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Baseline Levels of Metals in Volcanic Soils of the Azores (Portugal)

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Data on metal concentrations present in the soils of the Azores (Portugal) are scarce. The goal of this study was to measure the current levels of several metals in the top horizon of soils of two areas, distinguishable by their volcanic activity and physical characteristics, in order to establish some baseline concentrations of these elements. Soil samples were taken in similar ways from five sites in a volcanically active area and another five sites in an area without volcanic activity. Particle-size fractions, % organic matter, moisture content, pH, and major and trace elements compositions were measured. In general, the concentrations of trace metals in the soils from Santa Maria (inactive volcanism) were higher than those from Furnas (active volcanism), with the exception of Zn. The soils from Furnas, which have slightly lower pH and less % clay-silt than Santa Maria, will probably make such trace metals as Zn become more readily bioaccessible, and therefore pose a larger threat to living organisms inhabiting these soils.

Keywords Azores, trace metals, volcanic soils, volcanism

Introduction

Volcanism, which is evidence of the Earth's internal dynamic behavior, is one of the most powerful geological phenomena, and has a large range of associated processes such as lava emissions, diffuse degassing from soils, and hydrothermal activity. Rocks and volatiles of volcanic origins are responsible for the presence of metals in soils and waters (Aiuppa *et al.*, 2000; Cruz *et al.*, 1999; Ferreira and Oskarsson, 1999; Kelepertsis *et al.*, 2001), since diffusion of acidic volcanic gases through water permeable rocks contributes to the hydrological material transfer in volcanic strata (Cruz *et al.*, 1999). Volcanic activity is responsible for the release of metals such as arsenic (As), mercury (Hg), aluminum (Al), rubidium (Rb), lead (Pb), magnesium (Mg), copper (Cu) and zinc (Zn), among others (Delmelle and Stix, 2000; Durand *et al.*, 2004).

Some of the reasons why volcanic regions are important scenarios for the study of heavy metal contents in soils and the effects of those on living organisms are: (1) they are densely inhabited in some areas of the Earth; and (2) soils effectively retain chemicals acting as a reservoir affecting agriculture. Thus, factors controlling the total and bioaccessible concentrations of heavy metals in soils are of great importance for human toxicology and agricultural productivity (Alloway, 1995).

The Azores archipelago is made of nine islands, located in the North Atlantic Ocean between 36°45′–39°43′ N and 24°45′–31°17′ W (Figure 1), near the triple junction of Eurasian, African and North American plates. Therefore, the archipelago has a complex

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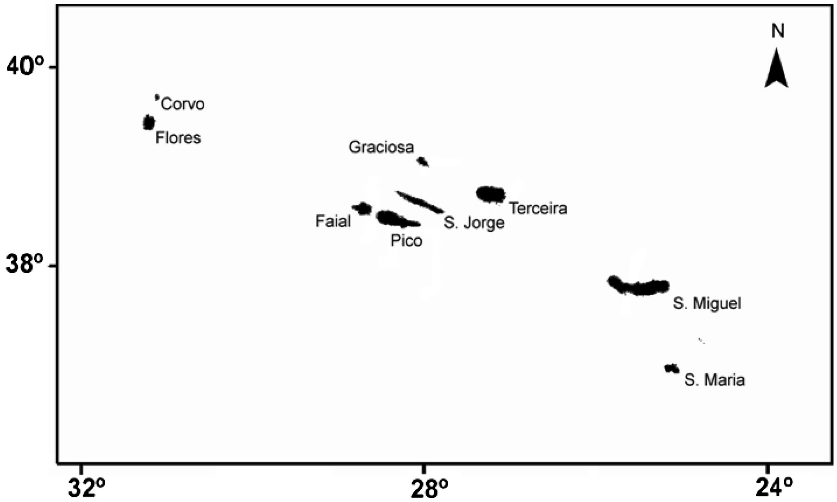

Figure 1. Location of the Azores archipelago in the North-Atlantic Ocean.

tectonic setting, where seismic-volcanic phenomena are common (Lourenço *et al.*, 1998; Nunes *et al.*, 1993). The Azores climate can be considered as oceanic temperate, with annual temperatures between 16.7°C (Terceira island) and 17.5°C (Santa Maria island), and humid, with relative humidity between 77% (Santa Maria island) and 82% (Terceira island). Precipitation increases from east to west, with average annual values of 775 mm in Santa Maria island (1961–1990) and 1716 mm in Flores island (1970–1990), and in altitude, with a 25% increase *per* 100 meters (e.g., Furnas in São Miguel island: 2252 mm) (Mata, 2001). São Miguel and Santa Maria are the two most eastern islands of this archipelago, and the latter is the oldest of all nine.

