



Anais da Academia Brasileira de Ciências

ISSN: 0001-3765

aabc@abc.org.br

Academia Brasileira de Ciências

Brasil

DE OLIVEIRA, SONIA M.B.; PESSENDA, LUIZ C.R.; GOUVEIA, SUZY E.M.; FAVARO, DEBORAH I.T.

Heavy metal concentrations in soils from a remote oceanic island, Fernando de Noronha, Brazil

Anais da Academia Brasileira de Ciências, vol. 83, núm. 4, 2011, pp. 1193-1206

Academia Brasileira de Ciências

Rio de Janeiro, Brasil

Available in: <http://www.redalyc.org/articulo.oa?id=32721028028>

- How to cite
- Complete issue
- More information about this article
- Journal's homepage in redalyc.org

redalyc.org

Scientific Information System

Network of Scientific Journals from Latin America, the Caribbean, Spain and Portugal

Non-profit academic project, developed under the open access initiative



Heavy metal concentrations in soils from a remote oceanic island, Fernando de Noronha, Brazil

SONIA M.B. DE OLIVEIRA¹, LUIZ C.R. PESSEDA², SUZY E.M. GOUVEIA²
and DEBORAH I.T. FAVARO³

¹Instituto de Geociências, Universidade de São Paulo, Rua do Lago, 562, 05508-080 São Paulo, SP, Brasil

²Laboratório de 14C, Centro de Energia Nuclear na Agricultura, Universidade de São Paulo,
Av. Centenário, 303, 13416-000 Piracicaba, SP, Brasil

³Instituto de Pesquisas Energéticas e Nucleares, LAN-CRPQ,
Av. Prof. Lineu Prestes, 2242, Cidade Universitária, 05508-000 São Paulo, SP, Brasil

Manuscript received on May 4, 2010; accepted for publication on March 10, 2011

ABSTRACT

This paper examines the role of parent rock, pedogenetic processes and airborne pollution in heavy metal accumulation in soils from a remote oceanic island, Fernando de Noronha, Brazil. We studied five soil profiles developed from different volcanic rocks. Mineralogical composition and total concentrations of major and trace elements were determined in 43 samples. The obtained concentrations range for heavy metals were: Co: 26-261 ppm; Cu: 35-97 ppm; Cr: 350-1446 ppm; Ni: 114-691 ppm; Zn: 101-374 ppm; Hg: 2-150 ppb. The composition of soils is strongly affected by the geochemical character of the parent rock. Pedogenesis appears to be responsible for the accumulation of Zn, Co, and, to a lesser extent, of Ni and Cu, in the upper, Mn- and organic carbon-enriched horizons of the soil profiles. Pedogenic influence may also explain the relationship observed between Cr and the Fe. Hg is likely to have been added to the soil profile by long-range atmospheric transport. Its accumulation in the topsoil was further favoured by the formation of stable complexes with organic matter. Clay minerals do not appear to play an important role in the fixation of heavy metals.

Key words: heavy metals, soils, anthropogenic mercury, Fernando de Noronha.

INTRODUCTION

The distribution of heavy metals in a soil profile is influenced both by parent rock composition and pedogenetic processes, which may cause the accumulation of metals in a specific horizon. For instance, the nutrient cycle of the vegetation can be responsible for the enrichment of transition metals in surface organic horizons (Blaser et al. 2000, Reimann et al. 2007). Mn and Fe can also play a role in the concentration of trace metals in soils due to the pronounced metal binding properties of their oxides (Kabata-Pendias and Pendias 1992). In addition to natural causes, local and regional

anthropogenic sources can also account for metal accumulation in soils. Furthermore, soils can be affected by long-range atmospheric transport of heavy metals (Nriagu 1989), and even in apparently pristine areas signals of airborne pollution can be detected. However, prior to assessing contamination, it is necessary to determine the local pedo-geochemical background of heavy metals (Baize and Sterckeman 2001, Salonen and Kirsti 2007). The geochemical inheritance of the parent rock can be evaluated by comparing soils developed from rocks of distinct composition under similar climatic conditions (Horckmans et al. 2005, Lasheras Adot et al. 2006). On the other hand, the variation of concentrations with depth and the degree of enrichment/depletion of an element in relation to the parent rock

Correspondence to: Sonia Maria Barros de Oliveira
E-mail: soniaoli@usp.br

in each soil horizon may help to estimate the role of pedogenesis and the extent of atmospheric input in the contamination of soils (Palumbo et al. 2000, Hernandez et al. 2003).

Here we studied five soil profiles developed from volcanic rocks of a remote oceanic island – Fernando de Noronha (FN) – situated in the South Atlantic Ocean. The aims of this study are (1) to assess the influence of the parent rock fingerprint in the composition of FN soils, (2) to determine the extent to which pedogenesis affected the heavy metal distribution within the soil profiles, and (3) to evaluate the possible contamination of FN soils by atmospheric deposition. FN is particularly suitable for this kind of study because of the variety of lithologies concentrated in a small area, the absence of industrial and other pollutive emissions in the archipelago and its remoteness from continental sources of dust.

MATERIALS AND METHODS

Fernando de Noronha (FN) is situated at 03°51' south and 32°25' west, approximately 400 km offshore from the Brazilian coast (Fig. 1). This island has an area of 16.9 km², making up 91% of the total area of the Fernando de Noronha archipelago, and reaches a maximum elevation of 320 m above sea level. At present, the climate is tropical, with two well defined seasons: a rainy season from January to August and a dry season for the remaining of the year. The average annual temperature is 25°C and the rainfall averages 1400 mm per year. Climate changes, as well as variations in the sea level, are thought to have occurred during the Pleistocene (Pessenda et al. 2008).

Although first settled around 1770, FN was scarcely inhabited until World War II. Its permanent population now numbers about 2,100. In 1988 about 70% of the archipelago was declared an environmentally protected area, and facilities for tourists were restricted. Human activity is mainly centered on the northern side of the island where the main village, Remédios, is situated.

GEOLOGIC SETTING

The geology and petrography of FN archipelago was first described by Almeida (1955), and is depicted in

the simplified geologic map in Figure 1. Rock geochemistry was reported by, among others, Gunn and Watkins (1976), Weaver (1990), Ulbrich et al. (1994) and Lopes and Ulbrich (2006). The main island is composed of two contrasting suites of igneous rocks. The Remédios Formation consists mainly of plugs and domes of phonolite, alkali-trachyte and alkali-basalt, cut by lamprophiric and basanitic dikes emplaced into pyroclastic tuffs. Unconformably overlying the Remédios Formation is the Quixaba Formation, which is dominated by highly mafic nepheline basaltic flows (nepheline basalts or ankaratrites). K/Ar age determinations (Cordani 1970) indicated an interval from 8 to 12 Ma for the older formation, and 1.7-3.0 Ma for the younger one.

