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Pedo-geochemical baseline content levels and soil quality reference values of trace elements in soils from the Mediterranean (Castilla La Mancha, Spain)

Research Article

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Abstract: To evaluate trace element soil contamination, geochemical baseline contents and reference values need to be established. Pedo-geochemical baseline levels of trace elements in 72 soil samples of 24 soil profiles from the Mediterranean, Castilla La Mancha, are assessed and soil quality reference values are calculated. Reference value contents (in mg kg^{-1}) were: Sc 50.8; V 123.2; Cr 113.4; Co 20.8; Ni 42.6; Cu 27.0; Zn 86.5; Ga 26.7; Ge 1.3; As 16.7; Se 1.4; Br 20.1; Rb 234.7; Sr 1868.4; Y 38.3; Zr 413.1; Nb 18.7; Mo 2.0; Ag 7.8; Cd 4.4; Sn 8.7; Sb 5.7; I 25.4; Cs 14.2; Ba 1049.3; La 348.4; Ce 97.9; Nd 40.1; Sm 10.7; Yb 4.2; Hf 10.0; Ta 4.0; W 5.5; Tl 2.3; Pb 44.2; Bi 2.2; Th 21.6; U 10.3. The contents obtained for some elements are below or close to the detection limit: Co, Ge, Se, Mo, Ag, Cd, Sb, Yb, Hf, Ta, W, Tl and Bi. The element content ranges (the maximum value minus the minimum value) are: Sc 55.0, V 196.0, Cr 346.0, Co 64.4, Ni 188.7, Cu 49.5, Zn 102.3, Ga 28.7, Ge 1.5, As 26.4, Se 0.9, Br 33.0 Rb 432.7, Sr 3372.6, Y 39.8, Zr 523.2, Nb 59.7, Mo 3.9, Ag 10.1, Cd 1.8, Sn 75.2, Sb 9.9, I 68.0, Cs 17.6, Ba 1394.9, La 51.3, Ce 93.5, Nd 52.5, Sm 11.2, Yb 4.2, Hf 11.3, Ta 6.3, W 5.2, Tl 2.1, Pb 96.4, Bi 3.0, Th 24.4, U 16.4 (in mg kg^{-1}). The spatial distribution of the elements was affected mainly by the nature of the bedrock and by pedological processes.

The upper limit of expected background variation for each trace element in the soil is documented, as is its range as a criterion for evaluating which sites may require decontamination.

Keywords: trace elements • regional geochemistry • baseline contents • reference values • soils

1. Introduction

Trace element compositions are important for assessing the environmental quality of soils. The first approach for contamination evaluation is the determination of the total trace element content. The natural background con-

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tents of trace elements in soils can be used as a reference. Therefore, to evaluate soil contamination it is important to establish background contents (or geochemical baseline contents) according to soil classes and properties [1, 2]. According to Tack et al. [3] and Reimann & Garrett [4]; the "natural background" contents are those derived solely from natural processes. The "actual background" content is defined as the typical content of an element found in a soil which has not been subject to point-source polluting impacts, e.g. contaminated with waste materials, polluted by industrial processes, etc. Since soils exposed to anthropogenic activities may accumulate large quantities of trace elements, it has become difficult to estimate the true geochemical background levels of trace elements in soils. Geochemical background contents should represent natural elemental contents in soils without human influence. Geochemical baseline contents (used to express a range of elemental content around a mean) in contrast, represent a content specific to one area and time and are not always true backgrounds [1, 5].

Moreover, there is a need to establish the levels of trace elements currently found in common soils. To achieve this objective previous studies have identified background levels, that is, the normal contents of soils before point-source pollution of anthropogenic origin [6–11]. These studies are initiated as a result of the need to evaluate human pollution [12, 13]. In recent decades soil quality reference values are being developed in different regions of Spain, revealing that their values may differ between geographical zones. The landscape-geochemistry variety of each zone or territory is determined by many factors, such as bedrock, lithology, pedology, etc. Several Spanish regions have established background and reference values: Catalonia [14]; the Basque Country [15]; Andalucia [16]; Castilla y Leon [17] and Madrid [18]. Royal Decree 9/2005 [19] proposes obtaining reference values for metals.

It is vital to know the background levels (reference values) for trace elements for each type of soil in each area of study [20]. However, two types of reference values are differentiated: generic, relating to a single value for the entire area of study, regardless of soil type; and specific, which depends on the properties of the type of soil in the area.

This study presents baseline contents and generic reference values of 38 trace elements (Sc, V, Cr, Co, Ni, Cu, Zn, Ga, Ge, As, Se, Br, Rb, Sr, Y, Zr, Nb, Mo, Ag, Cd, Sn, Sb, I, Cs, Ba, La, Ce, Nd, Sm, Yb, Hf, Ta, W, Tl, Pb, Bi, Th and U) for the Region of Castilla La Mancha (Central Spain) in order to obtain criteria that will identify potential contamination impacts and, therefore, determine whether or not a soil is contaminated.

2. Material and methods

2.1. Study area and sampling procedure

The region of Castilla La Mancha lies at the center of the Iberian Peninsula (Figure 1). It has a geological record from the Precambrian to the Quaternary, resulting from the superposition of several sedimentary and orogenic episodes. Its mean altitude is 830 m (2200 m maximum and 280 m minimum) and its basic physiographic features may be summarised as a large flat or nearly flat central area surrounded by an area of moderate relief. Lithologically one can find rocks from Cretaceous-Tertiary sediments (confined to the interior basins), such as limestone, marls, argillites, etc., to gneisses, migmatites, metasediments and granites, which have been subjected to several episodes of deformation and metamorphism. The region has varied ecosystems ranging from deciduous forests, Mediterranean forests, coniferous forests, steppes, moors, salt marshes and wetlands, although a substantial part (>50%) is dedicated to agricultural use. The region is characterized by generally warm temperatures, with winter or spring cold-rainfall, and dry and hot summers, with 300-800 mm average annual precipitation and 10-15°C average mean annual temperature.

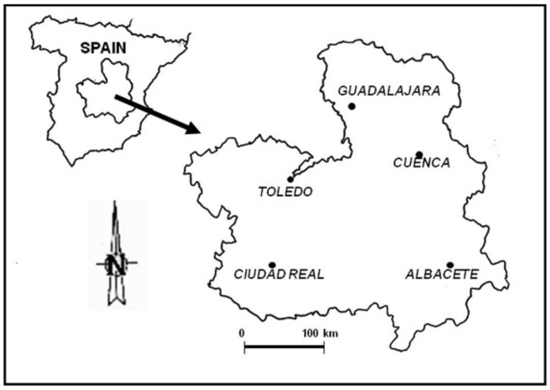

Figure 1. Location map of study area.

