ПОЧВОЗНАНИЕ АГРОХИМИЯ И ЕКОЛОГИЯ, ГОД. XLV, № 2
SOIL SCIENCE AGROCHEMISTRY AND ECOLOGY, VOL. XLV, № 2
София. 2011. Sofia

JAUME BECH*, SANDRA UGALDE*, NÚRIA ROCA*,, LUIS TONON***, GIOVANI LARRIVA***, MARIA SOKOLOVSKA******

**Universitat de Barcelona, Spain*
***Universidad Nacional del Centro de la Provincia de Buenos Aires, Argentina*
****Universidad de Cuenca, Equador*
*****Forest Research Institute, BAS, Sofia, Bulgaria*

Concentration and Distribution of Heavy Metals in Andisols and Vertisols of the Azuay Andes (Equador)

Abstract

At present many governmental and environmental bureaus are interested in establishing reliable soil quality criteria for heavy metals to enable the detection of polluted sites. To evaluate the variation of heavy metal natural concentration and to assess heavy metal contamination in soils, it is necessary to survey heavy metal baseline levels in order to understand their migration and distribution during pedogenesis. Many nationwide projects report elemental baseline values in soils. Baseline levels of heavy metals in soils have also been determined at local scales. Data is scarce on qualitative and quantitative trace elements content of Equatorian soils. The soils in the Azuay Andes (S of Equator) are thought to be generally non-contaminated. The objectives of this study are: 1) to determine the natural concentrations of seven heavy metals (Cd, Co, Cr, Cu, Ni, Pb and Zn) in soils of two orders, Andisol and Vertisol, in Azuay Andes, and 2) to evaluate the correlation between metal concentration and soil properties. Soil samples were ground in an agate mill prior to pseudototal heavy metal analysis. Cadmium, Co, Cr, Cu, Ni, Pb and Zn were determined by a masses spectrometer (MS-ICP) after aqua regia extraction according to ISO standard procedures. Soil particle size distribution, organic carbon, electrical conductivity and pH have been previously determined. Andisols are dominated by amorphous aluminium silicates and Al-organic complexes. The soils of volcanic area usually have an Ah-Bh-Bhs/Bw-C horizon sequence. The Ah horizon is dark-coloured and normally very high in organic matter, ranging from 6.4 to 15.2%. A strong rise in pH upon addition of a fluoride solution is used to signal the presence of allophane. The pH usually rises to 10.5 bellow 20 cm. The range of total soil values in $mgkg^{-1}$ is as follows: Cd (0.03-0.3), Co (0.8-5), Cr (7-15), Cu (9-25), Ni (2-4), Pb (11-41) and Zn (12-37). All heavy metal contents, except for Cd, are strongly correlated with pH. For the pseudototal fraction, there was significant difference between the soil layers, in regards to complex profile development. Vertisols are dominated by specific clay minerals with intersecting slickenside's in the subsoil and wedge-shaped structural aggregates in the subsurface soils (10-100 cm). These soils have an A-Bss-Bssg-Cg horizon sequence with deep and dark topsoils and strong gley in the subsurface soil (> 65 cm). The range of total soil values in $mgkg^{-1}$ is as follows: Cd (0.05-0.2), Co (9-40), Cr (11-72), Cu (7-50), Ni (7-45), Pb (11-18), Zn (67-110). Only Cu, Ni and Zn are strongly correlated with clay content. For the pseudototal fraction, there was no significant difference between the soil horizons, in regards to the strong homogenisation by shrinkage and swelling. In general, metal content in soils decreased significantly from Vertisol to Andisol reflecting the pedogenic factors that determine pH, organic matter and clay content variation between soil profiles.

Key words: trace elements, baseline values, soils orders

Introduction

Nowadays, trace elements from several origins can be found in the soil. These are categorized as lithogenic elements, directly inherited from the lithosphere or parent material; pedogenic elements, lithogenic in origin but subjected to pedogenic processes resulting in altered concentrations and distributions in soil layers and particles; and anthropogenic elements, due directly or indirectly to human activities (Kabata-Pendias, 2001).