SAMPLING

Soil sampling was performed as part of a previous study aiming to reconstruct the vegetation and climate changes during the Holocene (Pessenda et al. 2008). The soil profiles were identified as Haplic Cambisols according to the World Reference Base Classification System (FAO 1990).

In the present study, 43 soil samples were selected from five soil profiles (Table I). These are referred in this paper as Morro da Quixaba (MQ), Sancho Bay (SB), Mata Ponta Oeste (MP), Ponta de Atalaia (AB), and Leão Beach (LB) sites (Fig. 1). A precise characterization of the bedrock in each site is difficult because there are no unweathered exposure at the bottom of the profiles. For the purposes of this study, the sampling sites have been allocated to three lithological types according to the geological map of Almeida (1955). At MQ, SB and MP sites the bedrock is thought to be the highly mafic alkalic lava flows of the Quixaba Formation (nepheline basalts). The LB sampling site was located near the contact between the above described nepheline basalts and a small dome of alkaline trachyte (Remédios Formation). At the AB site, the soil profile developed from a sill formed by a coarse-grained equivalent of an alkaline undersaturated phonolite (essexite) of the Remédios Formation, cut by a mafic dike.

Soil of the five profiles was sampled systematically at every 10 cm. At the MQ site, a large pit was hand dug down to 3 m, and the soil profile was sampled from

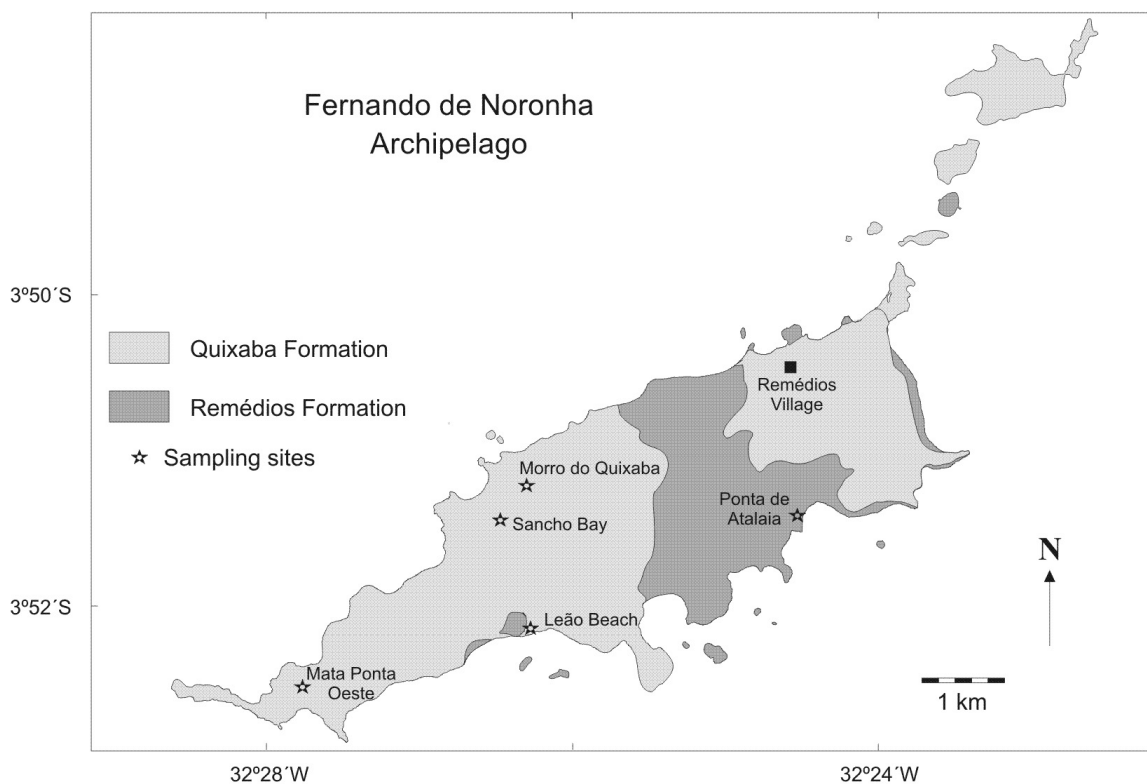


Fig. 1 – Simplified geological map of the Fernando de Noronha archipelago and location of the sampling sites: MQ = Morro do Quixaba; SB = Sancho Bay; MP = Mata Ponta Oeste; AB = Ponta de Atalaia; LB = Leão Beach.

TABLE I
Description of the sampling sites.

Profile	Location	Altitude	Bedrock	Horizon	Depth	Samples
MQ	Morro do Quixaba	170 m	Nepheline-basalt	A	0-30 cm	2
				A/B	31-190 cm	8
				B	191-290 cm	6
SB	Sancho Bay	65 m	Nepheline-basalt	A	0-30 cm	3
				B	31-110 cm	4
				B/C	111-140 cm	3
MP	Mata Ponta Oeste	100 m	Nepheline-basalt	A	0-30 cm	3
				B	31-120 cm	5
AB	Ponta de Atalaia	0 m	Essexite	A/C	0-10 cm	1
				B/C	11-70 cm	4
LB	Leão Beach	0 m	Ne-basalt + Trachyte	A/C	0-10 cm	1
				B/C	11-40 cm	3

the A organic-rich horizon (0-30 cm) through the A/B-horizon (31-190 cm) to the B horizon (191-290 cm). The remaining four soil profiles were sampled down to the B or B/C horizons using an auger. Table I summarizes the main characteristics of the sampled soil profiles.

ANALYTICAL PROCEDURES

Bulk mineralogical composition was determined by X-ray powder diffraction (XRD) in normal, ethylene glycol saturated and heated (at 500°C) oriented samples.

X-ray analyses were performed at the Institute of Geosciences, University of São Paulo, on a Siemens automated powder diffractometer equipped with a graphite monochromator. All slides were scanned over 2θ range $3-60^\circ$ with a step size of 0.05° using a $\text{CuK}\alpha$ radiation at 40 kV and 40 mA.

