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Trace and major element associations in basaltic ash soils of El Hierro Island

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ABSTRACT

Associations between major and trace elements (aqua regia) were studied in basaltic-ash soils from the island of El Hierro in order to distinguish possible non-lithological contributions to the large trace element concentration shown by the soils. Soil composition reflected the basaltic composition of the parent materials and their extended tendencies to ultrabasic and trachytic compositions. The obtained values did not differ from previously reported reference values for natural soils, pointing to a low intensity anthropic activity. Only Cd levels were above those predicted by parent materials. The large soil total phosphorus (P) concentrations were consistent with those reported for the parent materials, thus obscuring the hypothesis of the contribution of the phosphate-rich Saharan dust to soil Cd enrichment. The spatial distribution of trace and major elements helped to identify a larger concentration of trace elements in soils of the most humid zones where andic properties were more highly expressed. Anthropic influence was revealed by the association of P and Cd in a former intensive agricultural zone. The large metal concentrations could reach or exceed the Soil Quality Standards for heavy metal concentrations in relation to soil pH. Plant composition, however, did not approach hazardous levels, probably due to the effect of the organic and highly reactive mineral sorbing phases of the studied soil types.

1. Introduction

The knowledge of the origin of soil heavy metals (HM): pedogeochemical, anthropogenic, or long-range transport, can provide direct or indirect information on element reactivity, hence availability and mobility. This information is essential to derive Soil Quality Standards and soil management practices (e.g., biosolid applications). The relationships between major and trace soil elements is related to the lithologic origin of the elements (Takeda et al., 2004) and hence can help to discriminate from other inputs like management histories and pollution. Hamon et al. (2004) demonstrated that there are associations between the HM background and major elements like Fe or Mn in soils which appear to be consistent for several important heavy metals of environment concern. These authors warn that the use of a single element value may underestimate or overestimate the presence of metal contamination in soils since the binding action of structural or conservative elements (Fe, Al, Mn) are not considered.

Soils derived from basaltic materials contain large amounts of heavy metal (HM) concentrations (Kabata-Pendias and Pendias, 2001, Takeda et al., 2004). In the Canary Islands, reference values for trace metals have been derived for soils from natural ecosystems (Canarian Government); these values can be considered “Ambient Background Concentrations” or ABC values, since they were determined in soils distant from urban or industrial sources, in zones with low anthropogenic activity (McLaughlin et al., 2010). These large ABC values were consistent with the basaltic composition of the predominant rocks in the island. Some elements, however, presented concentrations exceeding the threshold values recommended by national and international organisms for certain soil use types and/or were not related to their lithogenic contents. This result could be explained by an allochthonous origin of contaminants. The Sahara is the most important source of dust to Canary Islands soils (Muhs et al., 2010). These authors showed that soil trace-element geochemistry was influenced by African dust. In the Island of Gran Canaria, Gelado-Caballero et al. (2012) found large enrichment factors for Zn and Cd during African dust outbreaks. The significance of dust deposits to Canarian soil ecosystems has been reviewed by von Suchodoletz et al. (2013) who underlined the transport of phosphorus (P). These authors suggested an increase of available P attributed to the accumulation of Saharan dust, unfortunately total P in soils and dust were not analysed in their study. Although desert

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dust appears as the most frequent source of P, high P concentrations are observed when the Saharan Air Layer is affected by emissions from open mines of P and P-based fertilizer industry and power plants from northern Africa (Rodríguez et al., 2011). Therefore, and considering the association between P and Cd and other trace elements in sedimentary rocks (Sauerbeck, 1993) and the large Cd concentrations of phosphate rock in northern Africa (UNEP, 2008), the probability of the allochthonous origin of Cd and other trace elements in the Canary Islands from Saharan aerosols is likely.

The aim of this work was to contribute to the knowledge of the anthropic and allochthonous origin of trace metals in the Canary Islands. To this end, the island of El Hierro was chosen because of its low anthropogenic influence; besides, the soils are low-weathered and the parent material is relatively homogeneous in terms of age and composition; therefore, the effect of the pedogenetic processes on the HM differential dispersion (Palumbo et al., 2000) is likely to be low. In order to test the hypothesis of the Cd origin from continental dust, different forms of phosphorus were determined.

The study area (300 to 1200 m a.s.l.) included the major natural pastures of the island, within which, the traditional pasture lands, former rainfed cultivated lands and shrub areas are found. Part of this zone was deforested after the Spanish settlement. Considering the large soil ABC values, plant sampling was also performed in the study zones in order to verify if plant composition was affected by such large concentrations. This study has an added interest since soils from the central plateau of the island, with highly favourable chemical and physical properties for plant growth, are transported to the lowlands for construction of terraces called "sorribas" for export crops. This is a common practice in the western, mountainous islands (Hernández-Moreno et al., 2007a). In the new, warmer environment, the soils are subject to irrigation and heavy fertilization, including some practices intending to acidify the soils (case of ananas). Therefore, this study may also provide a "starting point" for the appraisal of the HM potential hazards in intensively cultivated Andosols.