Elevated concentrations of trace elements in the soil-water-plant ecological system are of great concern because of possible influences on the food chain. The major external source of heavy metals in the soil is usually pollution caused by anthropogenic activities such as metal mining, smelting and processing. Additionally, diffuse pollution by wet and dry deposition has resulted in the long-term accumulation of heavy metals all over the world.

Although the soils in the Azuay Andes (South of Equator) are thought to be generally non-contaminated, there is a complex mining district near the studied area characterized by the influence of many superimposed geological events and ore-forming processes. Therefore, it is extremely important to establish the baseline abundance of elements in soils as reference values for evaluating changes in their concentrations and to be able to define the elements origins (Alonso Rojo et al., 2004).

Natural trace element concentrations are influenced by the parent material and weathering process, both of which participated in producing the soil, although they themselves are also a function of other soil forming factors such as topography, biota, and time. Therefore, baseline values are characterized by regional variability and it is a function of time. Data is scarce on qualitative and quantitative trace element content of Equatorian soils.

The objectives of this study are:

1) to determine the concentrations of seven heavy metals (Cd, Co, Cr, Cu, Ni, Pb and Zn) in soils of 2 orders, Andisol and Vertisol, in Azuay Andes, and

2) to evaluate the correlation between metal concentration and soil properties.

Material and Methods

The study area is located in the Paramo area of the Royal Andes at Azuay Province (Equador). The paramo is a high altitude neotropical grassland ecosystem, located between the continuous forest border (~3500 m) and the eternal snow line (~5000 m) (Dinerstein et al., 1995). The climate of the study area is characterized by rather high rainfall, between 1200 to 2000 mm per year, but well distributed and generally with low intensities. The yearly average temperature (7 °C) is constant with high diurnal amplitudes. In geological terms our study area is a valley formed over a pre-existing volcanic basement which consists of rhyolite and andesite volcanic tuff.

A representative four soil profiles of two soil orders (Andisol -A- and Vertisol -V-) were studied and sampled. The sampling depth was limited by the bottom of the soil profile and all the soil horizons were sampled. Since complete profiles were collected, the vertical and horizontal variability of the soil parameters (texture, pH, organic matter) were taken into account. The soil samples were analysed as follows: particle size was determined by the pipette method, soil pH was measured in a 1: 2.5 soil: water, 1: 2.5 KCl and 1N NaF; and finally, organic carbon was determined by the Walkley-Black methods (Burt, 2004). Soil samples were ground in an agate mill prior to pseudototal heavy metal analysis. Cadmium, Cr, Cu, Co, Cr, Ni, Pb and Zn were determined by a ICP-MS spectrometer (Elan 6000) after *aqua regia* extraction according to ISO standard procedures (ISO, 1995). Quality control was assured by the use of duplicate analyses performed on all samples and the use of reagent blanks. The detection limits for the metals were: Cd 0.02 $mg \cdot kg^{-1}$, Co 0.10 $mg \cdot kg^{-1}$, Cr 0.20 $mg \cdot kg^{-1}$, Cu 0.20 $mg \cdot kg^{-1}$, Ni 0.20 $mg \cdot kg^{-1}$, Pb 0.05 $mg \cdot kg^{-1}$ and Zn 0.50 $mg \cdot kg^{-1}$.

Arithmetic mean (AM) and arithmetic standard deviation (ASD) were used to estimate the central tendency of the data. The relation between the elements and between some soil parameters have been assessed by Pearson correlation.The mean comparison was determined with ANOVA at 95% of confidence and the Tukey test of signification. Before ANOVA normality was analyzed with the Test of Shapiro and Wills. Descriptive

statistics were calculated using SPSS (SPSS, 2000).

Results and Discussion

Table 1 shows selected properties of the soils at the different profile sites. Andisols are dominated by amorphous aluminum silicates and Al-organic complexes. The soils of volcanic area usually have an Ah-Bh-Bhs/Bw-C horizon sequence. The Ah horizon is dark-coloured and normally very high in organic matter, ranging from 6.4 to 15.2%. A strong rise in pH upon addition of a fluoride solution is used to signal the presence of allophane. The pH usually rises to 10.5 bellow 20 cm.