For chemical analyses, samples were dried overnight at 40°C and pulverized to about <0.062 mm in a tungsten carbide mill. Analytical data for the major elements (Si, Al, Fe, Mn, Mg, Ca, Na, K, Ti and P) and selected trace elements (Ba, Cu, Ga, Nb, Ni, Sr, V, Y, Zn, Zr) were obtained by conventional wave-length dispersive X-ray fluorescence (XRF). XRF analyses of standard reference material showed accuracy and precision to be better than 5% RDS (Mori et al. 1999). The loss on ignition (LOI) was determined at the interval 100 to 1000°C for 60 minutes. XRD and XRF procedures were carried out at the Institute of Geosciences, University of São Paulo. Additional trace (Co, Cr, Hf, Sc, Ta, Th, U) concentrations were determined by Instrumental Neutron Activation Analysis (INAA). Sample reference materials and synthetic standards were irradiated for 16 hours in a thermal neutron flux of $10^{12} \text{ n cm}^{-2} \text{ s}^{-1}$ in the IEA-R1 nuclear reactor at IPEN – Institute of Nuclear and Energetic Research (São Paulo). Mercury was measured by cold vapor-atomic absorption spectrometry (CV-AAS) technique in a flow injection mercury system (FIMS) after total digestion by a mixture of HNO_3 , H_2SO_4 and H_2O_2 at the same Institute. All Hg determinations were performed in duplicate, and the detection limit was 2 ppb. Results were consistently within 10% of each other. The INAA methodology validation was performed by measuring the reference materials NIST SRM 2704, IAEA and IWG-GIT, and the AAS methodology, NIST SRM 2704, NIST SRM 1646, and BCR CRM 280. The lower limit detection for the elements determined by XRF and INAA were well below the lowest measured concentrations in all samples.

RESULTS AND DISCUSSION

SOIL MINERALOGY

The mineralogical composition of the analysed soils is summarized in Table II. A general characteristic is the absence of quartz and the presence of significant

amounts of non-crystalline phases. The dominant components in all soils are clay minerals: kaolinite in soils derived from the nepheline basalts of the Quixaba Formation (MQ, SB and MP sites), and the 17A swelling clay (smectite) in soils derived from the more acid lithologies of the Remédios Formation (AB and LB sites). Goethite and hematite are present in small amounts in all soils. Some of the primary constituents of the volcanic rocks – magnetite, ilmenite, pseudobrookite, zeolite and pyroxene – can also be found in minor amounts in most soil samples.

MAJOR AND TRACE ELEMENT CONCENTRATIONS IN SOILS

In Table III, major element concentrations are listed for all of the 43 samples analysed. Also shown are TOC (total organic carbon), $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratios and CIA (Chemical Index of Alteration). CIA was calculated from the chemical analysis of the soils by taking the molecular proportions of the oxides (Nesbitt and Young 1982): $\text{CIA} = [\text{Al}_2\text{O}_3/(\text{Al}_2\text{O}_3 + \text{CaO} + \text{Na}_2\text{O} + \text{K}_2\text{O})]$.

The chemical composition of FN soils is dominated by SiO_2 , Al_2O_3 , Fe_2O_3 and TiO_2 . MgO is present in significant amounts only in the less weathered horizons of the soil profiles. Na_2O , K_2O and CaO contents are remarkably low throughout the profiles. The organic matter (TOC) content of soils decreases with depth, varying between 2.7-0.9% and 0.8-0.1%, respectively, for surface and deep horizons. CIA reaches high values within the group of soils developed at higher altitudes (from 0.95 to 0.99 in the MQ site, from 0.62 to 0.93 in the SB site, and from 0.82 to 0.94 in the MQ site), pointing to a high degree of pedological evolution. On the other hand, in soils developed at the sea level, CIA values are lower, ranging from 0.71 to 0.76 in the AB site, and from 0.66 to 0.67 in the LB site.

Table IV displays the overall results for the trace element concentrations. The distribution of the heavy metals with depth (Fig. 2) varies according to the element and to the different soil profiles. In MQ, SB and MP sites, the concentrations of Zn and Co decrease with depth. Hg, Cr and Ni concentrations display a similar pattern in the MQ site, but in SB and MP sites Cr and Ni do not show a systematic pattern with depth. In the AB site, the heavy metal contents increase slightly with depth, and in the LB site their concentrations slightly

TABLE II
Mineralogical composition of the Fernando de Noronha soils.
Kaol = kaolinite, Smec = smectite, Goe = goethite, Hem = hematite,
Anat = anatase, Non-cryst = non-crystalline phases.
XXX = very abundant, XX = abundant, X = present, (X) = trace.

Profile	Horizon	Kaol	Smec	Goe+Hem	Anat	Non-cryst
MQ	A	XXX		X	X	(X)
	A/B	XXX		X	X	(X)
	B	XX	(X)	X		(X)
SB	A	XXX		X		X
	B	XXX		X		X
	B/C	XXX		X		(X)
MP	A	XX		X		XX
	B	XX		X		XX
AB	A/C		XXX	X		X
	B/C		XXX	X	X	X
LB	A/C		XX	X		X
	B/C		XX	X	X	XX

TABLE III
Soil composition: major oxides (%), TOC = total organic carbon (%), CIA =
chemical index of alteration (Nesbitt and Young 1982), sd = standard deviation.

	MQ (n=16)		SB (n=10)		MP (n=8)		AB (n=5)		LB (n=4)	
	mean	sd	mean	sd	mean	sd	mean	sd	mean	sd
SiO ₂	29.05	4.16	28.97	1.65	24.20	1.97	40.21	1.52	34.77	0.52
Al ₂ O ₃	23.53	1.29	22.44	1.56	20.65	1.43	18.65	0.74	15.12	0.36
MnO	0.23	0.24	0.25	0.06	0.52	0.10	0.17	0.05	0.30	0.02
MgO	1.04	0.29	2.85	1.19	1.93	0.44	2.42	0.06	3.56	0.08
CaO	0.15	0.12	1.24	1.43	0.97	0.49	1.60	0.27	2.86	0.10
Na ₂ O	0.16	0.13	0.85	0.34	0.33	0.20	1.08	0.06	0.72	0.05
K ₂ O	0.04	0.05	0.16	0.07	0.25	0.04	1.58	0.16	0.90	0.01
TiO ₂	5.99	0.31	5.67	0.35	5.41	0.17	5.02	0.43	6.14	0.14
P ₂ O ₅	0.68	0.31	1.91	0.20	1.48	0.14	2.01	0.71	1.30	0.01
Fe ₂ O ₃	26.91	1.68	24.99	1.56	30.84	4.18	15.81	1.67	25.12	0.50
LOI	11.95	2.11	10.49	1.37	13.19	1.79	10.51	0.35	8.06	0.52
Si/Al	1.06	0.21	1.11	0.15	1.00	0.06	1.83	0.06	1.95	0.02
TOC	0.54	0.68	0.35	0.31	1.20	0.79	1.14	0.30	0.66	0.18
CIA	0.98	0.01	0.86	0.10	0.89	0.04	0.74	0.02	0.67	0.00

decrease, or remain rather stable, with depth. The concentrations of Cu present no systematic behavior with depth.

