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Metals in topsoil in Larsemann Hills, an ice-free area in East Antarctica: Lithological and anthropogenic inputs

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ABSTRACT

Although metal accumulation has been investigated in coastal Antarctic soil, the information about to what extent station activities influence soil quality remains limited, especially in East Antarctica. Here, we carried out an investigation on element accumulation (Pb, Zn, Cu, Ni, Mn, Cr, Ti, Zr, Fe, Ca, K, Al, Mg and Na) in topsoils collected from Larsemann Hills, the second largest oasis along East Antarctica. Results show that metal contents in soils generally fall within the ranges of local rocks, suggesting a dominant source of parent minerals. In spatial, a content gradient of Pb was found, with elevated values inside station areas, while no obvious trend was found for other metals. Contents of total organic carbon (TOC) and nitrogen are rather low, and no association exists between metals and TOC or nitrogen, suggesting a minor role of nutrients in soil metal accumulation in this cold-xeric environment. Chemical weathering assessment suggests a low degree of chemical weathering in topsoils in Larsemann Hills. The results of multivariate statistical analysis suggest that lithological inputs are the dominant source of soil metals, and the different metal groups are likely associated with different geochemistry of elements during weathering process. Among the observed 14 metals, only soil Pb levels was affected by local human activities, but this influence is only confined to inside station areas. The influences of marine inputs and long-range pollutant transport on metal levels in topsoils were found to be negligible.

1. Introduction

The metals (e.g., Pb, Cu and Zn) released by human activities can be accumulated in different environmental matrices (Audry et al., 2004; Shi et al., 2008; Shi et al., 2010), due to their characteristics of degradation-resistant (Bryan and Langston, 1992). Thus, metal contamination is of increasing concern worldwide over the past several decades. When metals were released into the atmosphere, they can be transported to remote areas, such as polar region, by the long-range atmospheric transport (Steinnes et al., 1997; Donisa et al., 2000; Gong and Barrie, 2005; Shi et al., 2015). The polar regions have been recognized as important sinks for long range transport of metals (e.g., Hg) originated from human sources in mid-low latitudes (Bargagli et al., 2007 and references therein). In the Arctic region, elevated levels of metals in ecosystems, especially the toxic elements Hg, Cd and Pb, were thought to be mainly associated with human inputs (Macdonald et al., 2000; McConnell and Edwards, 2008). In comparison with the investigations in Arctic, the surveys are still limited in Antarctica, possibly due to the logistical difficulties in sample collection. Antarctica is usually thought of as a pristine land untouched by human disturbance, due to no permanent human settlement and the wide expanse of the Southern Ocean around Antarctica. However, human inputs have already exerted an influence on trace metals in the atmosphere and snow in Antarctica (Shi et al., 2015; Hua et al., 2016), and anthropogenic contribution is thought to be an important factor affecting snow metal concentrations (Soon et al., 2007). Different from the snow/precipitation, the input of trace metals from long-range transport to the soils in Antarctica is generally negligible (Bargagli, 2000), possibly due to the dilution effects. It is noted that a long-term survey of Hg distribution in a coastal ice-free area near Victoria Land suggested an enhancement of soil Hg, possibly associated with anthropogenic emissions in the Southern Hemisphere (Bargagli et al., 2005; Bargagli et al., 2007).

In Antarctica, the investigations of soil metal occurrence and sources are mainly focused on the Antarctic Peninsula (AP) (Table 2), in particular the King George Island, where a number of scientific stations are distributed. Thus far, King George Island is found to be one of the most impacted regions in Antarctica, mainly due to the local anthropogenic emissions (Padeiro et al., 2016). Elevated levels of metals (e.g., Pb, Zn and Cu) were often found in soils in the station areas, e.g., soil Pb and Zn can be up to 418 and 949 μg g^{-1} respectively near Ardley Cove

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(King George Island), suggesting a severe human disturbance (Carrasco and Préndez, 1991; Lee et al., 2004; Padeiro et al., 2016).

In addition to the sites near AP, soil metals in McMurdo Station (Table 2), coastal Victoria Land, and the Dry Valleys have also been documented (Crockett, 1998; Bargagli et al., 2007). These investigations suggest that local human impact on Antarctic soil metal accumulation is generally low, mainly confined to restricted areas. In comparison with the investigations carried out in West Antarctica, the reports on metals in the cold-xeric East Antarctic soils remain very limited.

Chemical weathering is of importance to the soil formation. This process, however, is thought to play a minor role in Antarctic soil formation. For instance, the investigations performed in AP and areas near the Transantarctic Mountains proposed that chemical weathering is not a controlling factor in the formation of soil parent materials, but this process is significant (Campbell and Claridge, 1987; Lee et al., 2004). However, the chemical weathering degree of soils in the cold deserts of East Antarctica has been poorly understood.

Larsemann Hills (LHs), located in the Indian Ocean sector, is the second largest ice-free oasis along the East Antarctica (with an area of about 50 km^2), where five research stations (Zhongshan, Progress I, Progress II, Law Base and Bharati) have been established to date (Fig. 1). During 1990s–2000s, Gasparon and Matschullat (2006a, 2006b) have examined trace metal levels in rocks and lake sediments in LHs; however, metal distributions and their geochemical behaviors in LHs soils have not yet been investigated. Here, we carried out an investigation concentrating on topsoil metal abundance and source apportionment in LHs. The main aims of this research are: (1) to determine metal abundances and their spatial distribution patterns, (2) to assess chemical weathering and metal accumulation degree, and (3) to identify possible sources of metals. The results of this study will contribute to a better understanding of metal geochemistry in soils and related pedogenesis in East Antarctica.

