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ORIGINAL PAPER

Natural concentrations and reference values for trace elements in soils of a tropical volcanic archipelago

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Abstract Fernando de Noronha is a small volcanic archipelago in the Southern Atlantic, some 350 km NE of the city of Natal in NE Brazil. These remote volcanic islands represent a largely pristine environment, distant from sources of anthropogenic contamination. This study was carried out to determine the natural concentrations of Ag, Ba, Cd, Co, Cr, Cu, Mo, Ni, Pb, Sb, V and Zn in the A and B horizons of soils of Fernando de Noronha. The aims of the study were twofold: determine whether there is a relationship between the bedrock geology and soils and to establish quality reference values for soils from Fernando de Noronha. Soil samples were subjected to acid digestion by the USEPA method 3051A, and metals were determined by inductively coupled plasma emission spectrophotometry. The results showed that the trace element distribution largely reflects the geochemistry of the underlying volcanic rocks of the Remedios and Quixaba Formations. The results demonstrate that the concentrations of Ba, Cr, Zn, Ni and Cu from the soils of the volcanic Fernando de Noronha archipelago are higher than those found in soils from continental Brazil. However, concentrations of Ni, Cu and Co are lower in soils of the archipelago as compared to other volcanic islands throughout the world. The elevated trace element concentrations of the volcanic parent material of Fernando de Noronha soils seem to be the main factor governing the relatively high natural concentrations of trace elements.

Keywords Heavy metals · Volcanic soils · Soil contamination · Soil pollution · Volcanic island

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Introduction

Volcanism is an evidence of the earth's internal dynamic behavior and represents one of the most powerful geologic phenomena. Rocks and volatiles originating from volcanic activities are responsible for adding trace elements in soils and waters (Kelepertsis et al. 2001; Amaral et al. 2006; Doelsch et al. 2006). Volcanoes emit pyroclastites of which the ash is responsible for the transport of environmentally significant elements such as As, Hg, Ni, Cr, Pb, Zn, Cu, Sb, Mn and Cd over long distances (Gondal et al. 2009; Duplay et al. 2014). Some of the reasons why volcanic regions are important settings to trace element studies in soils are: (1) They cover more than 124 million hectares of the earth's surface and are densely populated in some of these areas; (2) they are generally rich in trace elements and plant nutrients therefore pose great importance to both human toxicology and agricultural production (Alloway 1990).

Despite their importance, very few studies have focused on the concentration or distribution of trace elements in soils formed from volcanic parent material (Doelsch et al. 2006; Mendoza-Grimón et al. 2014; Cabral Pinto et al. 2015). Soils formed from highly weathered basaltic lava in Hawaii presented high concentrations of Cr, Cu, Ni and Zn (Burt et al. 2003). Likewise, volcanic soils from Japan (Takeda et al. 2004), La Reunión (Doelsch et al. 2006), and El Hierro, Spain (Mendoza-Grimón et al. 2014), have found to be rich in these trace elements. These high values are mainly due to the large amounts of trace elements found in soils derived from basaltic materials (Alloway 1990; Kabata-Pendias and Pendias 2000).

The volcanic archipelago of Fernando de Noronha is located in the South Atlantic at 3°51′S and 32°25′W. The exposed parts of the archipelago cover a total area of 26 km^2, consisting of the main island of Fernando de Noronha and more than 20 smaller islands. The archipelago is situated some 350 km NE of the city of Natal in NE Brazil far away from any sources of anthropogenic contamination, numbers roughly 2500 inhabitants. The whole archipelago is mostly a natural reserve oversighted by the Brazilian Environmental Agency (IBAMA); hence, there are no mining or industrial activities in the islands and the only relevant economic activity is ecologically friendly tourism. Thus, this largely unaltered environment poses an ideal setting for studying the relationships between parent material and soils, as well as conducting reference studies to measure the natural concentrations of elements in volcanic soils.

