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Chemical Partitioning of Fe, Mn, Zn and Cr in Mountain Soils of the Iberian and Pyrenean Ranges (NE Spain)

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The bioavailability of heavy metals, and thus their possible harmful impact on ecosystems and humans, depends on metal partitioning. This study describes the chemical partitioning of iron, manganese, zinc and chromium, because the potential effect of soil contamination is better assessed through the knowledge of the forms in which a given metal is present rather than the use of its total concentration. In four soil types representative of mountain soils in the Iberian and Pyrenean ranges in Aragón, a total of 16 selected sites have been sampled and five subsamples were taken in each site to create a composite sample. The 4 heavy metals have been extracted by the sequential extraction procedure of Tessier et al. *(1979) and analyzed by emission atomic spectrometry of solid state (ICP OES).*

Little Fe, Mn and Zn (<1, 2.4–35.9, <1–24.5 mg/kg, respectively) were retrieved from the exchangeable phase, a readily available phase for biogeochemistry cycles in the ecosystems. Chromium was not detected in the potentially bioavailable forms. The largest contents of Fe, Zn and Cr were retrieved from the residual phase with mean values of 21100, 72 and 60 mg/kg, and maximum values of 35700, 279 and 271 mg/kg, respectively. Mn was mainly bound to oxide phases with mean and maximum values of 236 and 887 mg/kg, respectively. For all metals, the highest contents are found in Leptosols on igneous rocks due to the rich and diverse mineral composition of their parent materials. The knowledge of the chemical partitioning of Fe, Mn, Zn and Cr provides information to identify the soils in which their mobile forms may be transferred to the soil-water-plant system. This information is of interest for the management of fragile mountain soils to avoid the environmental risk of cycling these metals in the environment.

Keywords Fe, Mn, Zn, Cr, geochemical phases, heavy metals, Iberian and Pyrenean ranges, mountain soils, NE Spain, sequential extraction.

1. Introduction

The risk posed by environmental pollutants such as heavy metals depends on the physicochemical properties in soil and water that determine their bioavailability in the biotic and abiotic environment. Although the heavy metal contamination of soil is generally quantified from the total metal content, various reactive compounds (organic matter, oxides,

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carbonates) of soils can affect the retention of these metals (Cabral and Lefebvre, 1998). Therefore, depending on environmental conditions, soils can be a sink or a source for metals.

The distribution of trace metals in the various phases of a soil determines their behavior in the environment: their mobility (Rauret *et al.*, 1988), bioavailability (Szefer *et al.*, 1995), and toxicity (Borovec, 1996). The mobility of heavy metals in soils and thus their toxic potential, depends upon speciation that has become increasingly important in environmental studies such as soil remediation (Environment Canada, 1993) and risk assessment (Salim *et al.*, 1993).

Heavy metal retention by soils can be evaluated by investigating their partitioning among the various geochemical phases. This allows a better knowledge into the mechanisms of retention and release involved in the process of transference within the ecosystem. The partitioning of metals in soils is element specific and depends on soil properties such as soil pH, organic matter, clay, and oxide concentrations (Brümmer *et al.*, 1986).

Sequential extraction procedures are used widely to assess metal partitioning in soils (e.g., Zeien and Brümmer, 1989). Numerous studies have evaluated heavy metal concentrations and speciation in temperate soils (e.g., McLaren and Crawford, 1973; Shuman and Hargrove, 1985; Chlopecka *et al.*, 1996). The procedure of chemical partitioning assumes that the heavy metals retained can be removed from the geochemical phases by using appropriate extracting reagents; however, various authors (e.g. Bauer and Kheboian, 1987) point out that the reagents used may not be perfectly selective for a selected geochemical phase.

This study is part of a broader project undertaken to establish the background levels of heavy metals in soils of Aragón (NE Spain). This first survey analyzed the contents of 15 elements in a wide variety of soils to assess the risks of soil contamination in the region. In this work our objective is to determine the binding of Fe, Mn, Cr and Zn to the main fractions in soils of the Iberian and Pyrenean ranges because their presence in different forms, especially as labile forms, would facilitate their transference and migration through the soil and this might influence their final bioavailability in the ecosystem.