2. Materials and methods

2.1. Study area

The Larsemann Hills are consisted of a series of low rounded hills along the southeastern shore of Prydz Bay, East Antarctica (Fig. 1). Different from most East Antarctic coast, there are no moraine deposits in LHs. Due to low temperature and very sparse micro-organisms in soil (Hopkins et al., 2005; Signh et al., 2007), soils are found to be mainly derived by physical weathering of local basement rocks (e.g., gneiss, granulite and granite in Fig. 1) (Campbell and Claridge, 1987; Carson et al., 1995; Gasparon and Matschullat, 2006a). In research station areas, soils are strongly disturbed by human activities (e.g., vehicle grinding and building constructions), resulting in loose soils widely distributed. In the areas away from station, soils are mainly smaller rock fragments, with less fine fractions. According to the soil survey during field sampling, the solum was thinner than 75 cm and the fine fraction soils was generally low (< 20%). Therefore, in most cases the soils were assigned to the “lithic” subgroup. Considering the texture of sandy and loamy skeletal, the soils were mainly distinguished as “Lithic Crysols” following the World Reference Base (IUSS Working Group WRB, 2015).

This study is focused on Mirror Peninsula in LHs (Fig. 1), where two year-round operating stations are distributed, i.e., Zhongshan Station (69°22′25″S, 76°22′14″E), and Progress II Station (69°22′52″S, 76°24′6″E). The basement on Mirror Peninsula is relatively homogeneous from the geochemical point of view, and the contents of Pb in basement rocks are high (Gasparon and Matschullat, 2006a). The LHs mainly consist of upper amphibolite to granulite grade paragneisses intruded by a number of generations of pegmatitic and granitic bodies (Carson et al., 1995). The mafic granulite is distributed in metapelitic and leucogneiss in the LHs, and in the Mirror Peninsula orthopyroxene-pla-gioclase symplectites around garnet in mafic granulite is present (Wang et al., 1994).

2.2. Sample collection

In order to investigate the impacts of station activities on soil quality, four samples were collected from the main road inside the station areas in February 2011 (S1–S4, triangles in Fig. 1). Contents of fine fractions in the four soil samples are relatively high, as a result of the intensive station activities (e.g., tracked vehicle grinding). Considering that only Zhongshan and Progress II are year-round operating stations, five sampling sites were set (S5–S9 in the dashed square of Fig. 1) in vicinity of the two stations to evaluate potential influences of human activities. In general, the distances from the five sampling sites to the stations are generally < 500 m, and these sites are less visited by vehicles. In addition, 19 sites, with a near-even distribution, were set in the rest of LHs, and these sites were least disturbed by local human activities.

At Zhongshan station, the annual mean wind speed is 7.0 m s^{-1}, and wind directions between north and east-north-east account for 85.7% of all occurrences, i.e., the prevailing wind direction is from the northeast (Ma et al., 2010). In this case, most of the sampling sites are less likely to be influenced by station emissions, and the soils in the downwind direction, especially S6-S8 and S10 (Fig. 1), could potentially be affected by local emissions.

The topsoils were collected with a stainless steel spatula, and 4–6 sub-samples (the topmost 3-5 cm) were taken and then mixed thoroughly to obtain a bulk soil sample. At each sampling site, the subsamples were at least 10 m apart, and the sub-sampled sites are distributed in an area of ~0.5 ha. About 200 g soil was collected at each sampling site. Note that only the loose topsoil was sampled, with no crusts collected. In total, a set of 28 soil samples were collected. All the samples were kept in sealed polyethylene packages to avoid contamination, and then they were stored under freezing conditions (< − 20 °C) and transported to lab for treatment and analysis.

2.3. Sample treatment and analysis

Soil samples were air-dried in a clean hood, and then thoroughly mixed and gently crushed to pass through a 2 mm nylon sieve for the analysis (Sheppard et al., 2000). The fraction of the stones (i.e., > 2 mm), generally < 20% (w/w) of the whole soil, were discarded. Acid digestion method was used for soil treatment. Firstly, about 1.0 g soils were placed in polytetrafluoroethylene vessels, and then digested with HNO_3, HF and $HClO_4$ in a microwave oven following the operations of 0.3 MPa (3 min) → 0.6 MPa (2 min) → 1.0 MPa (2 min) → 1.5 MPa (2 min) → 2.0 MPa (6 min) (Shi et al., 2012). Total Pb, Zn, Cu, Ni and Cr were determined by a Perkin-Elmer AANALYST800 atomic absorption spectrophotometer analyzer. The other elements Mn, Ti, Zr, Fe, Al, K, Na, Ca, and Mg were measured by a Shimadzu XRF-1800 X-ray fluorescence spectrometer, using the raw soil samples.

During analysis procedure, sediment standard material, GSD-9, supplied by the national research center for certified reference materials of China, was used for QA/QC. The reference material was treated synchronously with samples, and the recovery of metals ranged from 88% to 111% (Table S1 in Supplementary material). Duplicated sample analysis was performed throughout all the experiments to check the analysis accuracy, with relative standard deviation < 5.0% (n = 5); meanwhile three blank determinations were also carried out through the whole digestion process for the examination of reagent quality. All of the containers used in this research were immersed in the diluted HNO_3 for at least 24 h; then they were washed with fresh water, lastly washed with Milli-Q water (18.2 MΩ) for three times.

Total organic carbon (TOC) content was measured on corresponding soils (~5 g) after HCl (10% v/v) digestion to remove the carbonate by using an automatic element analyzer (Elementar, VARIO EL III).