In response to this extraordinary variety of factors very varied soils have formed. According to the classification of the FAO [21], one can find Leptosols, Vertisoles, Fluvisols, Kastanozems, Gypsisols, Calcisols, Acrisols, Luvisols, Umbrisols, Cambisols and Regosols, and to a lesser extent Histosols, Antrosols, Technosols, Solonchaks, Chernozems, Phaeozems and Arenosols. Solontezs, Podsols, Nitisols, Ferralsols, Planosols, Stagnosols, Albeluvisoles, Alisols and Lixisols are rare. There are no Cryosols, Andosols, Plinthosols or Durisols. According to the US Soil Taxonomy [22] criteria, there are: Entisols, Inceptisols, Alfisols, Molisols and to a lesser extent Aridisols, Histosols, Vertisols and Ultisols, while Podsols are rare. No Andosols (despite the existence of various volcanic material), Oxisols nor Gelisols were found. The Castilla La Mancha region has a high soil diversity.

Due to high or medium temperatures, and medium to scarce rainfall, the predominant soils of this semi-arid region are Cambisols, Leptosols, Regosols, Calcisols, Vertisols, Umbrisols and Luvisols. These soils have therefore been selected for analysis (Table 1). Soil samples were collected from 24 geo-referenced locations throughout Castilla La Mancha. In each location a surface horizon (A), a subsurface horizon (B or C) and a depth horizon (C or R) were collected. The soil samples were collected with a steel blade and transferred into polyethylene bags for shipment to the laboratory. The samples were air-dried and sieved to remove rock fragments, roots, etc. Care was taken in sampling, preparation and storage to avoid accidental contamination. Soil samples were dried under 40°C and disaggregated.

2.2. Analytical methods

Once in the laboratory, the samples were air-dried and sieved using a 2 mm mesh. Sub-samples were ground in an agate mortar until obtaining a particle size of 74 µm. Total trace element contents of the <2 mm soil samples were determined using XRF, with an EMMA-XRF (Energy-dispersive Miniprobe Multielement Analyzer) unit by Key Analytical (Sudbury, *Canada), using Mo Kα or Mo Kß radiation.* Data quality was assessed by the analysis of duplicates. Clay identification was carried out using a SIEMENS D-5000 diffractometer, (X-ray diffraction of oriented aggreagates, glycolated with ethylene-glycol and heated at 550°C for 2 hours.). The semi-quantification of the components was done using the reflecting power method [23, 24]. Descriptive statistics (mean, median, etc.) were undertaken using SPSS (14.1)

3. Results and discussion

3.1. Trace element contents and clay mineralogy

The contents of trace elements in Castilla La Mancha are shown in Figure 2. These contents were controlled by the geochemical characteristics of the underlying rock and the nature of weathering processes [25]. Because of the small ratio of precipitation to evaporation, the migration of elements down the profile is scarce.

Trace element contents in the study area were similar to those reported for other regions of the world, [1–3, 7, 10, 26–28] or to those analysed in other areas of Spain [11, 14–18]. The baseline contents depend mainly on the geochemistry nature of bed rock.

The mineralogy of the clay fraction from the surface horizons is shown in Figure 6. Illite and kaolinite are dominant, occasionally accompanied by smectite. Calcite and gypsum are also occasionally present.

The basic statistical parameters for each variable (such as mean, minimum and maximum, etc.) are given in Table 2. Thirteen of the elements analyzed (Co, Ge, Se, Mo, Ag, Cd, Sb, Yb, Hf, Ta, W, Tl and Bi) have values at or under the detection limit for the analytical method used, imposing certain limitations on the interpretation.

The element content in profile (Figure 2) displays a variety of patterns, so that sometimes enrichment occurs at the surface, sometimes at depth, and sometimes at the intermediate depth horizon. Finally, some elements show no obvious vertical zonation as they neither increase nor decrease appreciably.

Trace element distributions in soils provide an insight into elemental behaviour during weathering and availability to plants. The low ratio of precipitation to evaporation generally does not favour downward percolations. Due to low rainfall, the semiarid environment provides the optimum conditions for trace elements to be sequestered in the B or C horizons. However, the carbonate content tends to increase with depth and appears to have a negative effect on the contents of trace elements, also noticed by Maqueda et al. [28] and Lachica et al. [29].

Considering the elements individually, Sc shows a slight tendency to increase with depth. V tends to occur in greater amounts in surface soils, with the highest content being found in the Valverde profile (17), developed on basalts. In this same soil (Vertisol), Cr is also high. In other soils element contents oscillate with depth. Although Co tends to occur in below detection limit quantities, it is present in this soil with a high content. This soil is rich in smectite (Figure 2).

Another element that tends to increase at the surface is Ni, but its content is conditioned by that of micaceous minerals and is independent of kaolinite. Cu, As and Ga tend also to increase in the surface horizons, as does Zn, although the latter sometimes falls. In profile 15 (S. Cruz de Mudela, on slates and quartzites) this element appears in high amounts. Mosser [30], remarks that Cr, Ni and Pb are associated with some micas, and Cr can substitute for octahedral Al. According to Hogdson [31] Zn and Cu can be easily retained by smectitic minerals. This occurs in profile 17 (Valverde) where there is also retention of Sc, V Cr, Ni, Rb Sr, Zr, Ba, La, Ce Nd and Cu, which are associated to type 2:1 clay. Knezeck & Ellis [32] remark

Table 1. General and pedological characteristics of investigated soils.