Mountain ranges have been relatively well preserved landscapes till recent times; nevertheless, anthropic pressure on these fragile environments is rising rapidly. By transforming forest in skiing resorts, new urban areas for tourism or by changing land uses including deforestation for wood manufactures or agricultural use, there is an increasing risk of cycling heavy metals contained in mountain soils.

The four heavy metals were chosen because they are of importance in agroecosystems as micronutrients (Fe, Zn and Mn) but also because of their toxicity (Cr). To determine their partitioning, a five-step sequential extraction procedure (Tessier *et al.*, 1979) based on the capacity of some extracting reagents to remove the heavy metals retained from the geochemical phases has been used. It was intended to examine if any enhanced heavy metal concentration in selected soils of the Iberian and Pyrenean ranges is caused by naturally occurring mineralization or if any derived anthropogenic impact on these soils may affect their cycling and accumulation in the environment.

2. Material and Methods

2.1. Study Area, Soil Sites and Sampling

The Ebro basin extends over a surface of 85.000 km^2 in northeast Spain. The Pyrenees and the Iberian range are their natural limits at the north and south of the basin in its

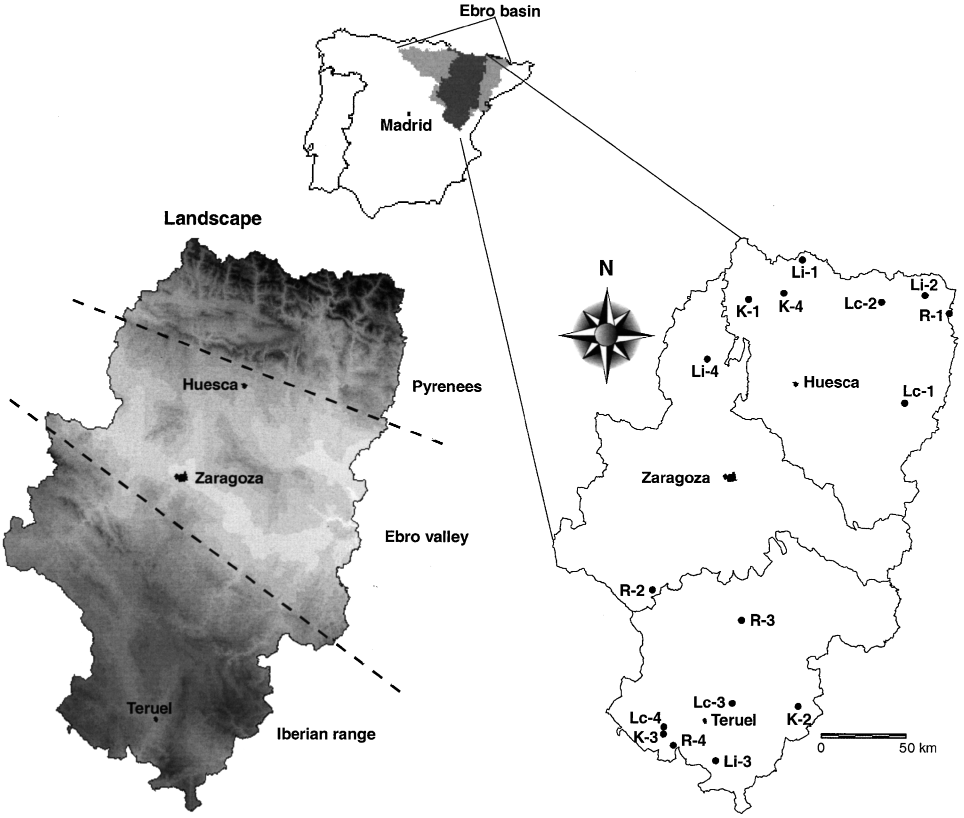

Figure 1. Location of the study area and sampling sites.

central part in Aragón (Figure 1). The Pyrenees and Iberian ranges are composed of a large variety of materials from clastic (conglomerates, sand, silt and clay) to carbonatic as well as igneous and metamorphic rocks covering since Precambrian times to Tertiary and Quaternary formations. The climate in the ranges is mainly continental with a large diversity following a gradient from the highest divides (3400 m a.s.l.) towards the central valley (180 m a.s.l.). The most representative soils in the ranges are Leptosols (Machín, 1984) that are developed on a large variety of lithologies. As a part of the soil system, Kastanozems are also abundant in the ranges. Leptosols on igneous rocks and Rankers are light soils (sand content is around 60%) and slightly acidic. Conversely, clay content is around 25% in Kastanozems and Leptosols on calcareous rocks that in turn have the highest organic matter content. Some main soil properties of these soils are presented in Table 1.