Vertisols are dominated by smectitic clay minerals with intersecting slickensides in the subsoil and wedge-shaped structural aggregates in the subsurface soils (10-100 cm). These soils have an A-Bss-Bssg-Cg horizon sequence with deep and dark topsoils and strong gley in the subsurface soil (> 65 cm) (Table 1).

Certain heavy metals correlate with some soil properties (Table 2). All heavy metal contents, except for Cd and Pb, are strongly correlated with pH. This parameter has importance for metal mobility and distribution, substantially increasing mobility because of the extreme acid environment (Sauve et al., 2000). Only Cu and Ni are strongly correlated with clay content. Close relationships between clay content and many trace elements have been found in other studies (Adriano, 1986), also organic matter has a marked affinity to trace elements forming organo-mineral complexes (Alloway, 1995). Understanding these relationships may help determine the influence of soil forming processes on the depth distribution of heavy metals of natural origin (Bech et al., 1998; Roca et al., 2008; Tume et al., 2008).

The range of pseudototal andisols values in $mgkg^{-1}$ is as follows: Cd (0.03-0.3), Co (0.8-5), Cr (7-15), Cu (9-25), Ni (2-4), Pb (11-41) and Zn (12-37) while the range of pseudototal vertisols values in $mgkg^{-1}$ is as follows: Cd (0.05-0.2), Co (9-40), Cr (11-72), Cu (7-50), Ni (7-45), Pb (11-18), Zn (67-110). The mean comparison and

Table 1. Some soil properties of the Andisol (A) and Vertisol (V) topographic sequence

Profile	Geographic position	Horizon	Depth, cm	pH			OC, %	Clay, %	Sand, %
				H_2O	KCl	NaF			
A1	02°46´39´´S 79°13´34´´W 3989 m	A1	0-5	4.8	4.0	8.3	6.4	27.5	58.2
		A2	5-8	5.1	3.9	8.2	15.3	-	-
		Bhs	18-38	5.0	4.0	11.2	8.5	-	-
		Bwc	38-55	4.4	4.0	11.7	3.9	27.2	63.4
		C	55-65	4.4	4.0	12.0	1.7	21.3	65.4
		R	>65	4.7	4.2	12.0	1.4	19.2	66.2
A2	02°46´22´´S 79°14´23´´W 4.200 m	A1	0-6	4.4	3.7	9.7	14.7	-	-
		A2	6-27	4.3	3.6	9.9	12.4	-	-
		Bh	27-47	4.8	3.9	10.5	15.7	-	-
		Bhs	47-58	5.5	3.9	11.6	4.8	26.7	48.4
		C	>58	4.4	4.0	10.9	1.0	26.9	28.7
V1	02°59´19´´S 3.122 m	A	0-15	5.6	-	-	5.8	52.9	18.4
		Bsso	15-48	5.8	-	-	3.4	50.9	20.0
		Bssg1	48-88	5.5	-	-	1.8	49.9	19.0
		Bssg2	88-120	5.7	-	-	2.1	51.4	16.6
		Cg	>120	5.4	-	-	0.7	43.0	29.3
V2	03°00´07´´ S 3.144 m	A	0-17	4.8	-	-	4.5	42.5	23.4
		Bssg1	17-66	4.4	-	-	3.4	68.7	4.9
		Bssg2	66-115	4.4	-	-	3.5	76.2	3.0
		BC	115-250	4.7	-	-	4.4	84.5	2.3
		C	>250	4.9	-	-	0.2	24.8	33.7

Table 2. Pearson's correlation coefficient of heavy metal with soil properties of Azuay soils profiles

	Cd	Co	Cr	Cu	Ni	Pb	Zn
pH	0,218	0.734[a]	0.719[a]	0.458[b]	0.679[a]	-0,362	0.567[a]
OC, %	0.541[a]	- 0.446[b]	-0,332	-0,172	-0,346	-0,259	- 0.546[a]
*Clay,%	-0,077	0,27	0,444	0.837[a]	0.496[b]	-0,304	0,41

Total soil samples, n = 22, *n = 17.

[a] Correlation is significant at the 0.01 level.