The Fernando de Noronha Archipelago is part of oceanic volcanic islands in NE Brazil. These islands are the emerged portions of a volcanic range that developed along an east–west submarine ridge, the Fernando de Noronha Ridge, which likely outlines the westward motion of the South American plate over a fixed 'hotspot' (Morgan 1983; Mizusaki et al. 2002; Almeida 2006; Perlingeiro et al. 2013). The volcanic rocks on Fernando de Noronha have been dated by Cordani (1970), Cordani et al. (2003) and Perlingeiro et al. (2013). The age of the two most widespread rock formations, Remedios and Quixaba Formations, spans from 12.5 to 1.3 million years (Ma). The volcanic Remedios Formation, made up of highly alkaline pyroclastics, intruded by phonolitic–trachytic domes, dikes and plugs, underly the central part of the island. The geochemistry of the main rock types of Fernando de Noronha are described by Almeida (1955, 2002), Ulbrich and Ruberti (1992), Ulbrich (1993), Ulbrich et al. (1994), Weaver (1990) and Horota and Wildner (2011). The age of volcanic rocks of the Remedios Formation ranges from 12.5 ± 0.1 to 9.4 ± 0.2 Ma (Perlingeiro et al. 2013). The volcanic rocks of the Quixaba Formation, made up of dark ferromagnesian, silica-undersaturated melanephelinite and ankaratritic flows and pyroclastics of the same composition lasted from 6.2 ± 0.1 to 1.3 ± 0.1 Ma (Perlingeiro et al. 2013). The melanocratic volcanic rocks of the Quixaba Formation are found mainly on the two plateaus in the eastern and western parts of the island.

Trace elements in soils can have a natural or anthropic origin. Their natural occurrence is due to the chemical composition of rocks and the precipitation of particulate matter present in the atmosphere. Anthropogenic sources are generally related to mining, industrial and agricultural activities, as well as to the indiscriminate disposal of industrial and domestic waste. As Fernando de Noronha is a largely unaltered archipelago, the concentrations of these elements in soils reflect the chemical composition of the geological source material and are dependent on the pedogenesis as well as the degree of soil development (Oliveira et al. 2011a; Biondi et al. 2011a).

Environmental contamination is a widely discussed geochemical topic. However, management policies for contaminated areas require prior local information, such as the concentrations of the substances naturally found in soil. Thus, the establishment of reference values allows verifying the level of contamination in soils. The reference values are known by different names in different countries. The Brazilian Council for the Environment (CONAMA 2009) subdivided these values into three categories: quality reference value (QRV) which refers to the natural content of trace elements in soil, with no interference of anthropogenic activities; investigation value (IV) which refers to the value above which there is a potential risk to human health and is based on a risk analysis considering the maximum acceptable dose absorbed by the body; and prevention value (PV) which indicates the maximum metal concentration in soil without compromising its functions, which is intermediate between QRV and IV. The establishment of guiding values provides decision-makers with assessment tools on natural background information and gives guiding tools for possible restoration of areas contaminated by trace elements.

In order to collect geochemical data on trace elements for the Fernando de Noronha Archipelago and to provide background concentrations of metals in volcanic-derived soils in a tropical environment, the aims of the study were: (1) to determine the natural concentrations for Ag, Ba, Cd, Co, Cr, Cu, Mo, Ni, Pb, Sb, V and Zn on soils of this remote oceanic archipelago, (2) to study and correlate the metals concentration in the soils with the geochemistry of the geological parent materials and (3) to calculate the QRV of metals in order to support the monitoring of potentially contaminated soils in this environmentally protected area.

Materials and methods

The Fernando de Noronha archipelago is situated some 350 km NE of the Brazilian coast far away from any sources of anthropogenic contamination (Fig. 1). The soils of the archipelago cover three soil groups (FAO 1998): Neosols, Cambisols and Vertisols (Ribeiro et al. 2005). The Neosols are related to strongly sloping hillside areas or dunes and beaches formed by marine sediments. The Cambisols occur in well-preserved positions of the plateau, near watersheds or in the lower third of hills, at various topographic levels. The Vertisols are associated with depressions and imperfectly drained areas (Marques 2004) and are mostly underlain by easily weatherable pyroclastic rocks of the Remedios Formation. The volcanic geological parent materials, with exceptions for small areas where marine sediments occur, form a unique geological zone in Brazil.

