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Heavy metals of Santiago Island (Cape Verde) top soils: Estimated Background Value maps and environmental risk assessment

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ABSTRACT

In this work we present maps of estimates of background values of some harmful metals (As, Cd, Co, Cr, Cu, Hg, Mn, Ni, Pb, V, and Zn) in the soils of Santiago Island, Cape Verde, analyse their relationships with the geological cartography, and assess their environmental risks. The geochemical survey (soil sampling at a spatial resolution of 3 sites per 10 km^2, sample preparation, geochemical analysis, data treatment, and mapping) was conducted following the guidelines proposed by the International Projects IGCP 259 and IGCP 360. The concentration of the selected elements was determined in the fraction <2 mm. Each sample was digested with aqua regia and analysed by ICP-MS.

The Estimated Background Value spatial distributions of the studied metals are found to be strongly linked to the geological cartography. These links are identified by a direct comparison of the geochemical maps with the geological cartography, and confirmed by either simple statistics and a Principal Component Analysis. The metals with higher loadings in the first Principal Component, Ni, Cr, Co, Cu, and V, clearly show the influence of a lithology rich in siderophile elements, typical of basic rocks and of its related minerals. The elements with higher loadings in the second Principal Component, Mn, Zn, Pb, As, Hg, and Cd, are chalcophile elements, except for Mn, but an anthropogenic contamination for these elements cannot be discarded.

We propose an index to numerically access the environmental risk of one element, which we denominate by Environmental Risk Index, and a Multi-element Index which is simply the average taken over all elements. The occurrence of values greater than 1 in the maps of the Environmental Risk Index shows where the content of the respective element is above the permissible levels according to the available legislation for agricultural and residential purposes. The same applies to the multi-element risk index maps. High values of these risk indices are found, both for agricultural and residential purposes, for Co, Cr, Ni, Cu, and V. These metals are precisely those with higher loadings in PC1, which are demonstrated to be of natural origin in Santiago. This behaviour is also shown in the Multi-element Environmental Risk maps computed with these five metals. The high natural concentration levels of heavy metals at some areas of Santiago should be of concern not only to scientists but also to policymakers. To further evaluate the environmental risks associated with the presence of these metals, their bioavailability should be assessed in future works.

1. Introduction

National geochemical surveys have been a priority in many countries given the importance and applicability of the resulting geochemical databases (Johnson et al., 2005; Garret et al., 2008; Smith and Reimann, 2008). These surveys provide the natural state of the environment (Appleton and Ridgway, 1993; Xie Xuejing et al., 1997; Tarvainen, 1997; Reimann and Caritat, 1998; Lech and Caritat, 2007; Salminen et al., 2005; Inácio et al., 2008) and allow the discrimination between geogenic sources and anthropogenic pollution (Darnley and Garrett, 1990; Darnley et al., 1995; Plant et al., 2001; Albanese et al., 2007) which is useful for mineral exploration (Levinson, 1974; Beus and Grigorian, 1977), agriculture (Reimann et al., 2003), geomedicine (Zatta et al., 2003; Komatina, 2004), and other fields. Initially, geochemical maps were used for mineral exploration and, therefore, were elaborated at high sample

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densities (from 1/1 km^2 to 1/25 km^2). Latter, in the late 1960s, the first national low-density geochemical survey was conducted in Africa, with a sampling density of 1/200 km^2. National and even continental surveys conducted in various parts of the world had, generally, sample densities ranging from 1/300 km^2 to 1/18,000 km^2 (Smith and Reimann, 2008).

Maps of baseline values are especially important in countries like Cape Verde, where intervention limits for soils are not yet established. Cabral Pinto (2010) conducted a high-density (aprox. 1/3 km^2) geochemical survey in Santiago Island, Cape Verde archipelago, and compiled the first environmental geochemical atlas for that region. The field work occurred from 2005 till the begin of 2008, over six champagnes.

Regional and national geochemical surveys usually include the construction of geochemical maps for the soil medium. Soils have a very important role in the environment as they are simultaneously a sink and reactor of various types of pollutants, which makes them also a source of pollutants for other ecosystems such as groundwater and crops which, in turn, affect public health. Among the soil pollutants, heavy metals and metalloids are especially dangerous due to their toxicity and persistence in the environment and, even, in the human body. Most studies of the geochemistry of heavy metals/metalloids have been conducted in urban environments, where the sources of contaminants in soils have strong anthropogenic origin, such as traffic emissions, industrial waste, residential activities (Manta et al., 2002; Lee et al., 2006; Rawlins et al., 2006; Zhang, 2006; Luo et al., 2007; Chen et al., 2008; Shi et al., 2008). Other works (Chen et al., 2009; Qishlaqi et al., 2009; Yang et al., 2009) were carried out at non-urban areas in order to evaluate soil contamination caused by agricultural activities.