[b] Correlation is significant at the 0.05 level.

Tukey Test of signification of 4 soils studied are shown in Figure 2. The variance analysis showed highly significant differences (p >0.01) for Cu, Cr, Co, Ni and Zn, being in higher concentrations in V3 profile. All metals, except Cu, showed significant differences for the both Vertisols. However, the Andisols only showed significant differences for the Cu. In general, metal content in soils decreased significantly from Vertisol to Andisol reflecting the pedogenic factors that determine pH, organic matter and clay content variation between soil profiles (Figure 1). Nevertheless, a study by Arbelo (2000) in natural soils from Canary Island, the total content of heavy metals was higher in Andosols than in Vertic soils, as a consequence of differential content and different alteration conditions of the basalts where they are developed.

The distribution of metals with depth represents a clear differentiation in heavy metal content based on their degree of profile development. In Profile V1, all elements, except Ni, follow the same pattern. Ni concentration increase abruptly between 88 and 120 cm (Figure 2). As for V2 profile Zn is accumulated at the 250 cm decreasing slightly towards the superficial horizons. Cu, Cr and Ni are accumulated from 115 to 17 cm, being concentrated more in the 115-250 cm. Pb almost does not presents variations, mean while

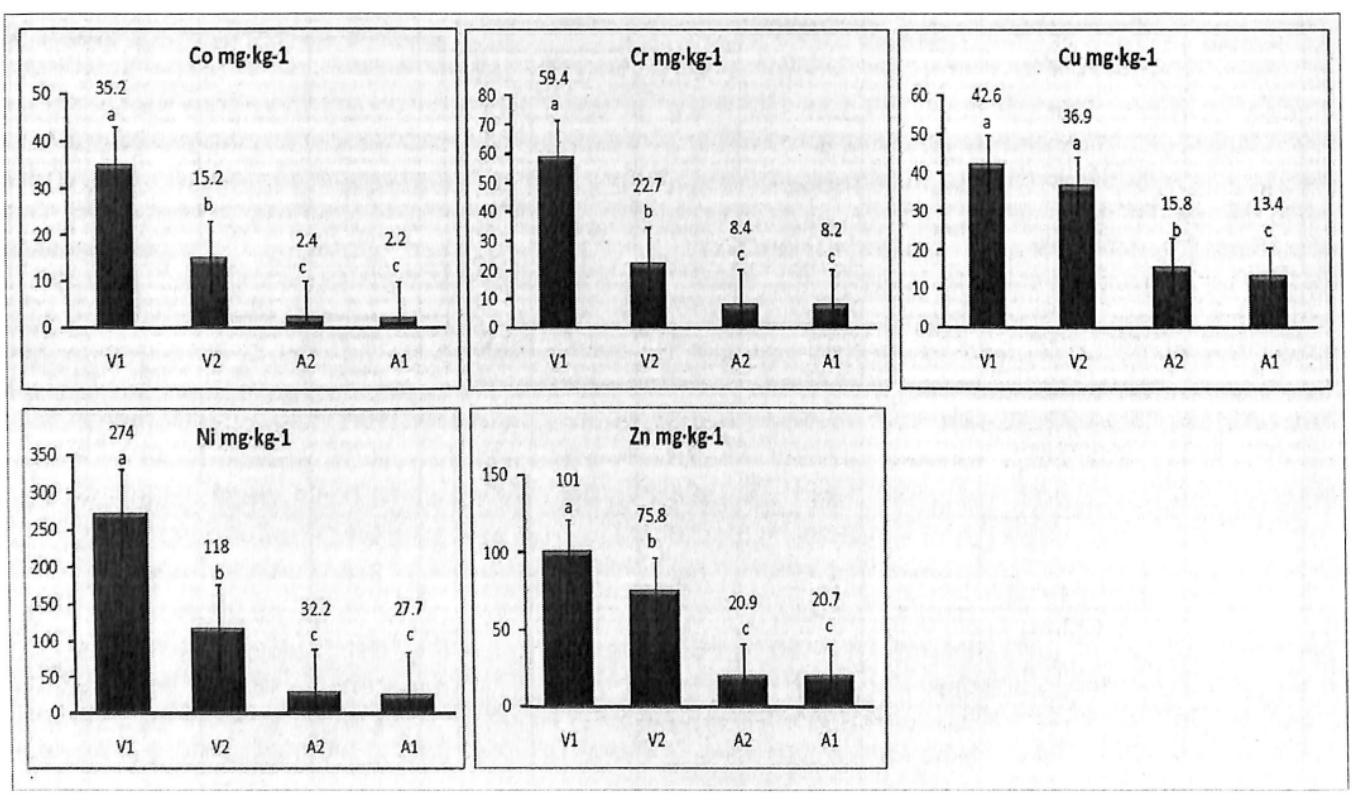


Fig. 1. Mean values, standard deviation and confidence intervals (mg·kg^{-1}) of heavy metals in Andisols (A) and Vertisols (V) of Azuay Andes. For any given element values followed by the same letter do not differ at p = 0.05