São Miguel, which is the largest island (757 km^2), has its geology dominated by three volcanic cores that correspond to the major active trachytic central volcanoes of Sete Cidades, Fogo, and Furnas, linked by rift zones. Their activity, throughout the last 5,000 years, is revealed by 57 volcanic eruptions, resulting in the production of over 4.6 km^3 of dense rock, and the current hydrothermal manifestations that occur mainly in the Fogo and Furnas volcanoes (Booth *et al.*, 1978; Cruz, 2003). Furnas is the easternmost of the three active volcanoes on the island of São Miguel. The Furnas volcano has an older caldera of about 7 × 5 km and with a 290-m-depth depression, enclosing a younger caldera, with a diameter of approximately 5 km, where two subsidence events took place in the last 5,000 years (Guest *et al.*, 1999). This explains the origin of the depressions where the Furnas village (Booth *et al.*, 1978) and the Furnas lake are found today (Zbyszewski, 1961). The growth of the Furnas central volcano started about 100,000 years ago, mainly as a result of eruptions of trachytic pumice. The last eruption at Furnas that occurred in the southern part of the caldera is dated at 1630 A.D. and had an explosive phase that produced a tuff/pumice ring complex (Cole *et al.*, 1995). Nowadays, Furnas presents active fumaroles and sulfataras. Santa Maria, one of the smallest islands (92 km^2), is also rural but, in contrast, has had no volcanic activity since approximately 3 million years ago (Feraud *et al.*, 1984). Soils in Furnas are mainly Udivitrands and the soils prevailing in Santa Maria are Dystrudepts. Udivitrands are the more or less well-drained and coarse-textured Andisols that have a udic moisture regime. These are relatively young soils that occur mostly near volcanoes. Dystrudepts are the acid and more or less drained Inceptisols with a udic or perudic moisture regime. The parent materials generally are acid, moderately or weakly consolidated sedimentary or metamorphic rocks, or acid sediments (Soil Survey Staff, 1999).

The present content of trace elements in the Azorean soils has not been fully studied. Thus, this study was undertaken to determine some baseline levels of trace elements in soils with different ages from active and inactive volcanic sites from the Azores archipelago, and to provide support information for future assessment purposes for bioindicators and biomarker studies regarding agricultural and public health interests.

Material and Methods

Soil Sampling and Analysis

Soil samples were collected from five sites in Furnas (A, B, D, E, R) and five sites in Santa Maria (C, G, H, I, S) in similar ways (Table 1). In each site samples were taken at two depths (0–30 and 30–60 cm). Samples were thoroughly mixed, air-dried and lightly crushed prior to the determination of particle-size fractions, organic matter (OM), pH-(H_2O), and major and trace elements. Particle-size fractionation was carried out by wet sieving, with an aperture lower than 63 μm, and simply separating two fractions, sand and clay-silt. The soil OM content was determined using hydrogen peroxide wet oxidation method (LNEC, 1967a). A WTW-pH 531 electrode was used to measure the soil pH in water (soil:water = 1:25 g.g^{-1}). The samples were stirred by hand several times. After one day, equilibrium was assumed and the pH was measured (LNEC, 1967b). Major element (SiO_2, Al_2O_3, Fe_2O_3, MnO, CaO, Na_2O, K_2O, TiO_2, P_2O_5) and trace element (Cd, Cu, Ni, Pb, Zn, Cr, Co, and S) content of soils was determined, respectively, by lithium metaborate/tetraborate fusion ICP and ICP/MS (Actlabs, Canada).

Table 1
Specific coordinates of sampling stations

	Coordinates	
Sampling stations	N	W
Furnas		
A	37° 46′ 20″	25° 18′ 08″
B	37° 46′ 05″	25° 19′ 10″
D	37° 46′ 09″	25° 18′ 58″
E	37° 46′ 19″	25° 18′ 36″
R	37° 46′ 09″	25° 18′ 18″
Santa Maria		
C	36° 58′ 11″	25° 09′ 25″
G	36° 59′ 40″	25° 06′ 29″
H	36° 57′ 38″	25° 03′ 26″
I	36° 57′ 26″	25° 06′ 19″
S	36° 59′ 55″	25° 04′ 24″

Statistical Analyses

Differences in element concentrations and between depths were examined by a one-way ANOVA, which produces a one-way analysis of variance for a quantitative dependent variable by a single factor variable and is used to test the hypothesis that several means are equal (Sokal and Rohlf, 1995) and considered significant when $p \leq 0.05$. Pearson correlations between physico-chemical properties and metal contents in soils were determined using the statistical package SPSS 11.5 (SPSS Inc.).

Results

Between Furnas and Santa Maria the soils analyzed did not differ significantly in pH and OM. However, they differed significantly in the percentage of clay-silt fraction (ANOVA, $p \leq 0.01$) and moisture content (Table 2).