Profile number	Soil Type (FAO, 2006)	Location	Parent Material	Land Use	Coordinates
1	Leptic Regosol (Gypsiric, Siltic)	Ontigola (Toledo)	Gypsums	Uncultivated	0450766 (X) 4425763 (Y)
2	Haplic Luvisol (Chromic, Profondic)	Madridejos (Toledo)	Marls	Dry farming	304534 (X) 4370675 (Y)
3	Vertic Luvisol (Profondic, Rhodic)	La Solana (C. Real)	Argillites	Dry farming	0479715 (X) 4306634 (Y)
4	Haplic Calcisol (Ruptic,Chromic)	Villahermosa (C. Real)	Sandstones/ quarzites	Forest/ dry farming	519091 (X) 4288625 (Y)
5	Haplic Leptosol (Skeletic, Novic)	Alcaraz (Albacete)	Quarzites	Pasture	544057 (X) 4211625 (Y)
6	Cutanic Luvisol (Clayic, Rhodic)	Povedilla (Albacete)	Argillites	Dry farming	0540151 (X) 4282000 (Y)
7	Leptic Luvisol (Humic, Chromic)	El Bonillo (Albacete)	Limestones	Forest/ Reforestation	0537754 (X) 4310260 (Y)
8	Endogleyic Cambisol (Humic, Dystric)	Velada (Toledo)	Granites	Pasture	331058 (X) 4431848 (Y)
9	Calcic Luvisol (Chromic, Abruptic)	Mirabueno (Guadalajara)	Limestones/ marls	Forest	0521246 (X) 4531563 (Y)
10	Haplic Leptosol (Calcaric, Skeletic)	Torremocha (Guadalajara)	Limestones/ calcarenites	Scrub/ pasture	0591915 (X) 4540195 (Y)
11	Leptic Cambisol (Calcaric, Chromic)	Alcolea del Pinar (Guadalajara)	Poligenic/ calcarenites	Dry farming/ pasture	543521 (X) 4543529 (Y)
12	Haplic Regosol (Gypsirc, Calcaric)	Tarancón (Toledo)	Marls/ gypsums	Uncultivated	0504409 (X) 4430745 (Y)
13	Cutanic Luvisol (Chromic , Clayic)	Belmonte (Cuenca)	Limestones/ calcarenites	Dry farming	0519693 (X) 4380744 (Y)
14	Haplic Cambisol (Calcaric, Yermic)	Olivares del Jucar (Cuenca)	Marls	Forest	0554157 (X) 4406257 (Y)
15	Leptic Cambisol (Dystric, Skeletic)	S. Cruz De Mudela (C. Real)	Slates/ quarzites	Uncultivated/ Dry farming	459873 (X) 4278354 (Y)
16	Calcic Luvisol (Rhodic, Profondic)	Bazán (C. Real)	Quarzites/ slates	Dry farming	0457194 (X) 4270927 (Y)
17	Calcic Vertisol (Humic, Pellic)	Valverde (C. Real)	Basalts	Dry farming	409417 (X) 4316228 (Y)
18	Calcic Luvisol (Skeletic, Rhodic)	Ocaña (Toledo)	Limestones	Uncultivated	455084 (X) 4423063 (Y)
19	Haplic Fluvisol (Calcaric, Skeletic)	Balazote (Albacete)	Fluvial sediments	Dry farming	0580442 (X) 4307137 (Y)
20	Leptic Cambisol (Humic, Dystric)	Almadén (C. Real)	Slates	Uncultivated/ Pasture	340446 (X) 4290941 (Y)
21	Cambic Umbrisol (Humic, Arenic)	Almorox (Toledo)	Granites	Forest/ Reforestation	0383535 (X) 4460106 (Y)
22	Haplic Acrisol (Ruptic, Profondic)	Viñuelas (Guadalajara)	Rañas	Forest	0470537 (X) 4515645 (Y)
23	Umbric Leptosol (Humic, Dystric)	Valdepeñas de la S. (Guadalajara)	Quarzites/ slates	Forest	0466594(X) 4529098 (Y)
24	Rendzic Leptosol (Humic, Brunic)	El Bonete (Albacete)	Limestones	Scrub/ Forest	0642565 (X) 4306691 (Y)

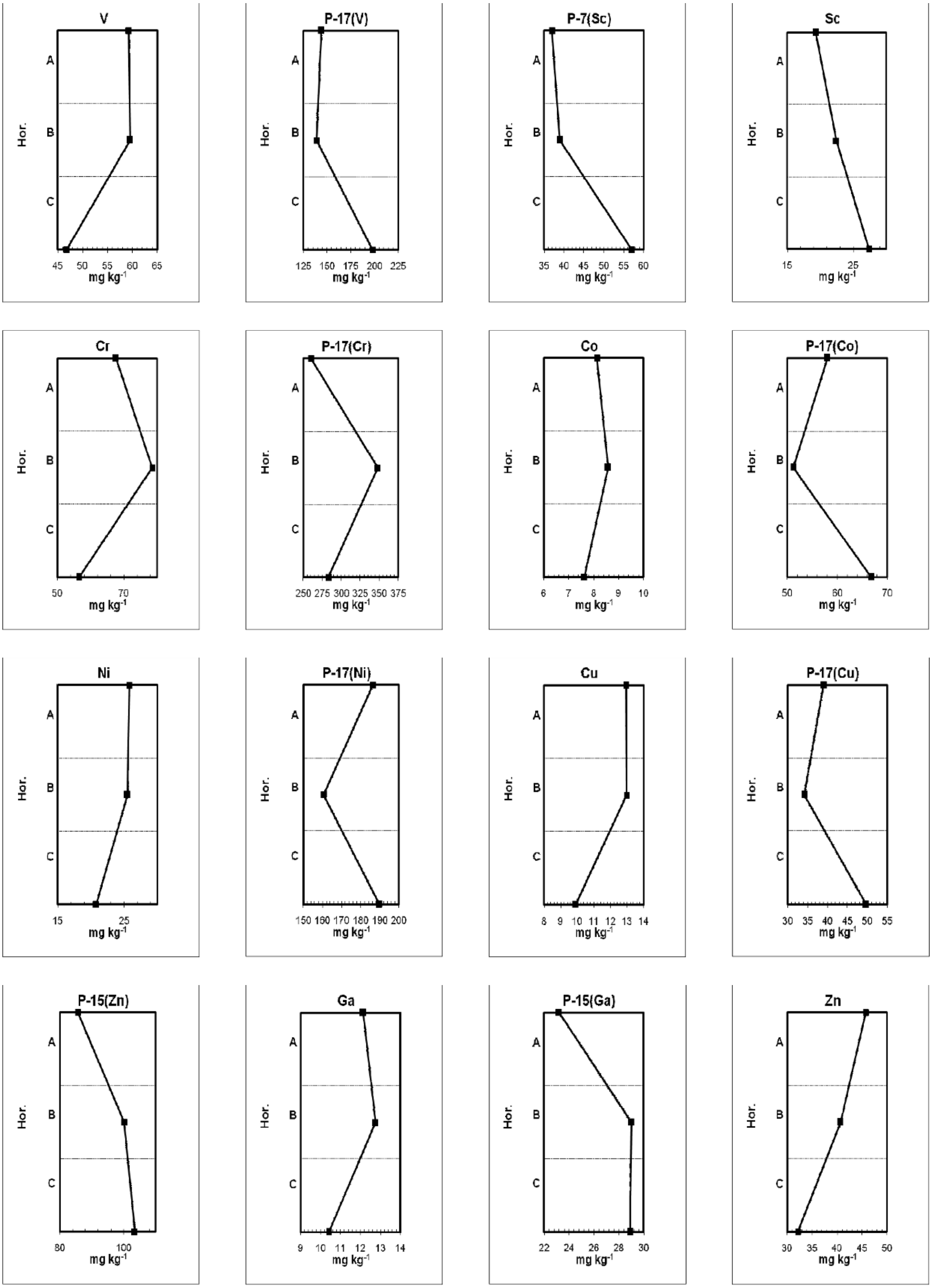

Figure 2. Soil profiles showing the distribution of trace elements with depth. U=element, P-1(U)= distribution in a selected soil profile.