Soil samples were collected from the A and B horizons of eight soil profiles from Fernando de Noronha Island covering two out of the three soil orders found in the archipelago. The samples were allowed to air dry and were passed through a 2-mm sieve for soil analysis using standard methods (EMBRAPA 2009). Soil pH was measured in a 1:2.5 soil/water suspension. Contents of exchangeable P, Na and K were obtained by Mehlich-1 extracting solution (HCl 0.05 mol L^{-1} + H_2SO_4 0.0125 mol L^{-1}) followed by colorimetry and flame photometry determination, respectively. Calcium, Mg and Al were extracted using a KCl 1 mol L^{-1} followed by titration measurement. Soil organic carbon (SOC) was measured using the Walkley–Black method by volumetric titration using ammonium ferrous sulfate. The soil particle-size distribution was determined using Bouyoucos hydrometer method. Information regarding the soil order, parent material and location, as well as the soils chemical and physical characterization is provided in Tables 1 and 2, respectively.

The soil samples were digested according to the method 3051A (USEPA 1998) to measure the environmental available concentrations. One gram of a macerated and sieved soil sample (0.03 mm) was transferred to Teflon tubes into which 9 mL HNO_3 and 3 mL HCl (high-purity Merck acids) were added. The tubes were kept in a microwave oven (Mars Xpress, CEM Corporation) for a period required for the equipment to reach 175 °C. After cooling, the extracts were transferred to 25 mL certified flasks (NBR ISO/IEC), filled with distilled water and filtering through a slow paper filter (Marcherey-Nagel®).

The digestions were performed in triplicate. Analysis quality control was carried out by using a NIST (National Institute of Standards and Technology, USA)-certified soil sample (SRM 2709—San Joaquin Soil Baseline trace element concentrations). The percentage recovery of trace elements in the certified sample was as follows: Ag (64), Ba (99), Cd (88), Cr (102), Cu (101), Mo (80), Ni (86), Pb (96), Sb (89), V (94) and Zn (101). The metals were determined by inductively coupled plasma atomic emission spectroscopy (ICP-OES/Optima 7000, PerkinElmer) with dual mode of observation (axial and radial) and a solid-state detector. The detection limits were 0.003, 0.0003, 0.004, 0.0002, 0.0002, 0.0009, 0.002, 0.0004, 0.001, 0.004, 0.0001 and 0.0002 mg L^{-1} for Ag, Ba, Cd, Co, Cr, Cu, Mo, Ni, Pb, Sb, V and Zn, respectively.

The data were subjected to descriptive statistics (mean, median and standard deviation) and a matrix correlation among trace elements and soil properties (SAEG 2007). The establishment of quality reference values (VRQ) was performed based on the 75th percentile after excluding the anomalous concentrations by a box-plot analysis as recommended in the Brazilian legislation (CONAMA 2009).