The average concentrations of Al_2O_3, Fe_2O_3, MgO, TiO_2, Cu, Ni, Cr, Co (ANOVA, $p \leq 0.01$), and P_2O_5 in the soils from Santa Maria were significantly higher than in Furnas. In contrast, the concentrations of SiO_2, Na_2O, K_2O (ANOVA, $p \leq 0.01$), and Zn were significantly higher in Furnas than in Santa Maria (Tables 3 and 4).

The metals Cu, Ni, Cr, and Co were significantly and positively correlated ($p \leq 0.05$) to the % clay-silt present in the soils, while Zn showed the opposite behavior.

Table 2
Some physico-chemical properties of the analyzed soils

		%		
Soil	pH (H_2O)	OM	Clay-silt	Moisture
Furnas				
A (0–30 cm)	5.7	1.42	30.88	31.78
A (30–60 cm)	5.5	0.25	29.78	34.19
B (0–30 cm)	6.4	1.33	36.70	40.67
B (30–60 cm)	6.5	0.34	21.19	51.44
D (0–30 cm)	6.1	1.40	64.94	30.78
D (30–60 cm)	5.9	1.23	66.96	34.95
E (0–30 cm)	6.1	7.11	25.57	50.99
E (30–60 cm)	6.2	0.39	37.25	36.80
R (0–30 cm)	8.6	1.27	11.03	23.71
R (30–60 cm)	8.0	1.59	20.14	31.05
Santa Maria				
C (0–30 cm)	6.9	1.62	79.79	17.72
C (30–60 cm)	7.1	1.69	63.29	21.77
G (0–30 cm)	4.2	3.11	93.57	33.77
G (30–60 cm)	4.5	1.92	92.49	34.09
H (0–30 cm)	6.0	2.08	14.61	31.03
H (30–60 cm)	6.0	1.27	88.09	30.21
I (0–30 cm)	8.3	0.92	72.63	23.23
I (30–60 cm)	6.3	0.11	86.19	29.25
S (0–30 cm)	6.5	2.57	85.70	28.75
S (30–60 cm)	6.6	1.58	86.75	30.26

Table 3

Major element concentrations of the analyzed soils [n.d. = not detectable]

	%									
Soil	SiO_2	Al_2O_3	Fe_2O_3	MnO	MgO	CaO	Na_2O	K_2O	TiO_2	P_2O_5
Furnas										
A (0–30 cm)	59.25	17.17	4.24	0.21	0.46	0.91	5.44	5.34	0.68	0.16
A (30–60 cm)	60.67	17.03	4.36	0.21	0.47	0.96	5.73	5.40	0.69	0.14
B (0–30 cm)	54.45	14.99	8.79	0.22	0.74	1.70	4.95	4.72	0.89	0.34
B (30–60 cm)	55.81	15.35	9.68	0.19	1.14	2.26	4.96	4.69	1.17	0.42
D (0–30 cm)	48.89	13.87	4.80	0.19	1.41	2.94	4.56	3.96	1.09	0.32
D (30–60 cm)	57.88	15.76	4.30	0.20	0.93	1.77	5.83	4.98	0.87	0.24
E (0–30 cm)	56.46	17.08	6.53	0.25	0.45	1.00	5.40	4.79	0.69	0.42
E (30–60 cm)	59.96	17.10	4.22	0.25	0.43	0.93	5.94	5.19	0.64	0.16
R (0–30 cm)	58.21	16.03	4.57	0.19	1.02	2.26	5.83	5.21	0.95	0.19
R (30–60 cm)	60.43	16.66	4.38	0.18	0.75	1.62	6.11	5.44	0.88	0.16
Santa Maria										
C (0–30 cm)	46.47	13.98	11.83	0.63	6.32	8.37	2.46	1.46	2.45	0.37
C (30–60 cm)	47.63	14.35	10.90	0.82	5.80	7.82	2.22	1.74	2.53	0.32
G (0–30 cm)	31.50	24.88	17.48	0.23	0.78	0.11	0.14	0.34	4.16	0.33
G (30–60 cm)	30.35	24.60	22.07	0.16	0.91	0.02	n.d.	n.d.	4.83	0.45
H (0–30 cm)	33.58	21.16	19.13	0.24	3.04	2.19	0.30	0.33	3.84	0.66
H (30–60 cm)	33.95	21.21	19.31	0.23	2.96	2.06	0.23	0.31	3.76	0.68
I (0–30 cm)	38.62	16.59	12.30	0.30	3.22	8.40	1.43	1.48	2.63	0.22
I (30–60 cm)	43.45	17.57	10.91	0.14	3.44	6.81	1.57	1.61	3.02	0.19
S (0–30 cm)	33.20	22.29	17.56	0.20	1.13	1.07	0.30	0.65	3.42	0.60
S (30–60 cm)	31.74	22.86	19.64	0.17	1.09	1.01	0.10	0.41	3.74	0.58

Between the two depths (0–30 and 30–60 cm) the soils analyzed did not differ significantly in any of the parameters.