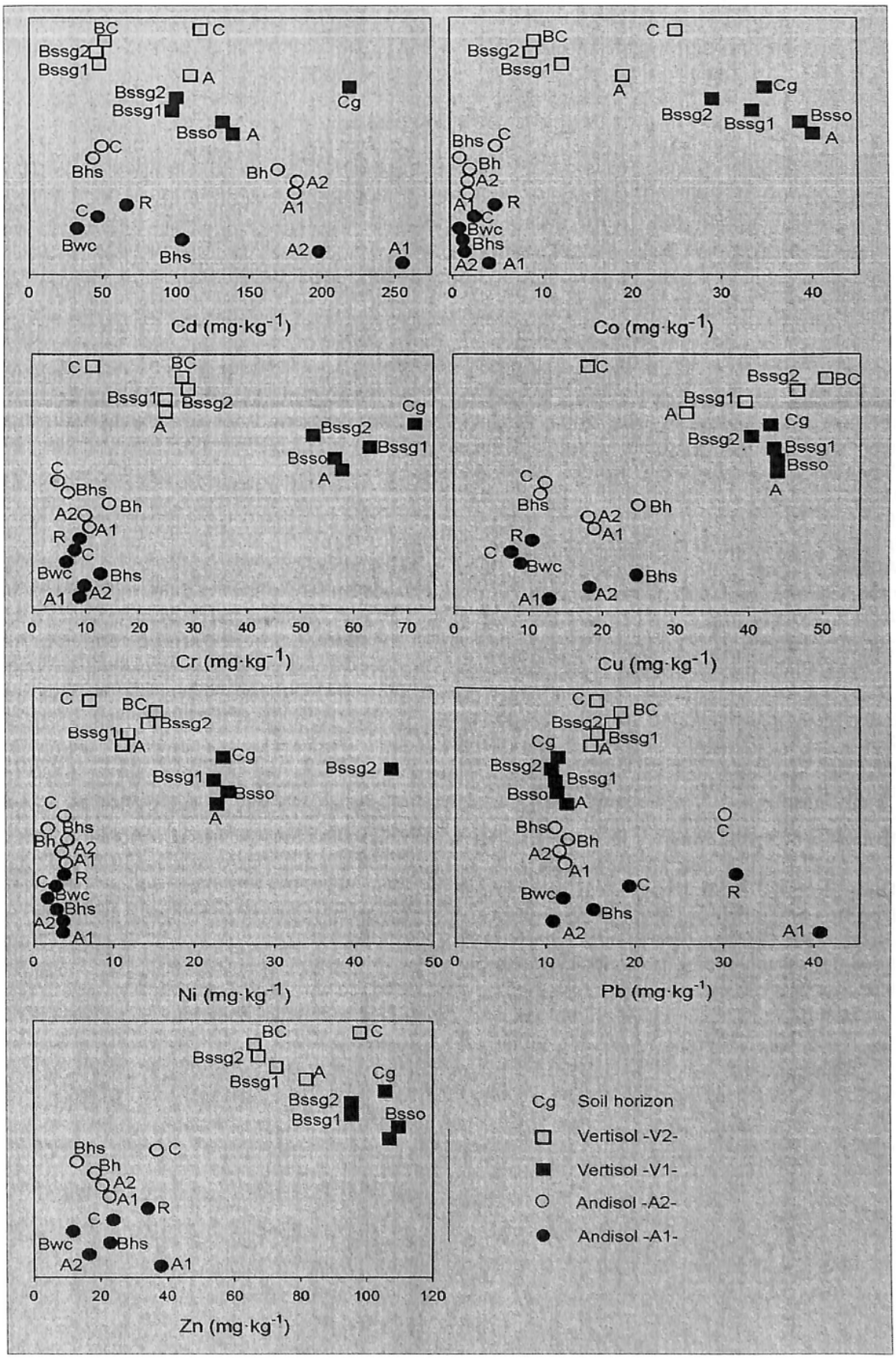


Fig. 2. Distribution of metals with depth

Co is being accumulated at the 250 cm. (Figure 2). There was no significant difference between the soil horizons in Vertisols, in regards to the strong homogenisation by shrinkage and swelling.

Conclusions

In terms of soil properties, most heavy metals, excluding Cd and Pb, significantly correlated with pH. The content of heavy metals is highly dependent on the soil order. In general, metal content in soils decreased significantly from Vertisol to Andisol reflecting the pedogenic factors that determine pH, organic matter and clay content variation between soil profiles. The approach applied to the Azuay soils profiles has allowed two dimensional descriptions (depth and length) to the spatial variability of heavy metal concentrations.

References

Alonso Rojo P, F. Santos Frances, A. García-Sánchez and E. Alvarez-Ayuso. 2004. Baseline Concentrations of Heavy Metals in Native Soils of the Salamanca and Valladolid Provinces, Spain. *Arid and Land Research and Management*, 18: 241-250

Adriano, D. C. 1986. Trace Elements in the Terrestrial Environment, Springer-Verlag, New York.

Alloway, B. J. 1995. Heavy Metals in Soils. Blackie Academic and Profesional. Londres.

Arbelo Rodríguez, C., R. Díaz Díaz and A. Rodríguez Rodríguez. 2000. Incidencia sobre el Suelo de las Emisiones de Dos Plantas Incineradoras de RSU's (La Palma, Canarias). Contaminación por Metales Pesados. *Edafología*, Vol. 7-3: 327-335