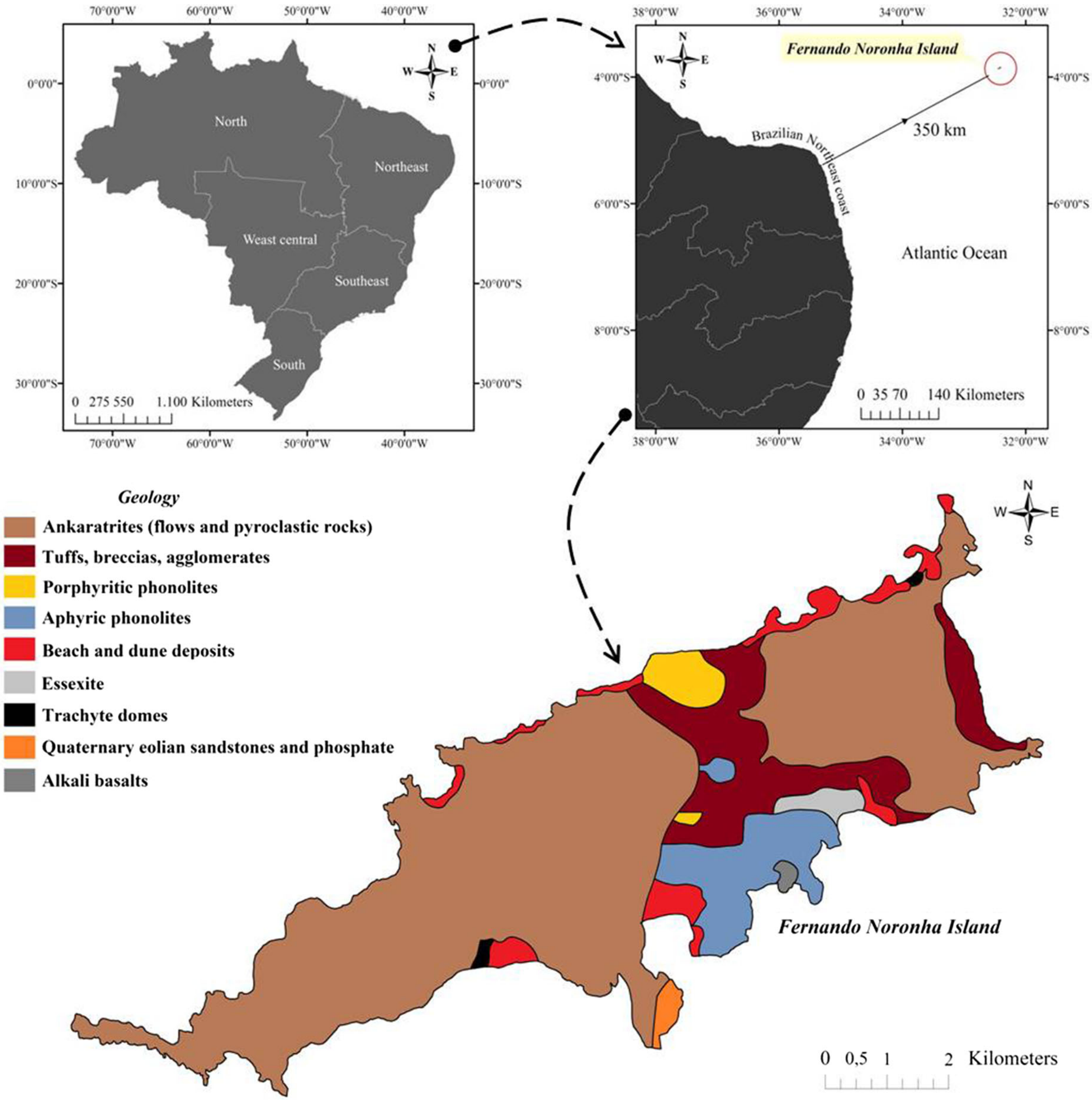

Fig. 1 Location and geological map of the Archipelago of Fernando de Noronha

Results and discussion

Soil properties and concentrations of trace elements in soils

Fernando de Noronha soils present high natural fertility (Table 2) due to the volcanic parent material and seabirds activities (guano deposits). Soil pH ranged from 4.9 to 7.9, i.e., from slightly acidic to slightly basic; owing to theses pH values, all available contents in soils are very low. Soil organic carbon showed a wide range from 4.54 to 51.18 g kg^{-1} with a mean value of 21 g kg^{-1}. These relatively high contents of SOC for tropical soils derive chiefly from the high amounts of guano deposited in the islands. The available P concentrations in soils of Fernando Noronha are very high (up to 1631 mg kg^{-1}) and are related mainly to the parent material with some contribution of guano deposition (Rocha et al. 2005). Soils are texturally

Table 1 Soil classification, source material and location of soil profiles from Fernando de Noronha. *Source*: [a] Ribeiro et al. (2005), [b] Marques (2004)

Profile	Soil classification[a]	Parent material	Coordinates UTM[b]
1	Cambisol	Basaltic rocks	3°48′43.16″S and 32°23′13.03″W
2	Cambisol	Phonolite	3°50′52.51″S and 32°25′15.73″W
3	Vertisol	Tuffs, breccias and agglomerates	3°51′21.75″S and 32°25′12.14″W
4	Cambisol	Basaltic rocks	3°51′03.69″S and 32°26′16.06″W
5	Cambisol	Ankaratrites	3°50′49.49″S and 32°24′39.77″W
6	Cambisol	Phonolite	3°51′20.65″S and 32°26′10.40″W
7	Cambisol	Basaltic rocks	3°51′26.3″S and 32°25′48.00″W
8	Vertisol	Tuffs, breccias and agglomerates	3°51′12.4″S and 32°25′14.90″W

classified as sandy loam, loam, clay loam and clay.