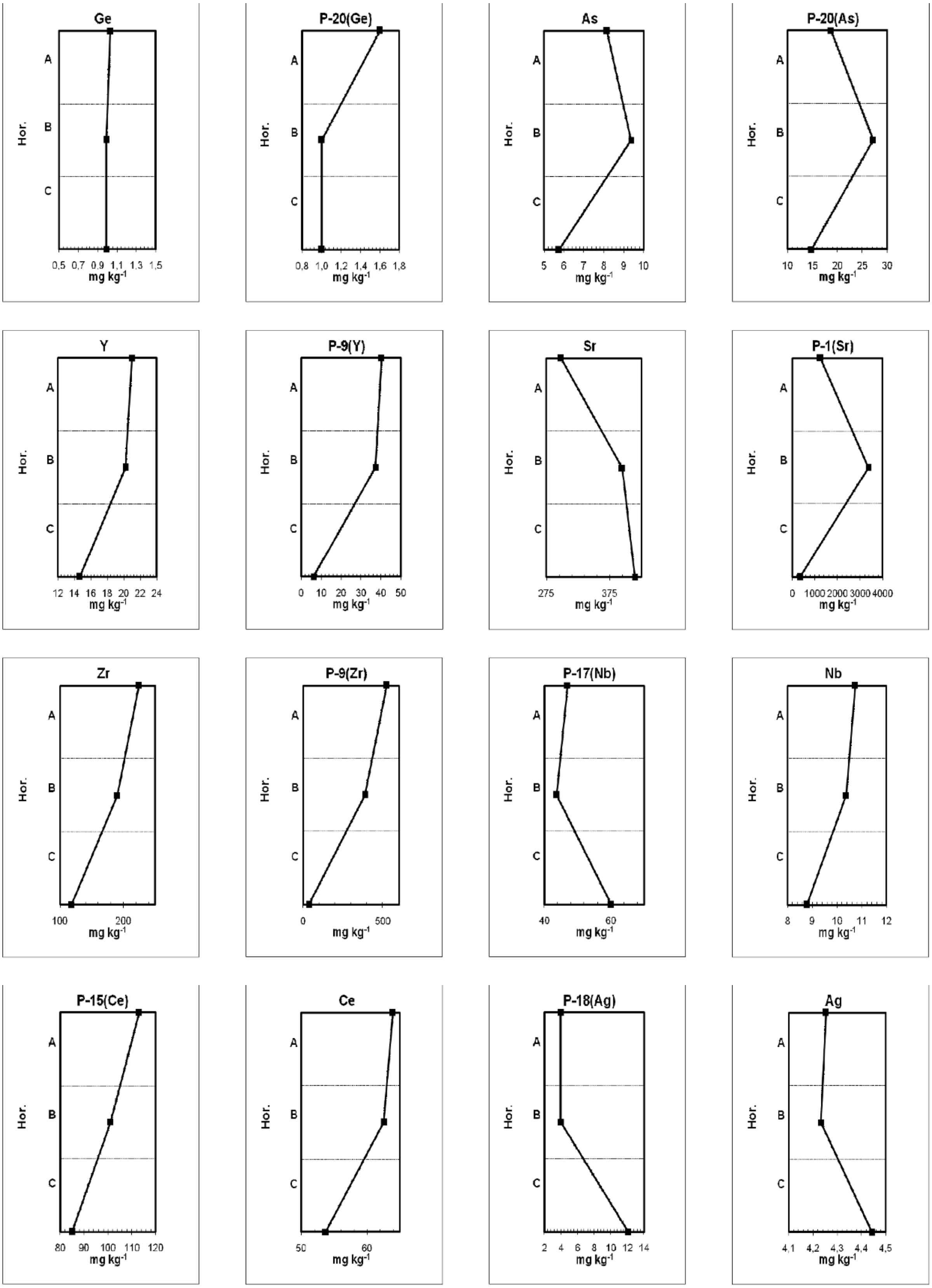

Figure 3. Soil profiles showing the distribution of trace elements with depth. U=element, P-1(U)= distribution in a selected soil profile (continuation).