For almost all soil samples, the heavy metal contents exceed the world range for non-polluted soils (Kabata-

Pendias and Pendias 1992), the Chinese environmental quality standard for soils (Chen et al. 1999), and the São Paulo State Environmental Agency (CETESB) standard for soils (Casarini et al. 2001) (Table V). However, this finding must be interpreted taking into account that

TABLE IV
Soil composition: trace elements (ppm), except Hg (ppb),
nd = not determined, sd = standard deviation.

	MQ (n=16)		SB (n=10)		MP (n=8)		AB (n=5)		LB (n=4)	
	mean	sd	mean	sd	mean	sd	mean	sd	mean	sd
Ba	471	140	503	160	755	99	771	87	833	11
Ga	41	3	38	3	37	1	32	0	29	1
Hf	11	1	13	1	10	1	13	1	9	1
Nb	167	9	125	8	148	4	160	11	170	4
Sr	343	57	326	205	364	62	513	33	528	7
Sc	44.6	2.3	38.7	2.1	40.8	1.7	23.8	1.8	31.2	1.4
Ta	8.9	0.7	8.5	0.7	8.2	0.5	9.3	0.8	8.9	0.7
Th	24.8	1.3	10.4	0.7	23.3	1.6	18.4	1.2	18.0	0.8
U	3.4	0.9	3.3	0.4	3.7	0.5	8.2	1.3	3.1	0.3
V	299	80	469	48	591	57	370	29	311	15
Y	38	24	44	9	47	3	30	1	45	1
Zr	478	26	545	35	416	16	632	32	410	1
Co	72	81	92	26	155	21	61	12	98	10
Cr	705	111	548	29	1081	182	397	50	590	40
Cu	60	9	67	15	70	4	39	5	96	1
Hg	30.8	43.3	nd	nd	nd	nd	nd	nd	nd	nd
Ni	222	75	600	53	344	21	130	10	221	2
Zn	157	67	180	28	219	28	166	24	304	3

the Fernando de Noronha soils were developed from already geochemically anomalous rocks when compared to the composition of the average upper continental crust (Wedepohl 1995) (Table V). Furthermore, pedogenesis on volcanic rocks is characterized by the neoformation of non-crystalline phases intimately associated with organic matter, known to show a strong retention of heavy metals (Hernandez et al. 2003). In the FN soils, such phases are abundant and can also account for the high concentrations of Cr, Co, Ni, Zn and Cu observed. On the other hand, compared with the products of weathering alteration of rocks of similar geochemical composition, such as the nepheline basalts from the French Massif Central (Soubrand-Colin et al. 2005), the FN soils are in the same range of heavy metal concentrations (Table V).

PARENT ROCK INHERITANCE

Soils developed from nepheline basalts (MQ, SB, and MP sites) present higher Fe₂O₃ contents and lower SiO₂

and K₂O contents than soils developed from more acid lithologies (AB and LB sites). In the MQ, SB and MP soils, SiO₂/Al₂O₃ ratios are lower compared with the ratios in the AB and LB soils, which reflects the presence of kaolinite in the former group of soils and smectite in the latter.

In order to investigate whether it was possible to distinguish different soils on the basis of similarities of their trace element composition, a cluster analysis was carried out. The dendrogram in Figure 3 shows two groups of soils based on the magmatic affinity of the parent rock: soils developed from the more unsaturated ultramafic rocks of the Quixaba Formation from those developed from the less unsaturated rocks of the Remédios Formation. Furthermore, within the latter, two sub-groups corresponding to different parent rocks could be detected: one formed by SB soils and another by AB soils. Overall, the results of the cluster analysis confirm that the chemical composition of soils is mainly determined by the parent material.

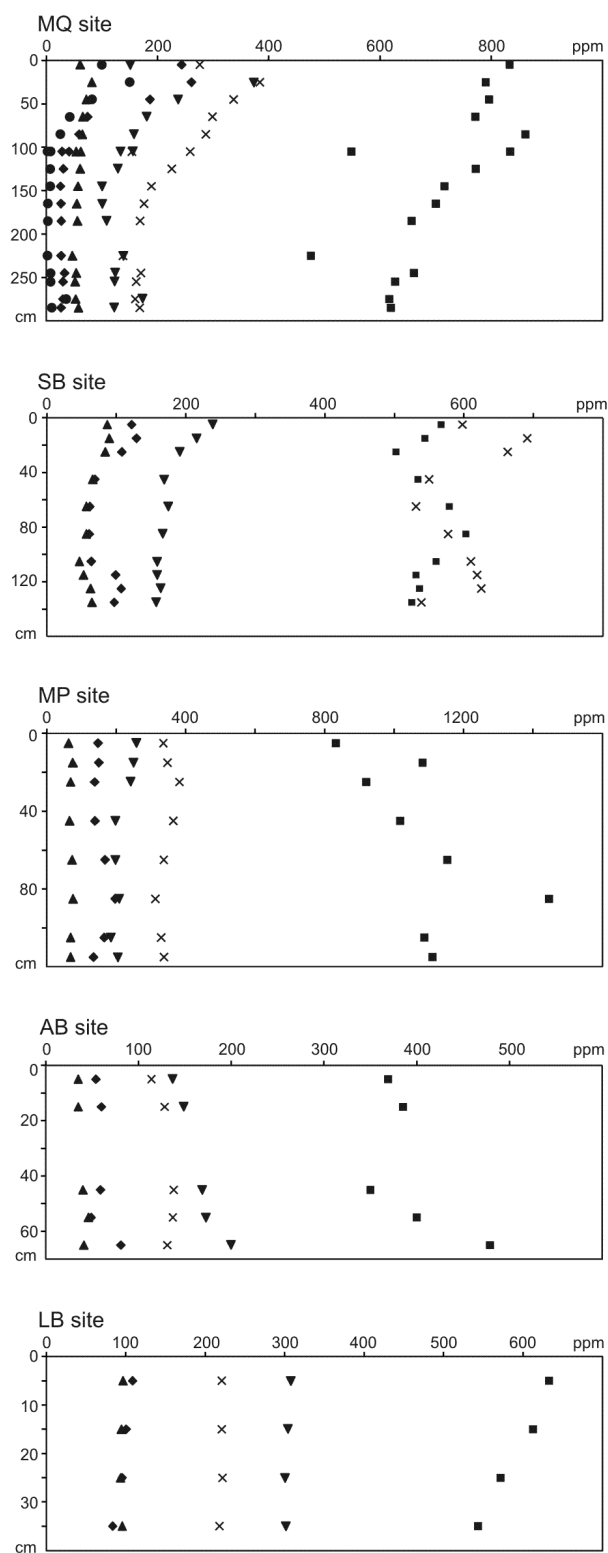


Fig. 2 – Total heavy metal concentrations (ppm) in soil profiles: Cr = solid squares; Zn = solid inverted triangles; Ni = crosses; Cu = solid triangles; Co = solid diamonds; Soil profiles: MQ = Morro do Quixaba; SB = Sancho Bay; MP = Mata Ponta Oeste; AB = Ponta de Atalaia; LB = Leão Beach.