A total of 16 sampling sites, 8 distributed in Leptosols and 4 in Kastanozems and Rankers, respectively, were chosen for their representativeness and edaphic features to conduct this study (Figure 1). The sampling procedure intended to obtain a characteristic average sample for each site made of five sub-samples. A total of 16 soil samples were composed from 80 subsamples collected at each site. Average depth of sampling was between 20 and 40 cm, and samples were extracted by using an automatic core driller.

Table 1
Main soil properties of the studied soils

Soil type	Sample no	pH KCl	OM %	Clay %	Silt %	Sand %
Leptosol on igneous rocks	5–2	6.61	6.9	15.0	49.6	35.5
	5–3	6.26	5.8	4.1	23.0	72.8
	5–9	6.22	0.5	1.5	11.7	86.8
	5–11	7.22	1.5	21.7	51.5	26.8
Leptosol on calcareous rocks	5–5	7.22	4.5	28.9	66.6	4.5
	5–12	7.23	1.1	17.5	40.5	42.0
	5–16	7.75	1.1	8.4	46.4	45.2
	5–17	7.97	0.1	19.3	74.1	6.6
Kastanozem	12–1	7.25	3.5	21.4	55.5	23.1
	12–9	6.68	6.7	26.1	60.3	13.7
	12–10	7.06	6.5	24.8	52.8	22.4
	12–14	7.76	2.1	22.9	65.7	11.4
Ranker	15–1	5.57	5.9	5.6	18.8	75.6
	15–2	5.08	6.9	7.1	28.4	64.5
	15–3	6.98	2.2	9.2	34.2	56.7
	15–4	6.80	1.7	9.8	58.0	32.2

2.2. Analytical Methods

Soil samples were air-dried and crushed to pass through a 2 mm sieve and representative subsamples were ground in an agate mortar. Analyses were performed by atomic emission spectrometry using an inductively coupled plasma with a detector of solid state (Perkin Elmer Optima 3200 DV). Digestion was made using a microwave (Milestone 1200 mls). Concentrations, obtained after three measurements per element, are expressed in mg/kg.

For the sequential extraction, the Tessier et al. (1979) five-step procedure was selected because it is well documented, widely used, has been adapted to the study of soils (e.g. Emmerson *et al.*, 2001) and allows comparison of the results obtained. Although various authors (e.g. Bauer and Kheboian, 1987; Usero *et al.*, 1998) reported inaccuracy in differentiation among geochemical phases and overlapping between the different extraction steps, reference to the original names of the fractions distinguished by Tessier *et al.* (1979) is maintained. The five fractions representing the following chemical phases are exchangeable metals, bound to carbonates, bound to Fe-Mn oxides, bound to sulphides and organic matter and residual fraction.

To check the results of the sequential extraction, the sum of the different fractions for each element was compared with the results obtained from the total digestion. The recovery rates were very good for iron and chromium (around 95%), whereas lower recovery rates (60–80%) were obtained for zinc and manganese. As quality control, duplicate analyses as well as analyses at an external laboratory were performed on 5 selected samples.

Granulometric analyses of the clay fraction were performed using Coulter laser equipment. Samples were stirred and ultrasound used to facilitate particle dispersion. The pH (1:2.5 soil:water) was measured using an Orion 901 pH-meter. Organic matter was determined by the Sanerlandt method (Guitian and Carballas, 1976) using a Mettler Toledo titrimeter and electrode.