The natural concentrations of trace elements in the soils of the Fernando de Noronha archipelago followed the descending order: Ba > Cr > V > Zn > Ni > Cu > Co > Sb (Table 3). The rock geochemistry of the archipelago reveals the same order for trace element concentrations (Lopes and Ulbrich 2015). Thus, the high trace element concentrations found for Fernando de Noronha soils are mainly due to the volcanic origin of the archipelago as the samples were collected from locations with no anthropic influence. Likewise, volcanic soils from Italy (Sicily), Japan, Portugal (Azores) and Cape Verde (Santiago) also presented high concentrations of Cr, Ni, Zn and Cu (Palumbo et al. 2000; Takeda et al. 2004; Amaral et al. 2006; Cabral Pinto et al. 2015). In general, the average concentrations (mg kg^{-1}) of Ba (522.15), Cr (237.70), Zn (97.48), Ni (45.81) and Cu (24.01) for the archipelago soils are higher than those likely found in soils from continental Brazil (Biondi et al. 2011a, b; Santos and Alleoni 2013; Preston et al. 2014) and similar or lower than trace element concentrations in volcanic soils around the world (Palumbo et al. 2000; Amaral et al. 2006; Mendoza-Grimón et al. 2014).

In general, the concentration of trace elements in the soils followed the order Cambisols > Vertisols (Table 4). Elevated concentrations of Ni, Cu, Cr and V are found in soils overlying melanocratic rocks of the Quixaba Formation (sites 1, 5 and 6). Relatively low concentrations of Ni, Cu, Cr and V occur in soils overlying tuffs and agglomerates of the Remedios Formation. High concentrations of V were also found in soils from the volcanic islands of Azores (Amaral et al. 2006) and El Hierro (Mendoza-Grimón et al. 2014) (Table 3). The data from rocks of the Remedios and Quixaba Formations demonstrate a clear geochemical difference as reported by Almeida (1955), Gunn and Watkins (1976), Weaver (1990), Ulbrich (1993), Ulbrich et al. (1994), Horota and Wildner (2011) and Perlingeiro et al. (2013). The chemical analyses presented by Weaver (1990) and Lopes and Ulbrich (2015) showed that Cr, Ni, Co and Ba as well as CaO, MgO, Fe_2O_3 and P_2O_5 are considerably higher in nephelinites and basanites of the Quixaba Formation than in phonolitic and trachytic rocks of the Remedios Formation. The analytical data from soils and rock geochemistry show clearly that the concentration of trace element in parent material is the main factor influencing the trace element concentration in soils of Fernando de Noronha.

The high Ba concentrations in Cambisol (Soil Profile 6, overlying ankaratrite) are common in feldspar and feldspathoid-rich rocks (Deer et al. 1981) and Lopes and Ulbrich (2015) reported over 1000 mg kg^{-1} of Ba in basanites and ankaratrites from Fernando de Noronha. The highest Ni concentration was found in a soil derived from melanocratic Quixaba rocks types (72.5 mg kg^{-1}) while the lowest (46.2 mg kg^{-1}) was associated with phonolites of the Remedios Formation. Despite higher than Brazilian continental soils (Table 3), Ni concentrations in Fernando de Noronha soils are lower than reported for other volcanic soils (Doelsch et al. 2006; Mendoza-Grimón et al. 2014; Cabral Pinto et al. 2015).

The soils showed a widely varied Cu concentration (from below detection limit to up to 55.74 mg kg^{-1}), but almost half of the concentration data were lower than 7 mg kg^{-1} (Table 4). The Cu concentrations in the Vertisols (Soil Profiles 4 and 9) were 2.05 and

Table 2 Chemical and physical characterization of soil profiles from the Fernando de Noronha Island. *Source*: Marques (2004)