TABLE V

Heavy metal concentrations (ppm) in: FN soils (this work), Non-polluted soils (Kabata-Pendias and Pendias 1992), Chinese environmental quality standard for soils (Chen et al. 1999), Fernando de Noronha rocks: Ne-basalts, Essexite and Trachyte (Gunn and Watkins 1976, Weaver 1990, Ulbrich et al. 1994, Lopes and Ulbrich 2006), UCC – upper continental crust (Wedepohl 1995), FMC – ne-basalts from the French Massif Central (Soubrand-Colin et al. 2005).

	Co	Cu	Cr	Ni	Zn	Hg ppb
FN soils	26-261	35-97	350-1446	114-691	101-374	2-150
Non poll soils	0.1-20	6-60	5-120	1-200	17-125	nd
Chinese stand	nd	35	90	40	100	150
Ne-basalts	56-65	22-70	252-686	70-451	103-128	nd
Essexite	20-21	19-20	62-110	55-83	99-100	nd
Trachyte	2-10	34-36	5-11	4-16	77-123	nd
UCC	12	14	35	19	52	56
FMC	nd	33-71	293-686	168-291	110-168	nd

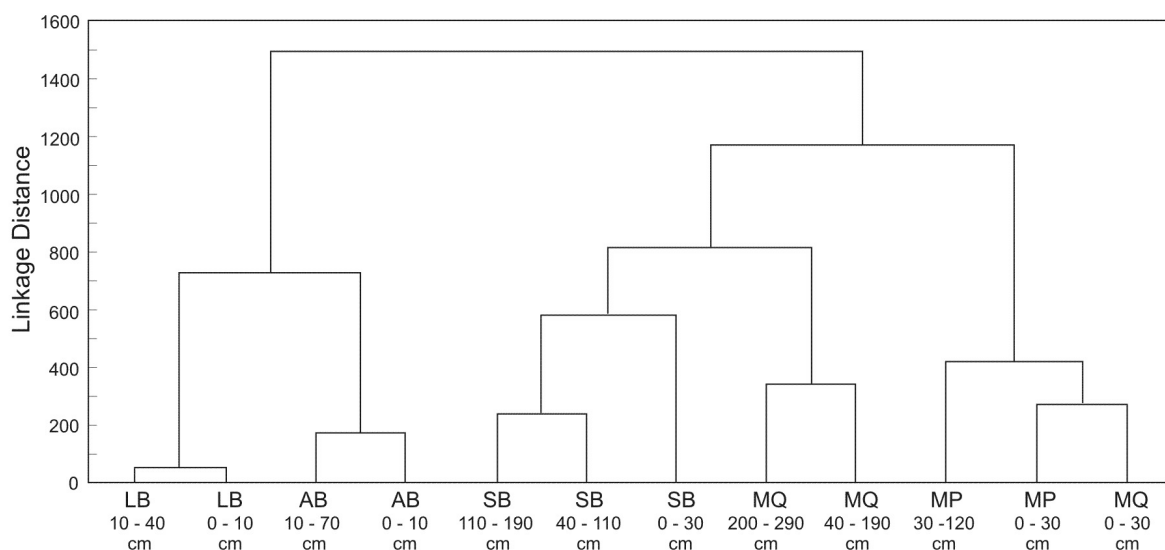


Fig. 3 – Dendrogram from cluster analysis based on trace element composition of soils. Ward's method, euclidean distances. MQ = Morro do Quixaba; SB = Sancho Bay; MP = Mata Ponta Oeste; AB = Ponta de Atalaia; LB = Leão Beach.

Soils developed from more mafic rocks, corresponding to MQ, SB and MP sites, present the highest Co, Ni and Cr contents, while the lowest concentrations are found in soil samples developed from the less mafic rocks (essexite) corresponding to the AB site. On the other hand, the AB soils present the highest contents of Ba, Sr, Zr, Hf and U. Soils developed under the influence of both a nepheline basalt and an alkaline trachyte (LB site) contain a characteristic heavy metal signature: Cu and Zn concentrations are the most elevated of all

soils analysed, while Cr, Co and Ni are in the range of the MQ soils.

INFLUENCE OF PEDOGENESIS ON HEAVY MINERAL DISTRIBUTION IN SOIL PROFILES

Relationships between major elements and heavy metals

Total organic carbon, aluminum, iron and manganese are generally considered important factors in evaluating heavy metal content in soils (Baize and Sterckeman

TABLE VI
Pearson correlation matrix for heavy metals, Mn, Fe and TOC in all soil samples
(n=43; *correlation is significant at $P < 0.001$; ** $P < 0.005$).

	TOC	Al	Fe	Mn	Co	Cr	Cu	Ni	Zn
TOC	1.00								
Al	-0.10	1.00							
Fe	-0.15	0.26	1.00						
Mn	0.59*	-0.07	0.41	1.00					
Co	0.60*	-0.05	0.32	0.98*	1.00				
Cr	0.20	0.12	0.85*	0.65*	0.55*	1.00			
Cu	0.09	-0.25	0.44**	0.47**	0.49*	0.32	1.00		
Ni	-0.10	0.29	0.19	0.24	0.34	0.03	0.33	1.00	
Zn	0.45**	-0.44**	0.08	0.60*	0.63*	0.17	0.74*	0.16	1.00

2001). The correlations between these variables for the Fernando de Noronha soils are presented in the form of a Pearson correlation coefficient matrix in Table VI.

A highly significant correlation was observed between Mn and Co ($r^2 = 0.98$, $n = 43$, $P < 0.001$) (Fig. 4a), which is probably related to the preferential association of this metal with the manganese oxides. Mn and Zn are also significantly correlated (Fig. 4b) considering all samples ($r^2 = 0.60$, $n = 43$, $P < 0.001$); this relationship becomes weaker with Cu ($r^2 = 0.47$, $n = 43$, $P < 0.005$) (Fig. 4c) and Ni (Table VI). For the SB soils only, the correlations Mn-Zn and Mn-Cu are much stronger (Mn-Zn $r^2 = 0.84$; Mn-Cu $r^2 = 0.90$, $n = 10$, $P < 0.001$) (Fig. 4b, c).