Table 2
Contents of Fe, Mn, Zn and Cr (mg/kg) in the lithosphere and soils and in similar soils of Aragón (Navas and Machín, 2002)

		Soil				
Metal	Lithosphere	Typical	Range	Leptosols	Kastanozems	Rankers
Cr	200	100	5–3000	34	26	17
Fe	50000	38000	7000–550000	22200	19500	21500
Mn	1000	850	100–4000	484	396	495
Zn	80	50	10–300	73	61	217

A cluster analysis was performed to form groups of soils with similar characteristics of the heavy metals in the fractions. The clustering method used was the furthest neighbor (complete linkage, distance metric: euclidean).

3. Results and Discussion

It is widely recognised (e.g. Maskall and Thornton, 1998) that the sequential extraction allows one to know the relative bonding of metals in different solid phases and therefore the forms that can be released in the soil solution under different environmental conditions. Table 2 presents the typical values for Cr, Fe, Mn and Zn in the lithosphere and soils and their total average contents for similar soils in the region. The concentrations of Fe, Mn, Zn and Cr in the five chemical phases for all soils are summarized in Table 3. These values fall into the normal ranges described by Navas and Machín (2002). There is a large variability in the amounts of heavy metals extracted from each fraction. The values of the coefficient of variation (CV) largely exceed 70%, the lowest variability is found for Fe in the residual fraction (CV: 34%).

In all soils, Cr in association with the exchangeable, carbonate and oxide phases was below the detection limit (25 μg/L). Zinc was found in the exchangeable phase of all Rankers (0.1–24.5 mg/kg). Insignificant amounts of Zn (0.1 to 0.9 mg/kg) were found in the exchangeable phase of most soils and it was below detection limits (30 μg/L) in two soils (Li-4, K-1). Similarly, very little Zn associated with carbonates was detected in only five of the soil samples. In all soils, very little Fe was found in the exchangeable phase and it was not retrieved from the exchangeable phase in a Kastanozem of Javierregay (K-1). In all soils, Mn was retrieved from all phases and its highest concentrations were bound to Fe-Mn oxides, carbonates and the residuals in that order. The rest of the heavy metals were mostly associated with the residual phase, followed by the organic and the oxide phases.

A measure of the analyzed elements in each fraction is shown for the studied soils in the box and whisker plots of Figure 2. Among the studied soils, differences in the amounts of the heavy metals extracted from the five chemical phases have been found. In the exchangeable phase the highest contents of Fe, Mn and Zn are in Rankers and the lowest Mn and Zn in Leptosols on igneous rocks. Associated with carbonates, the highest Fe and Mn contents are found in Kastanozems. The amounts of Fe and Mn retrieved from the oxide phase are higher in Leptosols on igneous rocks whereas of Zn are in Rankers. Associated with the organic phase, Zn is also higher in Rankers followed by Leptosols on igneous rocks, Cr in Leptosols on calcareous rocks and Mn in Kastanozems. In the residual phase the highest contents for

Table 3

Basic statistics of the contents of Fe, Mn, Zn and Cr (mg/kg) associated with the chemical phases in the studied soils of the Pyrenean and Iberian Ranges

	Exchangeable				Carbonates				Fe-Mn oxides				Sulphides + Organic				Residuals			
	Fe	Mn	Zn	Cr	Fe	Mn	Zn	Cr	Fe	Mn	Zn	Cr	Fe	Mn	Zn	Cr	Fe	Mn	Zn	Cr
Mean	0.3	14.4	2.1	BDL	6.6	65.9	0.7	BDL	1372	235.9	4.0	BDL	913	28.7	11.4	3.9	21103	103.2	72.1	60.4
Standard error	0.1	3.1	1.5	—	2.7	12.5	0.5	—	204	52.9	2.0	—	100	5.1	5.4	0.6	1807	34.8	16.4	14.5
Minimum	BDL	2.4	BDL	BDL	0.2	11.5	BDL	BDL	249	66.0	BDL	BDL	274	5.2	BDL	0.8	7677	10.0	7.8	9.8
Maximum	1.0	35.9	24.5	BDL	44.9	195.5	8.0	BDL	3341	887.0	34.0	BDL	1572	67.5	90.6	8.6	35713	603.0	278.5	270.7