Discussion

When comparing the moisture in the soils of Furnas and Santa Maria one verifies that the registered differences are mainly a result of the differences in precipitation regimes, i.e., 2252 mm of rain in the former against 775 mm in the latter, which may be one of the reasons for the observed dissimilarity. Another significant difference between physico-chemical properties of soils from Furnas and Santa Maria is the high % clay-silt content of the latter. This suggests a longer history of pedogenesis for the Santa Maria soils. Along with higher levels of clay-silt, Santa Maria soils also showed higher levels of Fe oxides than Furnas soils. Previous studies showed that young soils dominate in Furnas (Pinto Ricardo *et al.*, 1977) while older and clayish soils are dominant in Santa Maria (Madeira, 1981). This is compatible with the interval between the last eruption in Furnas (1630 A.D.) and Santa Maria (3 million years ago). According to Malucelli *et al.* (1999), a long history of pedogenesis may be inferred from a high mean content of clay and Fe oxides.

In general, the concentrations of major and trace elements in Santa Maria soils were higher than those of Furnas, with the exception of SiO_2, Na_2O, K_2O, and Zn. In the case

Table 4

Trace element concentrations of the analyzed soils [n.d. = not detectable]

	ppm							S
Soil	Cd	Cu	Ni	Pb	Zn	Cr	Co	%
Furnas								
A (0–30 cm)	n.d.	25	7	17	198	n.d.	2	0.09
A (30–60 cm)	n.d.	20	3	21	163	n.d.	2	0.13
B (0–30 cm)	n.d.	29	8	22	139	n.d.	3	0.03
B (30–60 cm)	n.d.	21	20	16	139	51	6	0.02
D (0–30 cm)	n.d.	23	18	24	133	55	5	0.06
D (30–60 cm)	n.d.	21	9	29	160	26	4	0.03
E (0–30 cm)	n.d.	58	13	83	258	20	4	0.04
E (30–60 cm)	n.d.	18	6	9	174	22	2	0.06
R (0–30 cm)	n.d.	18	18	11	144	40	5	0.01
R (30–60 cm)	n.d.	18	7	20	141	28	4	0.03
Santa Maria								
C (0–30 cm)	n.d.	66	233	74	197	850	96	0.04
C (30–60 cm)	n.d.	54	222	46	137	791	111	0.02
G (0–30 cm)	n.d.	99	411	40	102	820	46	0.06
G (30–60 cm)	0.8	117	483	38	106	975	53	0.06
H (0–30 cm)	n.d.	106	378	33	132	884	48	0.03
H (30–60 cm)	n.d.	107	379	30	121	893	66	0.02
I (0–30 cm)	n.d.	36	168	30	84	667	86	0.04
I (30–60 cm)	0.7	32	146	22	72	734	13	0.03
S (0–30 cm)	n.d.	70	197	43	145	784	40	0.05
S (30–60 cm)	0.6	64	204	43	123	958	41	0.04

of Cu, Ni, Cr, and Co, Santa Maria soils presented levels also much higher than some American, Chinese and Turkish soils (Holmgren *et al.*, 1993; Hseu *et al.*, 2002; Tsai *et al.*, 2002; Turkdogan *et al.*, 2002; Senwo and Tazisong, 2004). This may be related to the higher capability of Santa Maria soils, which are richer in fine grain size particles, to retain those elements, as suggested by the positive correlation between % clay-silt and those metals. This behavior is similar to the prodelta facies (silty clay and clayey silt) of the Yangtze estuary, which acts as a depositional sink for heavy metals (Chen *et al.*, 2004). According to Hooda and Alloway (1998), a soil with large amounts of clay has a greater metal sorption capacity and vice versa. The concentrations of Zn found in the soils of Furnas were higher than those of a volcanic region in Turkey (Turkdogan *et al.*, 2002) and were also similar to or higher than the permissible values established for European Union soils (Council of the European Communities, 1986) and mean level found in United States industrial/residential soils (Agency for Toxic Substances and Disease Registry, 1994) and in the vicinity of a Russian metallurgical factory (Van Straalen et al., 2001).

In summary, the Furnas and Santa Maria soils differed not only in age but also in particle size and in the amount of major and trace elements retained, making bioavailability different. Thus, elements such as trace metals will probably be more easily bioaccessible in the soils of Furnas, which is volcanically active. This is because inputs of metals to the soils are ongoing from fumaroles, sulfataras, and degassing and with soil pH reaching lower values than in the soils of Santa Maria, which is volcanically inactive and where higher adsorption rates occur. Based on this study and/or others, bioavailability studies need to be conducted in order to know if the levels of metals found in the present soils may pose any hazard to living organisms, especially humans, inhabiting the studied areas.

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