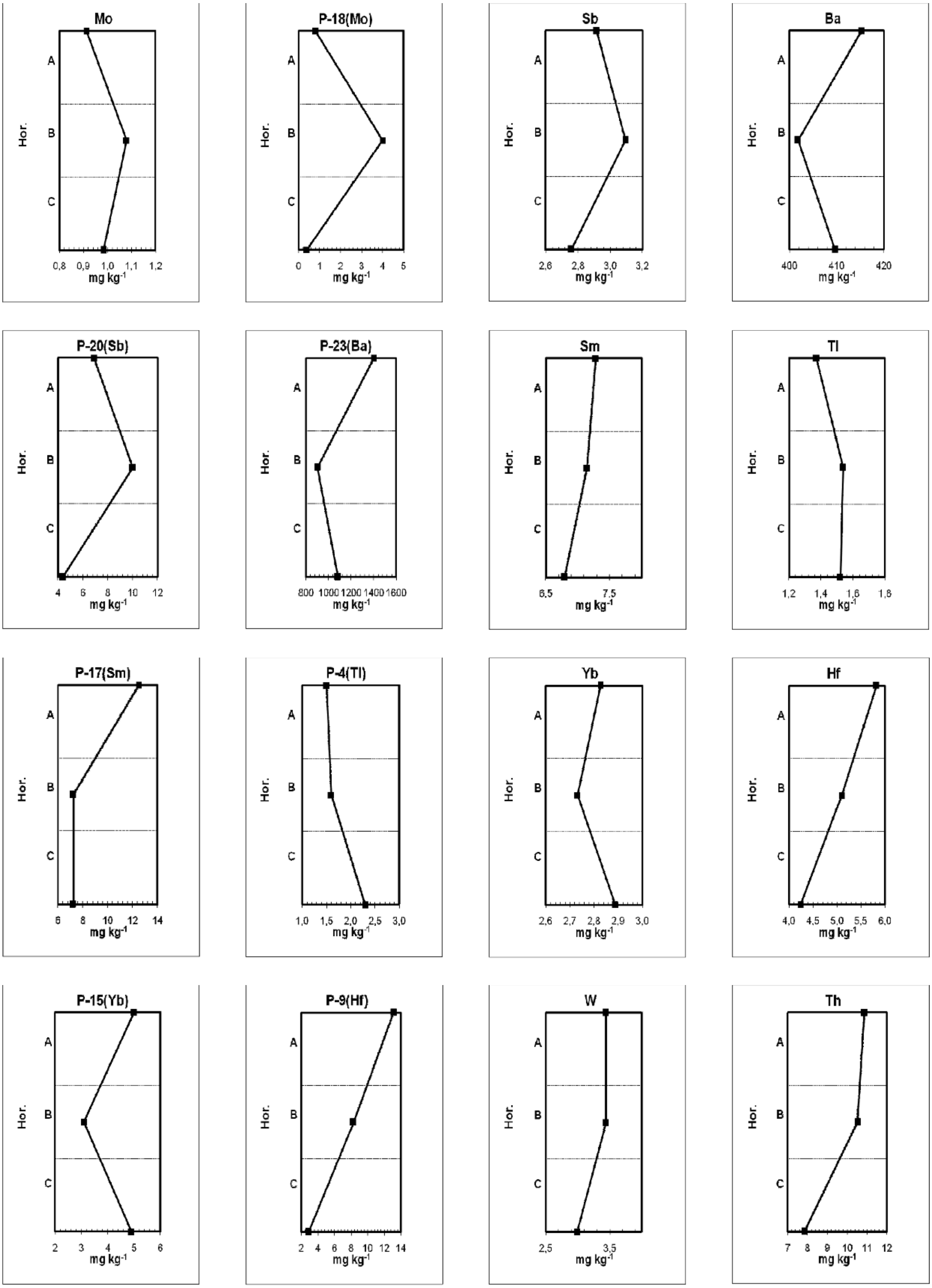

Figure 4. Soil profiles showing the distribution of trace elements with depth. U=element, P-1(U)= distribution in a selected soil profile (continuation).

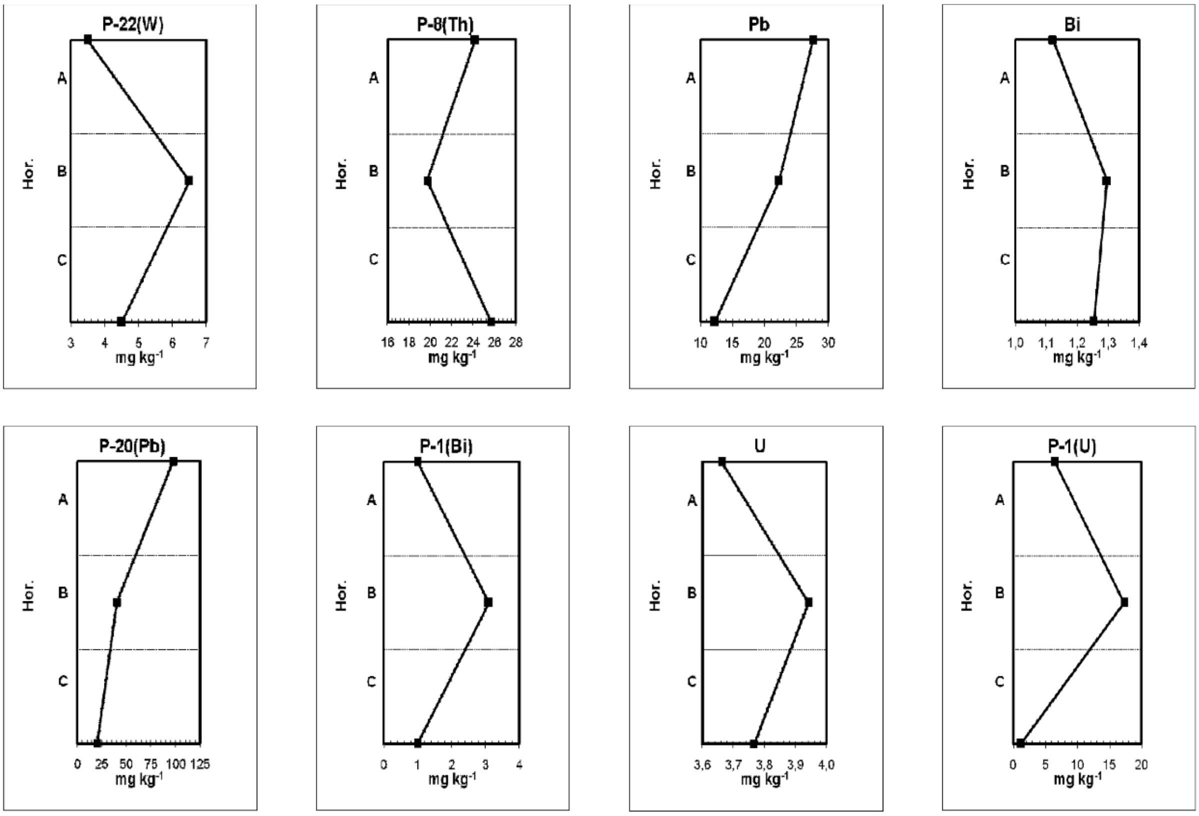

Figure 5. Soil profiles showing the distribution of trace elements with depth. U=element, P-1(U)= distribution in a selected soil profile (continuation).

Table 2. Summary statistics for the pooled soil profile data, 24 profiles and 3 horizons, n = 72.