A significant relationship was found between TOC and Co ($r^2 = 0.60$, $n = 43$, $P < 0.001$); this relationship is even stronger in the MQ site ($r^2 = 0.90$, $n = 16$, $P < 0.001$) (Fig. 4d). Between Zn and TOC the correlation is weaker ($r^2 = 0.45$, $n = 43$, $P < 0.01$), but considering only the SB soils, it is highly significant ($r^2 = 0.98$, $n = 10$, $P < 0.001$). Cr, Cu and Ni contents do not correlate significantly with TOC (Table VI). Ni shows no significant correlations with other elements when all of the soil samples are considered. However, Ni correlates significantly with TOC (Fig. 4e), as well as Mn (Fig. 4f) in the MQ soil profile (TOC-Ni $r^2 = 0.64$; Mn-Ni $r^2 = 0.78$; $n = 16$, $P < 0.005$) and with Mn in the SB soil profile (Mn-Ni $r^2 = 0.72$, $n = 10$, $P < 0.02$) (Fig. 4f).

Fe is significantly correlated with Cr considering all soil samples ($r^2 = 0.85$, $n = 43$, $P < 0.0001$) (Fig. 4g); the same was found for samples of each soil profile, which indicates a strong affinity of Cr for the iron oxides. The relationship between Fe and Cu is also positive, but less significant ($r^2 = 0.44$, $n = 43$, $P < 0.005$) (Fig. 4h). Fe did not correlate significantly with Co, Ni and Zn.

Considering only the MQ soils, Hg was strongly correlated with TOC and Mn (TOC-Hg $r^2 = 0.87$, Mn-Hg $r^2 = 0.97$, $n = 16$, $P < 0.001$). Fe did not correlate significantly with Hg (Hg-Fe $r^2 = -0.10$, $n = 16$).

No clear relationship between Al and the heavy metals was detected in this study, which suggests that the clay content does not control the amount of Cr, Cu, Zn, Co, and Ni of soils. On the other hand, the manganese oxides and/or the organic matter seem to be important controlling factors in the fixation of Zn, Co, Ni, Cu and Hg in the studied soils. Iron oxides and hydrous oxides play a major role only in the retention of Cr.

Enrichment factors

Enrichment factors (EF) were calculated in order to assess the enrichment or depletion of a trace element in a given soil horizon. EF considers the abundance of the element of interest relative to the abundance of a conservative, lithogenic element with no significant anthropogenic source. This ratio is then normalized to the corresponding ratio in the sample at the lowest soil

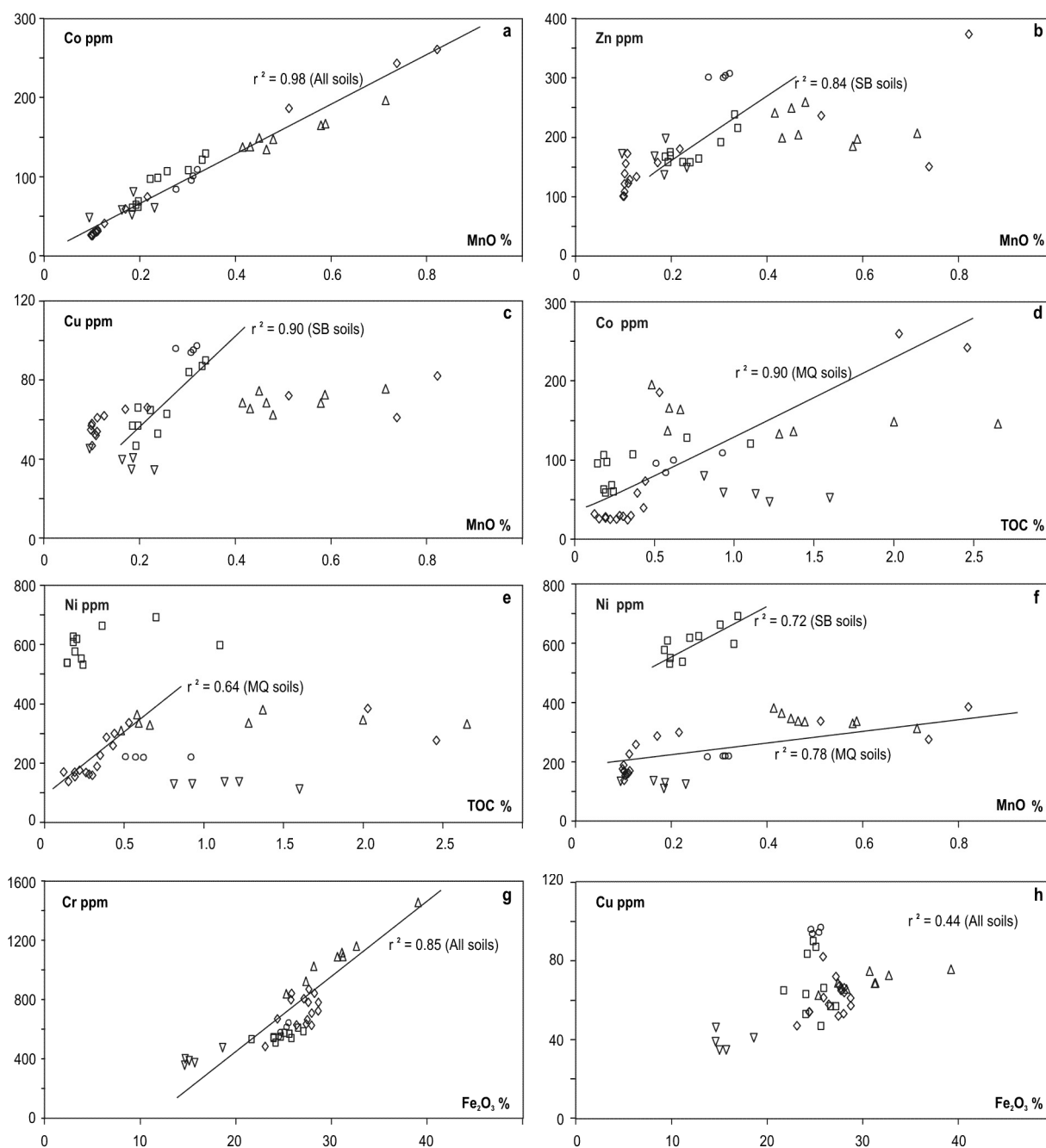


Fig. 4 – Relationships between the heavy metal contents and MnO, TOC and Fe₂O₃ in soil samples. Samples from MQ site: open diamonds; SB site: open squares; MP site: open triangles; AB site: open inverted triangles; LB site: open circles.