Horizon/depth	Profile 1 Cambisol		Profile 2 Cambisol		Profile 3 Vertisol		Profile 4 Cambisol		Profile 5 Cambisol		Profile 6 Cambisol		Profile 7 Cambisol		Profile 8 Vertisol	
	A (0–14)	Bi (14–51)	A (0–15)	BA (15–40)	Ap (0–15)	Cvn_1 (15–40)	A (0–15)	AB (15–45)	Ap (0–10)	BA (10–35)	Ap (0–15)	BA (15–40)	Ap (0–11)	Bi (11–43)	Apn (0–14)	Acn (14–32)
pH (H_2O) (1:2.5)	5.2	5.2	5.4	4.9	6.3	6.5	6.6	6.2	6.2	6.0	5.2	5.3	5.8	6.3	6.9	7.9
Ca + Mg ($cmol_c dm^{-3}$)	9.2	3.3	8.4	2.2	17.6	22.1	59.8	35.8	18.8	9.0	8.56	5.87	22.8	15.8	12.8	12.5
Al ($cmol_c dm^{-3}$)	0	0.8	0.3	1.9	0	0.1	0	0.3	0	0	0.4	0.5	0.1	0	0	0
Na($cmol_c dm^{-3}$)	0.9	0.7	0.4	0.2	0.8	2.0	1.3	1.1	0.5	0.3	0.3	0.3	0.5	0.9	3.8	7.3
K ($cmol_c dm^{-3}$)	2.0	1.0	0.8	0.1	0.2	0.5	3.2	1.3	2.0	1.3	0.4	0.2	0.7	0.1	0.3	0.1
P ($mg\ kg^{-1}$)	13,654	838	910	1010	218	107	1201	1631	1100	1407	350	270	332	306	270	212
O.C. ($g\ kg^{-1}$)	51.2	19.9	46.3	24.1	13.9	4.6	42.7	10.1	47.0	8.6	12.2	10.5	18.2	5.0	21.2	6.4
Total sand (%)	38	33	25	33	22	15	31	35	37	44	19	25	26	18	25	17
Silt (%)	32	28	28	29	17	11	35	23	26	24	24	24	23	9	18	7
Clay (%)	30	39	46	38	61	74	34	42	37	32	57	51	51	72	57	76
Bulk density soil ($Mg\ m^{-3}$)	0.91	1.04	0.84	0.89	1.46	1.57	0.7	0.92	1.01	1.10	1.11	1.26	1.2	1.3	1.08	1.44
Density of particles ($Mg\ m^{-3}$)	2.43	2.56	2.42	2.44	2.63	2.62	2.59	2.74	2.70	2.94	2.82	2.78	2.86	3.03	2.66	2.67

6.74 mg kg^{-1}, respectively, which are underlain by volcani-clastic rocks of the Remedios Formation. These concentrations are lower than those reported from Vertisols originating from non-volcanic rocks in Pernambuco state (Biondi et al. 2011b). This indicates the low potential of tuffs, breccias and agglomerates in providing Cu to the soils and corroborates the importance of the geochemical background on metal concentrations in soils. The mean concentrations of Zn observed for the Cambisols (Soil profiles 1 and 5) derived from melanocratic rocks of the Quixaba Formation are similar to data obtained by Oliveira and Costa (2004) for soils derived from basalt. The Cambisol group showed a small range of variation due to the different parent materials (95–112.1 mg kg^{-1}). For the Vertisols, the mean Zn concentration observed was 114.5 mg kg^{-1}. This figure is three times higher than found in Vertisols originated from non-volcanic parent material (Biondi et al. 2011b).

The natural concentrations of Cr ranged from 31.24 to 850.38 mg kg^{-1} (Table 4). The highest average concentration was observed for the Cambisols derived from Quixaba rocks (profiles 1 and 5). These means are only half of the concentrations found in soils from other volcanic island soils in the South Atlantic, e.g., the Azores (Amaral et al. 2006), similar to the Cr mean

Table 3 Average natural concentrations of trace elements in Fernando de Noronha soils compared with data compiled from volcanic soils in the world and Brazilian continental soils

Trace elements (mg kg^{-1})	Volcanic soils						Brazilian soils					World average soils[l]
	FN	Santiago[a]	La Réunion[b]	Açores[c]	Sicily[d]	El Hierro[e]	PE[f]	ES[g]	MG[h]	RN[i]	RO e MT[j]	
Cd	<LD	0.91	0.60	<LD	0.20	1.3	0.62	<LD[l]	0.5	0.07	<LD	0.01–2.0
Pb	<LD	5.00	8.74	44.00	8.50	ND	11.18	8.8	3.9	11.50	8.1	2–300
Zn	97.48	79.00	152.33	132.00	114.00	85.2	22.52	22.6	13.1	21.67	6.8	1–900
Cu	24.01	50.75	49.74	75.40	121.00	43.7	7.15	5.5	30.9	10.63	16.5	2–250
Ni	45.81	136.10	11,850	277.40	26.50	102.6	6.0	6.6	30.1	14.78	1.3	2–750
Cr	237.70	118.00	213.82	801.00	25.50	87.00	27.14	41.0	100.1	26.55	39.4	5–1500
V	122.24	169.00	ND	ND	ND	168.20	ND	ND	ND	22.39	ND	ND
Ba	522.15	ND	ND	ND	ND	ND	99.07	ND	190.96	53.41	ND	ND
Sb	4.60	ND	ND	ND	ND	ND	ND	ND	ND	0.13	ND	ND
Ag	<LD	ND	ND	ND	ND	ND	ND	ND	ND	0.58	ND	ND
Co	13.02	46.40	ND	63.20	ND	44.20	3.54	8.64	16.5	11.28	20.3	ND
Mo	<LD	ND	ND	ND	ND	ND	ND	1.43	ND	ND	ND	ND
As	<LD	0.60	ND	ND	ND	ND	0.44	6.80	17.78	ND	ND	ND
Hg	<LD	0.02	0.23	ND	ND	ND	0.09	ND	ND	ND	ND	ND