	Sc	V	Cr	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Rb	Sr	Y	Zr	Nb	Mo	Ag
Minimum	2.0	2.0	2.0	2.4	1.1	0.2	1.2	0.3	0.1	2.4	0.1	0.1	1.4	11.4	0.4	1.0	0.4	0.1	2.0
Mediane	22.5	35.5	57.0	2.4	12.5	7.9	32.8	10.3	1.0	7.2	1.0	5.2	76.7	111.6	18.3	156.2	8.0	1.0	3.9
Maximum	57.0	135.0	110.0	41.4	49.1	35.8	103.5	29.0	1.4	19.7	1.0	33.1	434.1	3384.0	40.3	524.2	20.1	4.0	12.1
Rank	55.0	133.0	108.0	38.9	48.0	35.6	102.3	28.7	1.3	17.3	0.9	33.0	432.7	3372.6	39.8	523.2	19.7	3.9	10.1
Arithm. mean	23.6	49.9	54.8	5.8	16.9	10.3	35.7	11.1	0.9	7.4	0.8	6.7	86.2	380.0	17.9	167.6	8.0	0.9	4.3
Var. of samples	184.8	1339.9	856.9	55.4	164.6	69.7	645.3	60.1	0.0	18.3	0.0	44.8	5506.0	553848.9	103.7	15059.7	28.1	0.2	2.9
Stimated var.	187.6	1360.5	870.1	56.2	167.2	70.8	655.2	61.1	0.1	18.6	0.0	45.5	5590.8	562369.7	105.3	15291.4	28.5	0.2	3.0
Std. deviation	13.5	36.6	29.2	7.4	12.8	8.3	25.4	7.7	0.1	4.2	0.2	6.6	74.2	744.2	10.1	122.7	5.3	0.4	1.7
	Cd	**Sn**	**Sb**	**I**	**Cs**	**Ba**	**La**	**Ce**	**Nd**	**Sm**	**Yb**	**Hf**	**Ta**	**W**	**Tl**	**Pb**	**Bi**	**Th**	**U**
Minimum	2.9	0.2	0.1	0.7	1.0	8.4	4.6	19.6	2.3	1.3	0.8	1.8	0.3	1.3	0.2	1.1	0.1	1.3	0.9
Mediane	4.0	3.5	2.3	4.1	6.0	330.3	24.5	56.2	22.7	7.2	2.6	4.1	2.4	3.2	1.6	17.4	1.0	8.9	2.8
Maximum	4.7	9.5	8.2	68.7	18.6	1403.3	49.2	113.1	44.3	11.1	5.0	13.1	6.6	6.5	2.3	45.0	3.1	25.7	17.3
Rank	1.8	9.3	8.1	68.0	17.6	1394.8	44.6	93.5	42.0	9.8	4.2	11.3	6.3	5.2	2.1	43.8	3.0	24.4	16.4
Arithm. mean	3.9	4.0	2.7	7.4	7.7	389.9	23.6	57.7	21.6	6.9	2.7	4.9	2.2	3.2	1.4	19.3	1.2	9.6	3.8
Var. of samples	0.0	5.2	2.1	80.2	10.5	108677.6	152.5	402.4	85.0	3.4	0.4	6.4	0.7	1.2	0.1	153.5	0.2	36.0	10.4
Stimated var.	0.0	5.3	2.1	81.5	10.7	110349.6	154.9	408.6	86.3	3.5	0.4	6.5	0.7	1.2	0.1	155.8	0.2	36.6	10.5
Std. deviation	0.1	2.2	1.4	8.9	3.2	329.6	12.3	20.0	9.2	1.8	0.6	2.5	0.8	1.1	0.4	12.3	0.4	6.0	3.2

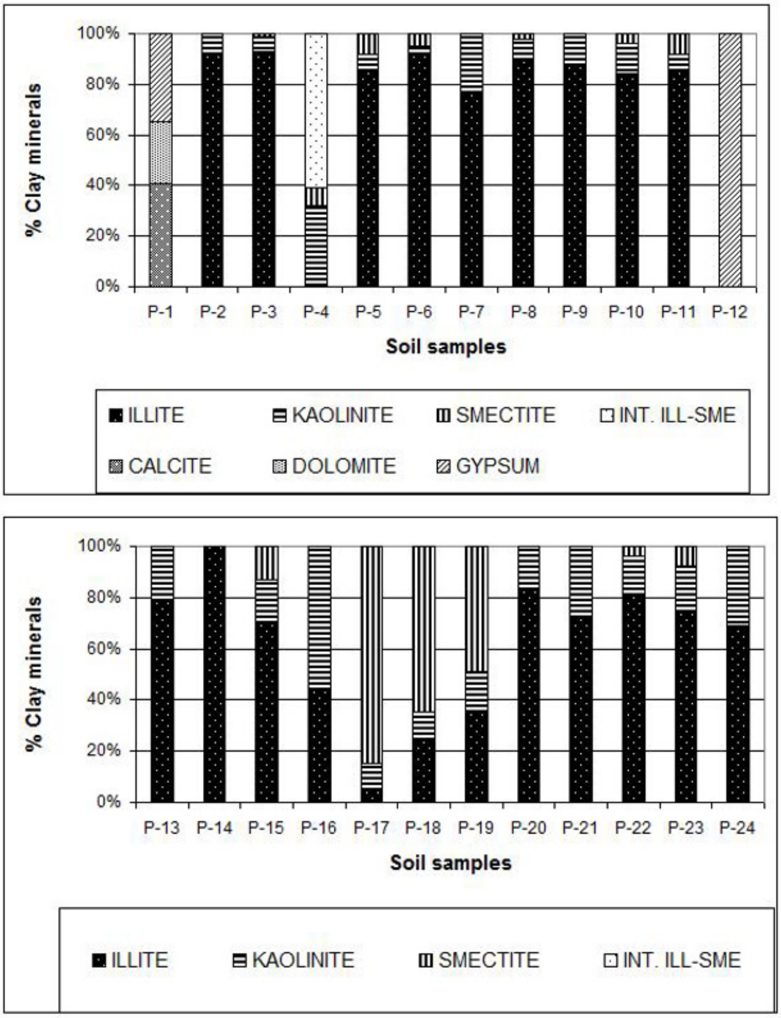

Figure 6. Percentage of clay minerals in the surface horizons of the investigated soils A: Profiles 1 to 12, B: Profiles 13 to 24.

that Cu and Zn have a strong association with smectitic materials.

Rb, which tends to increase with depth, appears in high contents in profile 8, (Velada), on granitic substrate. The main source of Rb in soils is micaceous minerals and K-rich feldspars (due to the similarity of the atomic radii of K and Rb). Sr is present in a wide range of contents, tending to increase with depth, with a high content in profiles 1 (Ontígola) and 12 (Tarancón). The Sr presence is linked to the content in micaceous minerals and Ca-rich feldspars, but the highest contents of Sr can be found in limestone and/or gypsiferous horizons (Figure 2). Due to its geochemical affinity with Ca, Sr is enriched in more carbonate-rich horizons [33]. Zr has a tendency to increase in the surface, but concentrations are variable. Pb shows a similar behaviour, as it tends to increase in the surface and is present in high contents in profiles 7, 9, and 10. Ba, which tends to increase in the surface, is the trace element with the highest contents (profiles 4, 7, 8, 9, 10, 11 and 16). Ba, Sr and Rb tend to be present in feldespars and micaceous minerals, substituting for K and Ca in crystal lattices.