TABLE VII
EF-Enrichment Factors calculated against the deepest horizon
values in the studied soil profiles.

	cm	Cr	Co	Ni	Cu	Zn	Hg
MQ	0-30	1.18	8.50	1.76	1.11	1.93	11.21
	31-190	1.14	2.04	1.33	0.98	1.08	2.20
	191-290	0.88	1.01	0.87	0.85	1.06	1.02
SB	0-30	0.89	1.07	1.04	1.16	1.18	nd
	31-110	0.92	0.56	0.89	0.74	0.90	nd
	111-140	0.94	0.97	1.03	0.87	0.95	nd
MP	0-30	0.77	0.97	0.95	0.90	1.11	nd
	31-120	0.99	1.13	0.94	0.97	0.92	nd
LB	0-10	1.05	1.17	0.92	0.91	0.92	nd
	11-40	1.06	1.11	1.01	0.99	1.00	nd
AB	0-10	0.91	0.78	1.02	1.00	0.81	nd
	11-70	0.91	0.82	1.10	1.06	0.93	nd

depth (Blaser et al. 2000). Here we used Sc as the lithogenic element. EF for Ba, Sr, Th, Ta, Hf, Zr, Nb, Cr, Co, Ni, Cu, Zn, and Hg in each horizon of the soil profiles were calculated:

$$EF = [(Me/Sc)_{\text{soil}} / (Me/Sc)_{\text{lowest soil sample}}],$$

where Me = total metal concentration, and Sc = total Sc concentration.

Results for the conservative elements Ba, Sr, Th, Ta, Hf, Zr were between 0.5 and 2.0 (not shown), which is considered in the range of natural variability (Hernandez et al. 2003).

EFs for the heavy metals are displayed in Table VII. Cr, Ni and Zn behave as conservative elements ($0.7 < EF < 1.9$). The only anomalous EF values are found in the MQ site for Co and Hg, particularly in the 0-30 cm horizon (8.50 and 11.21, respectively). In the 31-190 cm horizon, EF values for Co and Hg just slightly exceeded the upper limit considered to be in the range of natural variability (2.04 and 2.20, respectively).

The very high EF values for Hg in the uppermost soil horizon of the MQ profile are probably related to atmospheric deposition from anthropogenic sources. There is consistent evidence that long-range atmospheric transport and deposition of Hg emitted mainly from mining and industrial activities are responsible for Hg pollution in surface soils even in pristine areas (Fitz-

gerald et al. 1998, Hylander and Meili 2003, Lindberg et al. 2007). Furthermore, in the Fernando de Noronha island, a signal of atmospherically transported human-related Hg emissions was detected in the sediments of a small lake (Oliveira et al. 2009). On the other hand, the tendency to form quite stable complexes with humic compounds (Schlüter and Gaeth 1997, Valle et al. 2005) could have also contributed to the accumulation of Hg in the upper horizons of the MQ soil profile.

Co, unlike Hg, is not a volatile element and could hardly be atmospherically transported in the absence of local pollution sources. Moreover, Co presents a very high geochemical affinity for Mn, being incorporated in the octahedral layers of the secondary Mn oxides formed during weathering (Manceau et al. 1987). Thus, in the MQ soils, high concentrations of Co in the 0-30 cm horizon is probably related to the manganese oxides that are also very concentrated in the same horizon (the EF value for Mn = 6.9 is of the same order of that for Co = 8.5).

CONCLUSIONS

Soils of the Fernando de Noronha island developed from the highly alkaline and silica-undersaturated volcanic rocks of the Remédios and Quixaba Formations. The order of heavy metal abundances measured in these soils was: Cr > Ni > Zn > Co > Cu. The un-

usually high heavy metal concentrations of soils, generally well above the world averages, can be explained by the anomalous contents of these elements in the parent rocks, and the abundance of non-crystalline phases (particularly manganese and iron oxides and hydrous oxides) formed during pedogenesis.

The variations in the mineralogical and chemical composition among different soils can be interpreted as the result of variation in the composition of the lava flows. Soils developed from the nepheline basalts of the Quixaba Formation (MQ, SB, and MP sites) present higher Fe, Co, Ni and Cr contents than soils formed from the less mafic rocks of the Remédios Formation, corresponding to the AB site. These contain more Si, K, Ba, Sr, Zr, Hf, and U. LB soils, developed under the influence of a more acid lithology, which is a body of alkaline trachyte (Remédios Formation), are the most enriched in Cu and Zn of all soils examined.

The geochemical variations within the examined profiles allowed to identify the role of manganese oxides and/or organic matter in the distribution of Zn and Co, and, to a lesser extent, of Cu and Ni. Cr is probably adsorbed or coprecipitated mostly with iron oxides and hydrous oxides. Heavy metals do not appear to show a significant affinity for clay minerals. In the MQ site, Hg concentrations found in the 0-30 cm horizon are one order of magnitude above those in the deeper horizons of the soil profile. Such accumulation is probably related to global long-range atmospheric transport and deposition of anthropogenic Hg. The affinity for organic matter could have further favoured the accumulation of Hg in the topsoil.

ACKNOWLEDGMENTS

The authors are particularly grateful to Dr. René Boulet and Dr. Heloisa Filizola for their helpful assistance in soil sampling. Dr. A. Siffedine and Prof. E. Menor are also acknowledged for participation in fieldwork. Financial support was provided by the Brazilian Agencies Fundação de Amparo à Pesquisa do Estado de São Paulo (FAPESP) and Conselho Nacional de Desenvolvimento Científico e Tecnológico (CNPq). We also want to acknowledge Jim Hesson for revising the English.

RESUMO

Este trabalho examina o papel da rocha parental, dos processos pedogenéticos e da poluição aerotransportada na acumulação dos metais pesados nos solos de uma ilha oceânica remota, Fernando de Noronha, Brasil. Foram estudados cinco perfis de solo desenvolvidos a partir de diferentes rochas vulcânicas. A composição mineralógica e as concentrações totais de elementos maiores e traços foram determinadas em 43 amostras. Os intervalos de concentração obtidos para os metais pesados foram: Co: 26-261 ppm; Cu: 35-97 ppm; Cr: 350-1446 ppm; Ni: 114-691 ppm; Zn: 101-374 ppm; Hg: 2-150 ppb. A composição dos solos é fortemente afetada pelo caráter geoquímico da rocha parental. A pedogênese parece ser responsável pela acumulação de Zn, Co e, em menor grau, de Ni e Cu, nos horizontes superiores dos perfis de solo, enriquecidos em Mn e em carbono orgânico. A influência pedogenética pode também explicar a relação observada entre Cr e Fe. Hg foi provavelmente adicionado ao solo por transporte atmosférico de longa distância. Sua acumulação no horizonte do topo do perfil de solo foi adicionalmente favorecida pela formação de complexos estáveis com a matéria orgânica. Os minerais de argila não parecem ter tido papel importante na fixação dos metais pesados.

Palavras-chave: metais pesados, solos, mercúrio antrópico, Fernando de Noronha.