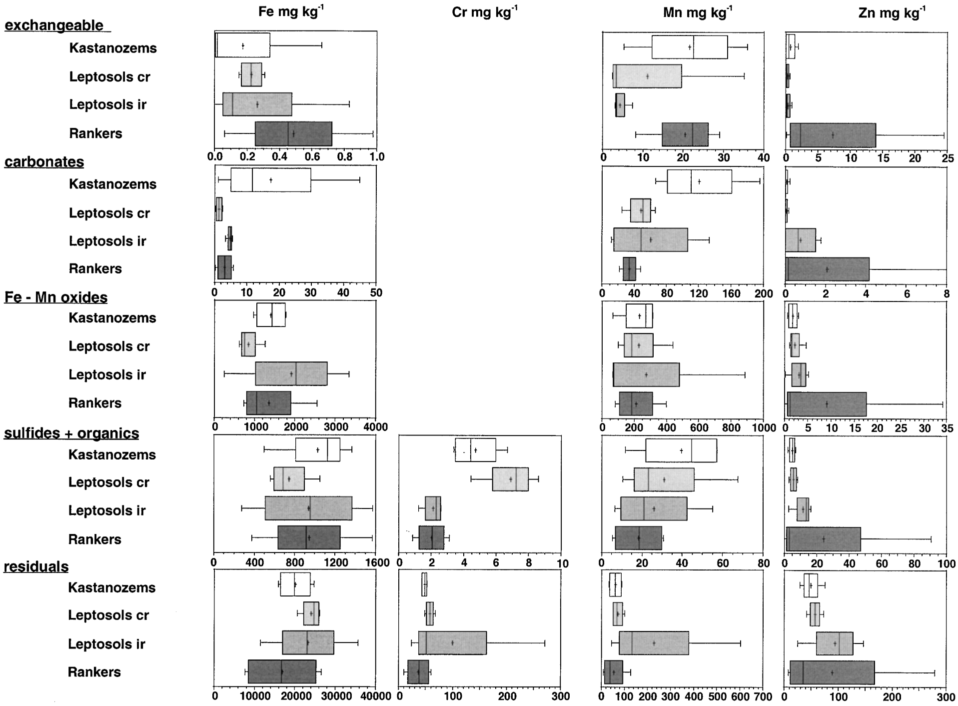

Figure 2. Box and whisker plots of Fe, Mn, Zn and Cr contents (mg/kg) for the studied soils. The lower boundary of the box is the 25th percentile, the upper boundary is the 75th percentile, the vertical line inside the box represents the median, mean is plotted as the small vertical line, individual points are outliers.

Cr, Mn and Zn are in Leptosols on igneous rocks. Land *et al.* (2002) also found differences in the extractability of elements in two soil profiles as a function of contamination as well as depending on the soil horizons. Besides variability in extraction efficiency, inaccuracy in differentiation among geochemical phases and overlapping of the chemical partitioning between the different extraction steps have been widely reported in the literature (e.g. Bauer and Kheboian, 1987; Usero *et al.*, 1998).

The distributions of Fe, Mn, Zn and Cr as percentages of the average total amount extracted from the soils are presented in Figure 3. The proportions of Cr, Fe and Zn extracted in the residual fraction are the highest. On average, they range between 91–98% of the total Cr, 88–94% of the total Fe and between 68–88% of the total Zn. Compared with the residual phase, much lower proportions of Zn and Fe are extracted in the organic and oxide phases that on average range, respectively, between 8–18% and 3–7% of the total Zn concentration and between 3–5% and 3–7% of total Fe. Between 2 and 11% of the Cr extracted was associated with the organic phase. Insignificant amounts of Fe and Zn were retained in the carbonate and exchangeable phases apart from Rankers where Zn retrieved from the exchangeable phase reached 5%. The percentage distribution of Mn is different from the rest of the heavy metals. Thus, approximately only 16% of Mn was associated with the residual phase, apart from Leptosols on igneous rocks, where it reaches 38%. The oxide phase retained most of the extracted Mn, between 46 and 62%. Lower proportions are extracted in the carbonate, organic and exchangeable phases, that range between 10–25%, 4–8% and