ND not determined, <LD below the detection limit

[a] Cape Verde: Cabral Pinto et al. (2015)

[b] Indian Ocean: Doelsch et al. (2006)

[c] Portugal: Amaral et al. (2006)

[d] Italy: Palumbo et al. (2000)

[e] Spain: Mendoza-Grimón et al. (2014)

[f] Brazil: Biondi (2010)

[g] Brazil: Paye et al. (2010)

[h] Brazil: Caires (2009)

[i] Brazil: Preston et al. (2014)

[j] Brazil: Santos and Alleoni (2013)

[l] World average: Alloway (1990)

Table 4 Natural concentrations, median, mean and standard deviation of Ni, Cu, Ba, Zn, Cr, Co, V and Sb in soils from the Fernando de Noronha

Profile	Ni mg kg^{-1}	Cu	Ba	Zn	Cr	Co	V	Sb
1-Cambisol	2.55	55.74	1167.25	116.51	257.12	<LD	70.41	6.33
2-Cambisol	36.25	6.65	259.38	117.58	58.03	47.05	36.89	<LD
3-Vertisol	7.24	2.05	96.69	139.95	55.03	0.98	61.43	1.03
4-Cambisol	94.38	44.05	834.88	118.18	266.13	<LD	207.04	5.11
5-Cambisol	58.75	40.64	1554.88	95.00	286.13	<LD	242.33	5.33
6-Cambisol	56.09	11.64	201.41	86.99	248.80	4.19	156.93	5.60
7-Cambisol	120.49	24.53	246.24	101.54	850.38	24.75	242.56	7.69
8-Vertisol	23.01	6.74	311.75	89.13	86.45	0.88	66.24	1.13
Median	46.17	18.09	285.57	109.03	252.96	4.19	113.67	5.33
Mean	49.85	24.01	584.06	108.11	263.51	15.57	135.48	4.60
SD	38.81	19.11	502.89	16.94	240.37	18.07	81.16	2.36

concentrations reported by Doelsch et al. (2006) for soils from La Réunion (Indian Ocean) and higher than those found in the soils of El Hierro, Spain (Mendoza-Grimón et al. 2014). The mean concentration of Co (13.02 mg kg^{-1}) in soils from Fernando de Noronha is similar (Santos and Alleoni 2013), higher (Biondi et al. 2011b; Preston et al. 2014) or lower (Caires 2009) than the average concentrations reported from other soils either from Brazil or other volcanic islands (Table 3).

Concentrations of V in soils from the Fernando de Noronha archipelago ranged from 16.30 to 242.56 mg kg^{-1}. Regarding Sb, 45 % of the soil samples posed Sb concentrations below 1.2 mg kg^{-1}, being the highest concentration (7.69 mg kg^{-1}) detected in a Cambisol (Soil Profile 8) originated from agglomerates of the Remedios Formation. The Sb concentration for most soils analyzed reflects the influence of the parent material as mafic igneous rocks exhibit relatively low concentrations of Sb (0.2–1.0 mg kg^{-1}). Besides the differences in rock composition within the same soil group, the residual effect during pedogenesis is indicated by some authors as an explanation for the high levels of Sb in soils derived from mafic rocks (Lintschinger et al. 1998; Vázquez and Anta 2009; Okkenhaug et al. 2011).