Nb, Sn, I, Cs, La, Ce, Nd and Br do not show any defined trends. Co, Ge, Se, Mo, Ag, Cd, Sb, Yb, Hf, Ta, W, Tl, and Bi occur frequently at contents below their respective detection limits. Although seleniferous soils are not recognized in the region in this study, Moreno et al. [34] have reported their presence on margo/gypsiferous materials.

Table 3. Correlation coefficients between trace elements (correlation significant at $p<0.05$).

	Sc	V	Cr	Ni	Cu	Zn	Ga	As	Br	Rb	Sr	Y	Zr	Nb	Sn	I	Cs	Ba	La	Ce	Nd	Sm	W	Pb	Th	U
Sc	1																									
V	**-0407**	1																								
Cr	**-0.580**	**0.883**	1																							
Ni	**-0.319**	**0.958**	**0.845**	1																						
Cu	**-0.331**	**0.923**	**0.824**	**0.960**	1																					
Zn	**-0.488**	**0.826**	**0.772**	**0.841**	**0.874**	1																				
Ga	**-0.642**	**0.844**	**0.839**	**0.777**	**0.775**	**0.876**	1																			
As	**-0.385**	**0.689**	**0.682**	**0.688**	**0.724**	**0.644**	**0.647**	1																		
Br	0.166	-0.217	-0.171	-0.164	-0.167	-0.159	-0.192	**-0.246**	1																	
Rb	**-0.511**	**0.343**	**0.420**	**0.277**	**0.310**	**0.461**	**0.619**	**0.353**	-0.074	1																
Sr	0.230	**-0.362**	**-0.507**	**-0.351**	**-0.339**	**-0.405**	**-0.397**	-0.154	0.052	**-0.303**	1															
Y	**-0.695**	**0.783**	**0.851**	**0.721**	**0.712**	**0.748**	**0.860**	**0.686**	-0.146	**0.507**	**-0.417**	1														
Zr	**-0.713**	**0.606**	**0.728**	**0.486**	**0.474**	**0.520**	**0.638**	**0.442**	-0.152	**0.408**	**-0.405**	**0.828**	1													
Nb	**-0.660**	**0.873**	**0.885**	**0.792**	**0.805**	**0.866**	**0.947**	**0.662**	-0.210	**0.566**	**-0.447**	**0.909**	**0.771**	1												
Sn	**-0.678**	0.242	**0.486**	0.171	0.212	**0.422**	**0.574**	**0.423**	-0.106	**0.519**	**-0.358**	**0.598**	**0.562**	**0.541**	1											
I	**0.434**	-0.174	-0.205	-0.134	-0.149	**-0.259**	**-0.272**	-0.223	**0.579**	-0.142	0.112	**-0.309**	-0.227	**-0.295**	**-0.270**	1										
Cs	-0.017	-0.009	0.051	-0.013	-0.055	-0.061	0.064	-0.055	-0.082	0.069	-0.218	0.090	0.045	0.074	0.035	-0.068	1									
Ba	**-0.561**	**0.573**	**0.715**	**0.488**	**0.504**	**0.528**	**0.683**	**0.525**	-0.182	**0.437**	**-0.357**	**0.648**	**0.562**	**0.712**	**0.653**	-0.235	-0.005	1								
La	**-0.549**	**0.828**	**0.887**	**0.785**	**0.765**	**0.782**	**0.830**	**0.632**	-0.194	**0.411**	**-0.486**	**0.895**	**0.809**	**0.904**	**0.483**	**-0.257**	0.057	**0.629**	1							
Ce	**-0.300**	**0.819**	**0.809**	**0.781**	**0.750**	**0.717**	**0.736**	**0.615**	-0,123	**0,350**	**-0.471**	**0.804**	**0.710**	**0.817**	**0.305**	-0.030	0.091	**0.490**	**0.892**	1						
Nd	**-0.449**	**0.832**	**0.845**	**0.802**	**0.768**	**0.767**	**0.812**	**0.627**	-0.156	**0.385**	**-0.478**	**0.865**	**0.745**	**0.858**	**0.370**	-0.126	0.090	**0.518**	**0.929**	**0.946**	1					
Sm	-0.067	**0.262**	0.184	**0.266**	**0.246**	0.219	0.217	0.116	-0.114	0.130	-0.101	0.239	0.236	**0.262**	-0.041	0.007	0.092	0.001	**0.294**	**0.334**	**0.358**	1				
W	**-0.272**	0.168	**0.261**	0.084	0.172	0.170	**0.305**	**0.420**	0.034	**0.297**	-0.129	**0.349**	**0.338**	**0.319**	**0.452**	0.122	0.096	**0.358**	**0.269**	**0.259**	**0.250**	0.149	1			
Pb	**-0.537**	**0.466**	**0.592**	**0.444**	**0.468**	**0.679**	**0.630**	**0.400**	-0.062	**0.447**	**-0.498**	**0.685**	**0.615**	**0.673**	**0.568**	**-0.304**	0.022	**0.469**	**0.689**	**0.599**	**0.633**	0.136	0.227	1		
Th	**-0.720**	**0.583**	**0.674**	**0.495**	**0.528**	**0.738**	**0.869**	**0.516**	-0.152	**0.657**	**-0.337**	**0.822**	**0.735**	**0.854**	**0.709**	**-0.247**	0.100	**0.556**	**0.774**	**0.661**	**0.743**	0.227	**0.414**	**0.692**	1	
U	-0.030	**-0.286**	**-0.374**	**-0.285**	**-0.257**	-0.192	-0.138	-0.047	0.015	-0.051	**0.904**	-0.177	-0.224	-0.227	-0.060	-0.009	-0.147	-0.214	**-0.299**	**-0.342**	**-0.294**	-0.046	-0.019	**-0.250**	0.009	1

Table 4. Soil quality reference values (mg Kg^{-1}) of 38 trace elements from Castilla La Mancha (Central Spain)