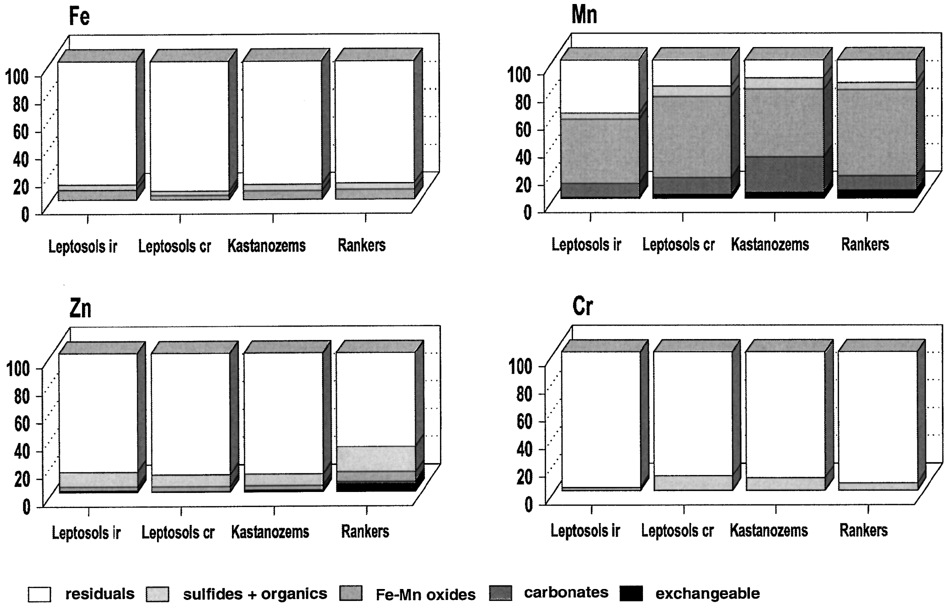

Figure 3. Percentage distributions of Fe, Mn, Zn and Cr in the studied soils.

0.7–6% of total Mn, respectively. In tropical soils, Wilcke *et al.* (1998) also found that Mn is bound to oxides, whereas Fe and Zn are mainly associated with silicates. However, in semiarid soils of the central Ebro valley, Mn was mainly associated with carbonates (Navas and Lindhorfer, 2003).

To examine the influence of soil properties in the mobilization of the studied heavy metals, correlations between pH, organic matter and clay percentages and contents of Fe, Mn, Zn and Cr in the five chemical phases of the sequential extraction have been established for all soils. As can be seen in Table 4, apart from Cr associated with the organic phase, no significant correlations between clay contents and the heavy metals were found. Between pH and the heavy metals the only significant and negative relationships are with Fe from the exchangeable phase and with Zn from the exchangeable and carbonate phases. Chromium from the organic phase is positively related to the organic matter content. This agrees with findings by Balasoiu *et al.* (2001) that reported high retention of Cr in organic rich soils. The authors also found great differences in the partitioning of Cr and Cu between mineral and organic soils. The processes of metal mobilization-immobilization are affected by a variety of soil properties and although the size of our data set does not allow us to obtain better results, the main trends reported in the literature, such as positive correlations with organic matter and clays (e.g. Labib *et al.*, 1989; Li, 1993), have also been observed in our soils.

It was intended to determine similarities between soils in relation to their contents for Fe, Mn, Zn and Cr in all chemical phases. The results of the cluster analysis applied for Fe indicate that Kastanozems and Leptosols on igneous rocks form a group separated from Rankers that, in turn, are separated from Leptosols on calcareous rocks. For Mn and Cr, the cluster shows that Leptosols on igneous rocks are separated from the the remaining three soils. In the case of Zn, Rankers are apart from the group formed by the other three soils. In this latter group, Leptosols on igneous rocks are in turn differentiated from Leptosols on

Table 4

Correlations between pH, organic matter content and clay percentages with the contents of Fe, Mn, Zn and Cr (mg/kg) associated with the five geochemical phases in the studied soils