Concentrations of Ag, Cd, Mo and Pb were below the detection limit of the equipment, and therefore natural concentrations were not established. Cadmium was also undetected in the volcanic soils of Santa Maria island, Portugal (Amaral et al. 2006) and presented very low values (0.02–0.7 mg kg^{-1}) in soils from La Réunion (Doelsch et al. 2006), a volcanic island located in the Indian Ocean. Low concentrations of Pb in volcanic-derived soils are reported by Davies (1990), Doelsch et al. (2006) and Mendoza-Grimón et al. (2014); for instance, 83 % of the soil samples from La Réunion (Doelsch et al. 2006) were below the detection limits for the element. Oliveira et al. (2011b) also reported undetectable concentrations of this metal in four out of five soil profiles from the Fernando de Noronha Archipelago, whereas Mendoza-Grimón et al. (2014) found Pb values normally below detection limit in volcanic soils from El Hierro Island.

Significantly, high correlation coefficients were found between Ba, Ni, Cr, V e Sb while Zn and Co were not correlated with any other trace elements (Table 5). Positive correlations between elements may indicate that they have similar sources (Lv et al. 2015). Taking into account the pristine conditions of the Fernando Noronha, these elements are derived mainly from the soil parent material. There was no significant correlation between trace elements concentrations and soil properties, except for Ba and pH (−0.80) and Zn and P (0.71).

Establishment of the quality reference values (QRV)

Environmental monitoring agencies continually assess the environmental impacts of anthropogenic activities in order to prevent heavy metal pollution in soils. Part of their mandate involves establishing guideline values that help identify polluted areas based on QRV and help assess the risks that such areas pose to

Table 5 Quality reference values (mg kg^{-1}) for soils from Fernando de Noronha

Metal	Ni	Zn	Cu	Cr	V	Sb	Co	Ba
QRV[a]	58.75	117.58	41.49	266.13	207.04	5.96	19.61	834.88
PV[b]	30.00	300.00	60.00	75.00	–	2.00	25.00	150.00
IV[c]	70.00	450.00	200.00	150.00	–	5.00	35.00	300.00
IV[d]	100.00	1000.00	400.00	300.00	–	10.00	65.00	500.00
IV[e]	130.00	2000.00	600.00	400.00	1000.00	25.00	90.00	750.00

[a] Quality reference value

[b] Prevention value

[c] Investigation value for agricultural areas

[d] Investigation value for residential areas

[e] Investigation value for industrial areas (CONAMA 2009)

the environment and to human health (Santos and Alleoni 2013).

The QRV established for Ba, Cr, Ni, Sb and Zn (Table 4) for the soils from Fernando de Noronha are higher than those documented from other Brazilian states, such as São Paulo, Minas Gerais and Pernambuco as well as to other areas in the world (Martínez-Lladó et al. 2008; Su and Yang 2008).

The values for Ba, Cr and Sb exceed the investigation value (IV) indicated by the Brazilian law (CONAMA 2009) which means that the area would represent potential risks to human health or the local ecosystem and should be cleaned up. However, it is more likely that the values established for these metals are underestimated in the current resolution. Biondi et al. (2011a) mentioned the need to establish QRV in cases where the legislation erroneously considered anomalous what in fact due to factors inherent to the geology of the site. This shows not only the variation of metal concentrations in soils originating from different parent materials but also supports the need for regional studies for the establishment of guiding values of trace elements in soils.

Conclusions

The results of this study indicate that the concentrations of Ba, Cr, Zn, Ni, Cu and V for the soils from the volcanic Fernando de Noronha archipelago are higher than those found in soils from continental Brazil. On the other hand, concentrations of Ni, Cu and Co are lower in soils of Fernando de Noronha as compared to other volcanic islands throughout the world. Trace element concentrations varied as a function of the soil order and geological parent material. Geochemical analyses of trace elements in soils and rocks clearly show a relationship between elemental concentrations in parent material and overlying soils. Thus, the volcanic parent material in Fernando de Noronha is reflected in the high natural concentrations of trace elements in soils on the archipelago. Quality reference values calculated for Ag, Co, Cu, Mo, V and Zn indicate that the evaluated soils have these metals in concentrations that meet the CONAMA quality benchmarks. Taking into account the relatively small sample size in the present study, i.e., eight soil profiles, the establishment of QRVs for soils of Fernando de Noronha needs further validation. Concentrations of Ni, Cr, Sb and Ba exceeded the prevention values adopted by CONAMA. These data illustrate the importance of the regional geology with regard to establishing soil guidelines for trace elements.

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