Bech, J., F. J. Tobías, N. Roca, J. Rustullet. 1998. Trace Elements in Some Mediterranean Red Soils from the NE of Spain. *Agrochimica*, XLII (1-2): 26-40

Burt, R. 2004. Soil Survey Laboratory Methods Manual. Soil Survey Investigations Report n 42.

Dinerstein, E., D. M. Olson, D. J. Graham, A. L. Webster, S. A. Primm, M. P. Bookbinder and G. Ledec. 1995. A Conservation Assessment of the Terrestrial Ecoregions of Latin America and the Caribbean. The World Bank: 174

ISO (The international Organization for Standardization). 1995. Soil Quality –Extraction of Trace Metals Soluble in *Aqua Regia*. International Standard ISO 11466.

Kabata-Pendias, A. 2001. Trace Elements in Soils and Plants, CRC Press, Boca Raton, FL, USA.

Roca, N., M. S. Pazos and J. Bech. 2008. The relationship between WRB soil units and heavy metals content in soils of Catamarca (Argentina). *Journal of Geochemical Exploration*, 96: 77-85

Sauve, S, W. Henderson and H. E. Allen. 2000. Solid Solution Partitioning of Metals in Contaminated Soils: Dependence on pH, Total Metal Burden, and Organic Matter. *Environmental Science Technology*, 34: 1125-1131

Tume, P., J. Bech, L. Tume, J. Bech, F. Reverter, L. Longan and P. Cendoya. 2008. Concentrations and Distributions of Ba, Cr, Sr, V, Al and Fe in Torrelles Soil Profiles (Catalonia, Spain). *Journal of Geochemical Exploration*, 96: 94-105

Wolf, T. 1975. Geografía y Geología del Ecuador. Ed. Casa de la Cultura Ecuatoriana. Quito (Ecuador).