Trace element	Mean	Standard Deviation	Reference value
Sc	23.6	13.5	50.8
V	49.9	36.6	123.2
Cr	54.8	29.2	113.4
Co*	5.8	7.4	20.8
Ni	16.9	12.8	42.6
Cu	10.3	8.3	27.0
Zn	35.7	25.4	86.5
Ga	11.1	7.7	26.7
Ge*	0.9	0.1	1.3
As	7.4	4.2	16.1
Se*	0.8	0.2	1.4
Br	6.7	6.6	20.1
Rb	86.2	74.2	234.7
Sr	380.0	744.2	1868.4
Y	17.9	10.1	38.3
Zr	167.6	122.7	413.1
Nb	8.0	5.3	18.7
Mo*	0.9	0.4	2.0
Ag*	4.3	1.7	7.8
Cd*	3.9	0.1	4.4
Sn	4.0	2.2	8.7
Sb*	2.7	1.4	5.7
I	7.4	8.9	25.4
Cs	7.7	3.2	14.2
Ba	389.9	329.6	1049.3
La	23.6	12.3	48.4
Ce	57.7	20.0	97.9
Nd	21.6	9.2	40.1
Sm*	6.9	1.8	10.7
Yb*	2.7	0.6	4.2
Hf	49	2.5	10.0
Ta*	2.2	0.8	4.0
W	3.2	1.1	5.5
Tl*	1.4	0.4	2.3
Pb	19.3	12.3	44.2
Bi*	1.2	0.4	2.2
Th	9.6	6.0	21.6
U	3.8	3.2	10.3

* Preliminary estimacion
(under detection limit)

3.2. Correlations between elements

Table 3 shows the correlation coefficients between total contents. The normality of the populations was determined by the Kolmogorov-Smirnov test, showing that they follow a normal or almost normal pattern. Pearson's product moment correlation coefficient gives strong correlations (>0.7) for: Sc with Zr and Th; Ni with Cu-Zn-Ga-Y-Nb-La-Ce-Nd; Cu with Zn-Ga-As-Y-Nb-La-Ce-Nd; Zn with Ga-Y, Nb-La-Ce-Nd-Th; Ga with Y-Nb-La-Ce-Nd-Th. Correlations higher than 0.7 are found for several elements, which is attributed to their siderophilous nature, that is, they have an affinity for Ni and Fe [35], such as V, which is also very significantly related with Cr-Co-Ni- Cu-Zn- Ga- Y- Nb- La- Ce- Nd; and Cr with Ni-Cu- Zn, Ga, Y, Zr, Nb, Ba, La- Ce- Nd, where both elements associate with the same elements. Cr, Co and Ni follow a similar pattern. Pb and Zn are related because they are very calciphilous, following the patterns of Goldschmidt [35]. Cu and Zn are closely correlated due to their similar ionic radius.

Certain other pairs appear in moderate levels: La with Sm; Ce with Nd; U with Rb. Pb and Zn showed a significant correlation to one another. Arsenic shows no correlation, in general with trace elements, with the exception of Cu. Sr shows correlation with Pb, Bi Th and U, albeit at medium levels.

Sc and Sr have a negative and significant relationship with many elements: V, Cr, Cu, Zn, Ga, Ge, As, Rb, Y, Zr, Nb, Sn, Sb, I, Ba, La, Ce, Nd, Hf, W, Pb and Th. On the contrary, V, Cr, Ni, Cu, Zn, Rb, Y, Zr and some others are positively related with many elements (although at times with a low significance).

3.3. Baseline content levels and reference values

The background content of trace elements in soils can assist in estimating a true reference level for the extent of soil pollution by these elements [36]. The trace element content of soils varies widely, making it inappropriate to use universal background contents for more than initial screening. The term geochemical background was introduced to differentiate between normal element contents and anomalies, which might be indicative of an ore occurrence. Hawkes & Webb [37] and Reimann & Garrett [4] defined background as the normal abundance of an element in barren earth material.

According to Bak et al. [38] few countries have detailed information on trace element or heavy metal contents for soils in contaminated areas. The background values for trace elements in soils are established as is, and may have received input from contaminant sources. We rule out those locations/samples that have received point-source contaminants, as proposed by Holmgren et al. [26] and Esser [39]. The background population consists of values lying between the minimum and maximum values of the population, following the removal of statistical outliers and other discordant values. The method for selecting discordant values is by the creation of box diagrams, as proposed by ISO/DIS 19258 [40]. After discarding the outliers and discordant values, an estimate of the reference value can be made for that type of distribution.

The recent publication of Royal Decree 9/2005 [19] is an attempt to limit the difference of criteria and its criteria are used in this study. Background levels are characterised by the mean, population median or percentiles. Soil attributes as clay and organic matter content did not contribute to the explanation of the trace element distribution and variability and were not considered important for the interpretation of reference values. When the distribution is normal (as is the case for most of the soil trace elements) the arithmetic means are used.

The upper limit of the background value or reference value is determined by the formula:

$$VR = VF + 2SD \qquad (1)$$

where VF is the background value calculated from the arithmetic or geometric mean taken as a function of the adjustment of the distribution of frequencies, and SD is the standard deviation.

Conde et al. [25] analysed the same soils and found that there was no significant difference between the superficial and sub-superficial horizons, and proposed searching for the "generic reference levels" through either one. The reference values obtained (Table 4) derived from the methodology of BOE [19] provide the information needed to set the criteria for polluted soils.

Normative values for environmental legislation concerning soil remediation should not be copied from other countries or regions but rather be determined locally. In this way, misinterpretation of abnormally high trace element contents can be avoided [41]. The reference values to provide a guide to evaluate soil quality and to help establish the maximum limit value for trace elements in soils of Castilla La Mancha are established.

4. Conclusions

Baseline content levels and reference values serve as the first piece of information required for identifying soil contamination. This study determines such background levels for the Castilla La Mancha region of Central Spain, which is characterized by a wide variety of geological substrates. The data presented here may be used to define background trace element contents for a range of soils and at different spatial resolutions.

The proposed reference values for the Castilla La Mancha region (in mg kg^{-1}) are: Sc 50.8- V 123.2- Cr 113.4- Co 20.8- Ni 42.6- Cu 27.0- Zn 86.5- Ga 26.7- Ge 1.3- As 16.7- Se 1.4- Br 20.1- Rb 234.7- Sr 1868.4- Y 38.3- Zr 413.1- Nb 18.7- Mo 2.0- Ag 7.8- Cd 4.4- Sn 8.7- Sb 5.7- I 25.4- Cs 14.2- Ba 1049.3- La 348.4- Ce 97.9- Nd 40.1- Sm 10.7- Yb 4.2- Hf 10.0- Ta 4.0- W 5.5- Tl 2.3- Pb 44.2- Bi 2.2- Th 21.6- U 10.3.

The present procedure constitutes a valuable first approach in evaluating potential soil contamination. When reference values are comparable to baseline content levels for the total concentration of trace elements in soils of Castilla La Mancha, it may be assumed that no hazardous effects are expected to occur. The results should be considered to assess the extent of the contamination and plan any necessary remediation.

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