REFERENCES

- ALMEIDA FFM DE. 1955. Geologia e petrologia do Arquipélago de Fernando de Noronha. Departamento Nacional da Produção Mineral – DNPM, Brasil, Monografia 13, 181p. (Unpublished).
- BAIZE D AND STERCKEMAN T. 2001. On the necessity of knowledge of the natural pedo-geochemical background content in the evaluation of the contamination of soils by trace elements. *Sci Total Environ* 264: 127–139.
- BLASER P, ZIMMERMANN S, LUSTER J AND SHOTYK W. 2000. Critical examination of trace element enrichments and depletions in soils: As, Cr, Cu, Ni, Pb and Zn in Swiss forest soils. *Sci Total Environ* 249: 257–280.
- CASARINI DCP, DIAS CL AND GAETA MN. 2001. Relatório de estabelecimento de valores orientadores para solos e águas subterrâneas no Estado de São Paulo, CETESB, 245 p.
- CHEN HM, ZHENG CR, TU C AND ZHU YG. 1999. Heavy metal pollution in soils in China: status and counter-measures. *Ambio* 28: 130–131.

- CORDANI UG. 1970. Idade do vulcanismo do Oceano Atlântico Sul. *Bol Inst Geoc Astron Univ S Paulo* 1: 1–75.
- FAO. 1990. Guidelines for Soil Profile Description. Third edition (revised). Soil Resources, Management and Conservation Service, Land and Water Development Division, FAO, Rome.
- FITZGERALD WF, ENGSTROM DR, MASON RP AND NATER EA. 1998. The case for atmospheric mercury contamination in remote areas. *Environ Sci Technol* 32: 1–7.
- GUNN BM AND WATKINS ND. 1976. Geochemistry of Cape Verde Islands and Fernando de Noronha. *Geol Soc Am Bull* 87: 1089–1100.
- HERNANDEZ L, PROBST A, PROBST JL AND ULRICH E. 2003. Heavy metal distribution in some French forest soils: evidence for atmospheric contamination. *Sci Total Environ* 312: 195–219.
- HORCKMANS L, SWENNEN R, DECKERS J AND MAQUIL R. 2005. Local background concentrations of trace elements in soils: a case study in the Grand Duchy of Luxembourg. *Catena* 59: 279–304.
- HYLANDER LD AND MEILI M. 2003. 500 years of mercury production: global annual inventory by region until 2000 and associated emissions. *Sci Total Environ* 304: 13–27.
- KABATA-PENDIAS A AND PENDIAS H. 1992. Trace elements in soils and plants. 2nd ed., CRC Press, London, 413 p.
- LASHERAS ADOT E, PLANO ISC, REIXACH JG AND VALENCIA DE. 2006. Geochemical inheritance of soils that develop from volcanic rocks (Navarra, Western Pyrenees). *Geoderma* 135: 38–48.
- LINDBERG S, BULLOCK R, EBINGHAUS R, ENGSTRON D, FENG X, FITZGERALD W, PIRRONI N, PRESTBO E, AND SEIGNEUR C. 2007. A synthesis of progress and uncertainties in attributing the sources of mercury in deposition. *Ambio* 36: 19–32.
- LOPES RP AND ULBRICH MNC. 2006. Rochas vulcânicas da Formação Quixaba de Fernando de Noronha, PE: química mineral e litogeoquímica. *Rev Bras Geoc* 36(1): 35–48.
- MANCEAU A, LLORCA S AND CALAS G. 1987. Crystal-chemistry of cobalt and nickel in lithiophorite and asbolane from New Caledonia. *Geochim Cosmochim Acta* 51: 105–113.
- MORI PE, REEVES S, CORREIA CT AND HAUKKA M. 1999. Development of a fused glass disc XRF facility and comparison with the pressed powder pellet technique at Instituto de Geociências, São Paulo University. *Rev Bras Geoc* 29(3): 441–446.
- NESBITT HW AND YOUNG GM. 1982. Early Proterozoic climates and plate motions inferred from major element chemistry of lutites. *Nature* 299: 715–717.
- NRIAGU JO. 1989. A global assessment of natural sources of atmospheric trace metals. *Nature* 338: 47–49.
- OLIVEIRA SMB DE, PESSEDA LCR, GOUVEIA SEM, BABINSKI M AND FAVARO DIT. 2009. A geochemical and lead isotopic record in a small pond in a remote equatorial island, Fernando de Noronha, Brazil. *Holocene* 19(3): 433–442.
- PALUMBO B, ANGELONE M, BELLANCA A, DAZZI C, HAUSER S, NERI R AND WILSON J. 2000. Influence of inheritance and pedogenesis on heavy metal distribution in soils in Sicily, Italy. *Geoderma* 95: 247–266.
- PESSEDA ET AL. 2008. Interdisciplinary paleovegetation study in the Fernando de Noronha Island (Pernambuco State), northeastern Brazil. *An Acad Bras Cienc* 80: 677–691.
- REIMANN C, ARNOLDUSSEN A, ENGLMAIER P, FILZMOSER P, FINNE TE, GARRET RG, KOLLER F AND NORDGULEN O. 2007. Element concentrations and variations along a 120-km transect in southern Norway – Anthropogenic vs. geogenic vs. biogenic element sources and cycles. *Appl Geochem* 22: 851–871.
- SALONEN VP AND KIRSTI KN. 2007. Influence of parent sediments on the concentration of heavy metals in urban and suburban soils in Turku, Finland. *Appl Geochem* 22: 906–918.
- SCHLÜTER K AND GAETH S. 1997. Modelling leaching of inorganic Hg(II) in a Scandinavian iron-humus in a podzol-validation and long-term leaching under various deposition rates. *Water Air Soil Poll* 96: 301–320.
- SOUBRAND-COLIN M, BRIL H, NÉEL C, COURTIN-NOMADE A AND MARTIN F. 2005. Weathering of basaltic rocks from the French Massif Central: origin and fate of Ni, Cr, Zn and Cu. *Can Mineral* 43: 1077–1091.
- ULBRICH MNC, MARINGOLO V AND RUBERTI E. 1994. The geochemistry of alkaline volcanic-subvolcanic rocks from the Brazilian Fernando de Noronha Archipelago, South Atlantic Ocean. *Geochim Brasil* 3(1): 21–39.
- VALLE CM DE, SANTANA GP, AUGUSTI R, EGREJA FB AND WINDMOLLER CC. 2005. Speciation and quantification of mercury in Oxisoil, Udisoil, and Spodosol from Amazon (Manaus, Brazil). *Chemosphere* 58: 779–792.

- WEAVER BL. 1990. Geochemistry of highly-undersaturated ocean island basalt suites from the South Atlantic Ocean: Fernando de Noronha and Trindade islands. *Contrib Mineral Petr* 105: 502–515.
- WEDEPOHL KH. 1995. The composition of the continental crust. *Geochim Cosmochim Acta* 59(7): 1217–1232.