A reliable geochemical baseline can only be established if pristine soil sites are sampled. The human influence was very limited in the Cape Verde archipelago when the Cabral Pinto (2010) survey was conducted, when compared to developed countries. However, cities and traffic are expanding and tourism-related structures, such as international airports and tourist villages, were built, namely in Santiago Island where the capital of the country is located. Thus, the input of pollutants from human activities may have been leading to the contamination of the Santiago soil environment since then, and so it will be increasingly difficult to get pristine soil sites in the future. These arguments demonstrate the importance of the geochemical database provided by Cabral Pinto (2010).

Using the data of Cabral Pinto (2010), Cabral Pinto et al. (2012) reported the mineralogy of Santiago soils, presented the soil cartography, proposed baseline values for some chemical elements, and calculated the enrichment in metal content of Santiago soils relatively to the upper crust reference values. The authors showed that Santiago soils are dominated by primary silicate minerals such as feldspar, pyroxene, and olivine, while the main secondary minerals are phyllosilicates (smectite, kaolinite, mica/illite), calcite, hematite and also quartz. Furthermore, they also found leucite, apatite, nepheline, magnetite, titanomagnetite, ilmenite, chromite, garnet, zeolites, siderite, opal, barite, sphene, zircon, halite, aragonite, dolomite, brucite, and chlorite. Cabral Pinto et al. (2012) also argue that the mineralogical composition of Santiago soils is primarily governed by the mineralogy of the bedrock, climatic conditions (precipitation, temperature, and wind direction) in conjunction to the topography. Chemical weathering is not so intense in Santiago, due to the semiarid climatic conditions and the vigorous relief. The soil mineralogy is a combination of minerals inherited from the original lithology, minerals resulting from the alteration of these primary minerals, some of them associated with pedogenic soil processes (hematite, phyllosilicates, and calcite), and probably also wind-transported minerals, mainly from the Sahara Desert (quartz, phyllosilicates).

In the present paper we use the geochemical database provided by Cabral Pinto (2010) and present baseline value maps, referred to as Estimated Background Value (EBV) maps of As, Cd, Co, Cr, Cu, Hg, Mn, Ni, Pb, V, and Zn, which are potentially harmful elements to human health, delineate their main sources, and relate them with the geology of the island. Furthermore, we assess the environmental risk of these potentially toxic elements using an index, proposed herein, that numerically evaluates the enrichment of the concentration of each metal relative to permissible levels defined by the Canadian legislation for agricultural and residential purposes. We denominate this index as Environmental Risk Index (ERI). After mapping the agricultural and residential ERI for each metal, we assess the potential risk of all the studied elements by mapping the agricultural and residential Multi-Element ERI (ME-ERI) which are simply the average of the ERIs taken over all elements.

The layout of this works is as follows. After describing the general geography and lithology of Santiago Island in Section 2, the experimental procedure followed in the geochemical survey of Cabral Pinto (2010) is summarised in Section 3. Section 4 presents the analytical and statistical analysis used to obtain the results of this work: the EBV fields, their relationship with the geological cartography, and the agricultural and residential ERI and ME-ERI maps. Finally, the major conclusions are summarised in Section 5.

2. Cape Verde archipelago and Santiago Island: location and geology

2.1. Settings of the archipelago of Cape Verde and Santiago Island

The archipelago of Cape Verde is located at the eastern shore of the Atlantic Ocean, 500 km west from Senegal's Cape Verde, in the African western shore, that names the archipelago, between the latitudes of 17°13′N (Santo Antão Island) and 14°48′N (Brava Island) and the longitude of 22°42′W (Boavista Island) and 25°22′W (Santo Antão Island) (Fig. 1). It is composed by 10 islands (Fig. 1), nine of them inhabited, with land areas that vary from 35 km^2 (Santa Luzia Island, uninhabited) to 991 km^2 (Santiago Island). According to INE (2010, see www.ine.cv) over half the population lives in Santiago Island (273,919 habitants).

Santiago Island is located in the southern part of the archipelago (Fig. 1) and is the biggest island of the Archipelago, representing 25% of the entire land area. It is elongated in the NNW–SSE direc-

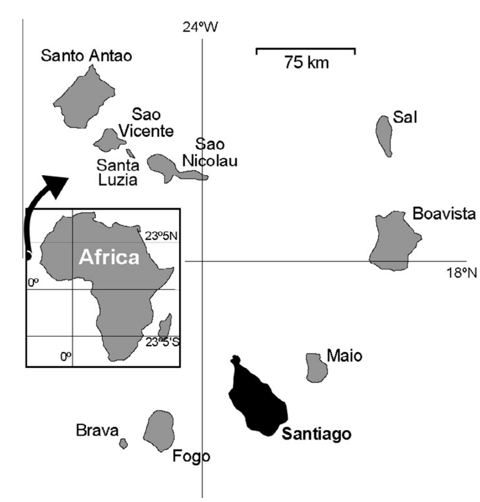

Fig. 1. The Cape Verde Archipelago and its location in Africa's western coast.