	pH	Organic matter	Clay
Fe			
Exchangeable	**−0.71**	0.24	−0.33
Carbonates	0.25	−0.23	0.15
Fe-Mn oxides	−0.25	−0.01	−0.37
Sulfides + organics	−0.14	0.23	−0.07
Residuals	0.34	0.06	−0.03
Mn			
Exchangeable	−0.40	0.14	0.15
Carbonates	0.45	0.01	0.46
Fe-Mn oxides	−0.11	0.47	0.15
Sulfides + organics	0.21	**0.55**	0.37
Residuals	0.09	−0.31	−0.47
Zn			
Exchangeable	**−0.51**	0.10	−0.35
Carbonates	−0.50	0.12	−0.41
Fe-Mn oxides	−0.41	0.15	−0.35
Sulfides + organics	−0.41	0.08	0.41
Residuals	−0.28	0.07	−0.44
Cr			
Sulfides + organics	0.32	**0.56**	**0.74**
Residuals	0.23	−0.35	−0.36

calcareous rocks and Kastanozems. Therefore it appears that apart from Fe, Leptosols on igneous rocks are the most distinctive soil type for the rest of heavy metals. Moreover, their soil properties, such as lower pH (KCl), organic matter and clay contents, in comparison with the remaining soils differentiate them from the rest, although they do not differ as much from Rankers that also have low pH and clay content. The properties of these light soils can be a source of easily available heavy metals. In comparison with the other soils, Leptosols on igneous rocks have the highest contents for all metals in the residual phase but the lowest for Cr in the organic phase that may be due to their lowest organic matter content.

Rankers differ from the other soils in their highest Zn contents that are found in the exchangeable, oxide, organic and residual phases. The reason for this could be their mineralogical composition that might contain these metals in argillaceous minerals or as single sulfides.

The results of the sequential extraction show that, apart from Zn in Rankers, most of Cr, Fe and Zn are strongly retained in the residual phases bound in the crystal lattices of minerals. In the case of Mn, its higher proportion (56–74%) is associated with oxides and carbonates. In the case of a change towards reducing conditions, Mn would be released from oxides and, if conditions became acidic, it would be released from carbonates.

The mobile and bioavailable heavy metal fractions are associated with the exchangeable phase. In this phase, the heavy metals have the weakest bounds and can be easily released into the environment. The presence of heavy metals in this phase where they can be taken up by plants from the soils is the most hazardous to the ecosystem. In the studied soils, little Mn and Fe are present in this phase and in the amounts that have been detected they are not dangerous for the ecosystem. According to Chapman (1966), the content of Mn that might affect plants is around 400–500 mg/kg, whereas almost no toxic effect due to iron excess has been documented in the literature (Bergmann, 1992). Zinc associated with the exchangeable phase has been found in most soils, although contents are very low. Only in Rankers can relatively higher Zn be released from the exchangeable phase, reach surface and groundwaters and be cycled in the environment.

Because the highest concentrations of the heavy metals studied have been found in soils of the ranges (Navas and Machín, 2002), there is a risk of cycling these metals in the environment by unsuitable management of these easily erodible soils. Furthermore, the risk of contamination can be enhanced if different forms of heavy metals accumulate in water bodies. This can be an environmental concern in the ranges, especially if, as in the case of the Iberian and Pyrenean ranges, many reservoirs that are located at their foot hills retain considerable amounts of sediments (Navas *et al.*, 1998).

4. Conclusion

This study served to evaluate the contents and association to different chemical phases of Fe, Mn, Zn and Cr in selected mountain soils of the Iberian and Pyrenean ranges in Aragón. The results obtained are a first approach to assess the environmental levels of these metals in function of their availability to the ecosystems. Some cycling of mobile forms of Fe and Mn in the ecosystem would be expected and in particular of Zn in Rankers, where it may be involved in downward migration in the soil profile as well as transferred to the water and plant systems. Apart from Mn, which is mainly associated to the oxide phase, most of Fe, Zn and Cr are strongly retained in the soil minerals. Nevertheless, because they are present in the remaining phases, although not as easily soluble forms, they might be released to the ecosystem favored by the acid pH conditions of Leptosols on igneous rocks and Rankers. Moreover, these soils, and especially Rankers that are light soils, can be easily eroded and disaggregated soil particles bearing heavy metals may represent an environmental risk if they reach surface and ground waters. Therefore, special care regarding the management of these fragile mountain soils is highly recommended to avoid the environmental risk of cycling these metals in the environment. To this respect, awareness on off-site contamination hazard derived from the accumulation of different forms of heavy metals in reservoirs should also be taken into account to restrict anthropic impacts and to promote a rational land use in the ranges.

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