2. Materials and methods

2.1. The study area and samples

El Hierro (269 km^2) is the westernmost island of the archipelago and also the youngest one, about 0.8 Ma old; most of the island's surface is covered by relatively young material (<160 ka) with predominant basaltic composition (Carracedo et al., 2001). It is situated at a latitude between 27° 38′ and 27° 51′ N, with a maximum height of 1500 m a.s.l.. The climate of the island varies greatly depending on altitude, the orientation of the mountain systems, the influence of the trade winds. The north and northeast sides, which are influenced by the trade winds, have a humid and cool climate, whereas the south is more arid and hot. The bioclimatic characteristics of the island have been described by del-Arco et al. (1996, 1999). The soils of the island and their distribution have been studied by Padrón Padrón (1993). The recent basaltic materials and the climate features can explain the dominant soil types of the island: Andosols with more or less vitric character: Vitric and Silandic Andosols (IUSS Working Group WRB, 2007) and Vitrands and vitric sugroups of other Andisol greatgroups (Soil Survey Staff, 2010). The natural vegetation in the pasture areas at mid-high altitudes is arbustive shrubs and forage grasses and legumes. Sampling locations were selected so that the different climate zones (dry, semiarid and subhumid) and vegetation of the natural pastures and rainfed zones were represented; accordingly, four zones were defined: zone 1 (abandoned intensive cultivated area, dry), zone 2 (Nisdafe plateau, subhumid), zone 4 (La Dehesa, semiarid) and zone 3 which is a transition between zones 2 and 4. The sampling points were labelled with the corresponding zone numbers in Fig. 1. Soil samples were taken from the top 15 cm soil. The forage (shoots) sampling was done using a 25 cm diameter ring, thrown 3 times at random. In all, 53 sites were sampled (Fig. 1).

2.2. Soil analysis

Soil samples were allowed to air dry and were sieved to 2-mm mesh for laboratory analysis. Soil pH was measured in a 1:2.5 soil/water suspension (Chapman and Pratt, 1982). Soil organic carbon (SOC) and nitrogen were determined by dry combustion with a LECO CNS 2000 analyzer. Available nitrate was determined by extraction with 0.01 M calcium chloride of the 1:5 (soil to water ratio), and analysed by ionic chromatography. Available soil P was determined by sodium bicarbonate extraction, according to Olsen et al. (1954), noted Olsen-P. Exchangeable cations (K, Ca, Mg, and Na) were extracted with buffered 1 M ammonium acetate at pH 7, and were analysed by inductively coupled plasma optical emission spectrometry (ICP-OES). Andic properties (Soil Survey Staff, 2010) were determined in representative profiles of the four sampling zones: Oxalate-extractable Al, Fe, and Si and phosphate retention (ΔP) were determined according to Blakemore et al. (1981). The percentage of volcanic glass was determined in the 0.02- to 2-mm fraction, according to Eden (1988). These properties were determined in representative soil profiles in each of the studied zones. Soil bulk density was determined in all samples and was measured by obtaining undisturbed cored samples under field moisture conditions (Klute, 1986).

Major and trace elements soluble in aqua regia (AR) were analysed in Actlabs Laboratories (Ontario, Canada). Total P (fusion) analysis was also performed in these laboratories. The concentrations resulting from AR extractions are normally referred to as "pseudototal contents" (Gupta et al., 1996). The elements extracted with AR were noted with the AR- prefix, e.g., AR-Cu.

2.3. Plant analysis

Dry matter (DM) of plant samples was determined by drying in an oven at 60 °C to constant weight. Plant samples were subjected to microwave digestion with nitric acid. The following elements were analysed by inductively coupled plasma optical emission spectrometry (ICP-OES): P, K, Ca, Mg, Na, B, Cu, Fe, Mn, Zn and Cd.

2.4. Data analysis

Statistical analysis was performed using the package SPSS 17.0 for Windows (SPSS Inc.). Pearson correlations between trace and major elements were determined. One-way ANOVA was used to compare soil properties and AR-extracted elements between the four studied zones; differences between means were tested using LSD post-hoc tests with a level of significance $P < 0.05$

3. Results and discussion

3.1. Soil properties, element contents and associations

The summary statistics of relevant soil properties and heavy metal concentrations are listed in Table 1. Lead values were normally below the detection limit (<2 mg·kg^{-1}), and were not included in this table. Soil reaction ranged from slightly acidic to slightly alkaline, according to the limited soil development and type of parent materials. Andic properties of the selected profiles generally coincided with the soil distribution types reported by Padrón Padrón (1993). Silandic Andosols were more frequent in the Nisdafe plateau (Zone 2), which can be related to a more humid regime. Average bulk density was 0.95 t m^{-3}, which exceeded slightly, but significantly, the density values of the natural soils of the zone, probably due to soil management practices. The heavy metal concentrations obtained did not show significant differences with the soil ABC values reported by the Canarian Government.