.kg⁻¹
r= -0.5
Ni mg.kg⁻¹
r= -0.2
SOM
Pb mg.kg⁻¹
r= -0.4
Sb mg.kg⁻¹
r = 0.3
Sc mg.kg⁻¹
r= -0.6
Se mg.kg⁻¹
r= 0.8
Sm mg.kg⁻¹
r= -0.7
Sn mg.kg⁻¹
r= -0.2
Sr mg.kg⁻¹
r= 0.8
Tb mg.kg⁻¹
r= -0.7
U mg.kg⁻¹
r= -0.2
Zn mg.kg⁻¹
r= 0.8
P mg.kg⁻¹
0
50000
100000
150000
● Non-influenced
● Southern giant petrel
● Southern elephant seal
● Brown skua
● Chinstrap penguin
● Imperial shag

◂**Fig. 6** Correlation (Spearman *r*) between chemical elements and phosphorus levels (P mg kg^{-1}) content in marine vertebrate-influenced and non-influenced soils from Admiralty Bay, King George Island, South Shetland Islands

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 elements which could, in turn, be apparent in differences between specific elements in colonies or vertebrate species. Significant positive and negative correlations were found between SOM content, P levels and different elements, suggest that both enrichment and differential leaching are occurring in areas influenced by marine vertebrates. These are indicative that the concentrations of elements and organic matter in Antarctic soils are a result of interplay between local geology, vertebrate diet and colony size.

Supplementary Information The online version contains supplementary material available at https://doi.org/10.1007/s00300-022-03091-8.

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Author contributions LSTC, ESC and JPMT conceived and designed the research project; JPMT obtained funding for the Antarctic expedition; JSK, LSTC, ESC and JPMT conducted the field sampling; TAS performed the sample processing; JSK performed the laboratory, statistical and data analysis; PN supervised the laboratory analysis; JSK wrote the first draft of the manuscript; JSK, TCP, PC, LSTC, KZ and PN contributed to data interpretation and discussion; JSK and PN obtained funding for analytical analysis; JSK, TCP, PC, LSTC, TAS, KZ and PN revised the manuscript. All authors read and approved the final version of the manuscript.

Declarations

Competing interests The authors declare no competing interests.

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