



Soil–metal interactions: Associations of macroconstituent fractions in selected soils

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Abstract

The study of soil processes provides new information about soil chemistry, but, frequently, simplified models or approximation techniques have to be used as tools in order to understand this complex system. One of these tools, metal speciation or sequential extractions, was applied in order to determine the distribution of major cations (Na, K, Ca, Mg and Fe). An analytical procedure of speciation was adapted for this study from published methods and it was applied to several soils collected at three different locations (one industrial area and two rural areas). Na, K, Mg and Fe were mainly accumulated in the residual fraction. In the case of Ca, the fraction associated with carbonates was the most important one. Based on speciation results, Ca was concluded to be the element which was more easily released to the soil solution. Variable classification by numerical taxonomy was applied to relate general soil properties with metal fractions. Individual studies for each element reveal that carbonate content was related to a large amount of the fractions. The selective extractants also used in this study were not specifically related to any fraction.

1. Introduction

When an element is added to a soil, it can be found in one of the following forms:

- dissolved in the soil solution,
- bound to inorganic or organic constituents,
- occluded or fixed in the soil minerals,
- incorporated into soil biological material [1].

The kinetics that rule the attainment of chemical equilibrium between the distribution of an element in the soil solution and the solid phase is very complex, and it can simultaneously involve several solid phases. As a consequence of the heterogeneity

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and variability of chemical, physical and mineralogical properties in soils, the results of many studies can only be applied to known systems. In spite of this, a great deal of work has been carried out on metal mobility, accumulation, and toxicity in sediments and different kinds of soils [2–4].

Because of the complexity of soil interactions, simplified models or approximation techniques have to be applied to understand soil variation and behavior because total metal determinations do not provide complete information about bioavailability, toxicity or mobility. One of those techniques involves computer programs such as GEOCHEM, WATSPEC or MINTEQ [5] which have been designed to determine the speciation of individual elements in natural waters and in soil solutions. However, the major weakness of these computer programs is that all naturally occurring complexes are not usually included in the models because all their formation constants have not been determined exactly in natural systems. Another technique is the procedure of sequential extraction to be applied to the solid phase of soils. Although imperfect [6], it provides information about the origin, mode of occurrence, biological and physicochemical availability, mobilization, bonding strength and transport of metals in the solid phase of natural systems [7].

The distribution of metals in soils and sediments can be investigated assuming that they can be found in different species or fractions. Tessier et al. [8] established the following fractions: 1 – exchangeable fraction; 2 – fraction bound to carbonates; 3 – fraction bound to iron and manganese oxides; 4 – fraction bound to organic matter and sulphurs; 5 – residual fraction. This fraction can contain mainly primary and secondary minerals, which may hold metals within their crystal structure. In order to determine those fractions in sediments and soils, different extraction methods have been proposed [9–12], which have been applied to study selected metals such as Cu, Pb, Zn and Cd [2, 4, 13–16].

The purpose of this study was to determine the distribution of major soil constituents (Na, K, Ca, Mg and Fe) in the solid phase of soils. Those major constituents, whose distribution into sequential fractions has scarcely been investigated, influence the behavior of other 'environmentally troublesome' metals because increased levels of major cations in soil solution compete for negatively charged surface sites on secondary minerals, reducing heavy metal sorption [17]. Studies of desorption processes in dynamic conditions revealed that the extent of desorption of cations like Pb^{2+} , Cu^{2+} and Cr^{3+} can vary under the influence of cations like Ca^{2+} , K^+ , Mg^{2+} and NH_4^+ [18]. As a consequence, the distribution of macroconstituents in the solid phase of selected soils was studied to determine their main forms of occurrence and possible relationships with general soil parameters and selective extractants. These associations among variables have been investigated using multivariate statistical methods like *classification by numerical taxonomy*.

2. Experimental

2.1. Soil sampling

In this study, three sampling locations were selected in the Basque Country (Northern Spain): locations 1 and 3 were selected in two different rural areas and location 2 was

chosen in an industrial area. In each sampling point soil samples were taken at four different distances from the main road (0, 10, 25 and 50 m), and at two depth intervals (0–5 cm and 5–10 cm) to ensure that the samples would be representative of each soil. Consequently, 24 samples were collected. All the samples were air dried and passed through a 2 mm sieve.

2.2. Analytical methods

The general characteristics of the soil samples collected at the three sampling locations were determined (Table 1). pH values of the soils were measured using a 1:2.5 suspension (soil weight:water volume). The method to determine cationic exchange capacity was basically the one used by Blakemore et al. [19]. Particle size analysis was performed according to D-2487 ASTM standard and only two fractions were considered: a fine fraction (clay and silt) whose particle size is smaller than 0.08 mm and a sand fraction (fine sand and medium sand) whose particle size ranges from 2 to 0.08 mm. Organic matter was determined by spectrometric adaptation of the Walkley and Black method [20]. Soil carbonate content was determined by using the Bernard calcimeter. The Fe and Mn oxide content was determined by using the speciation method explained below. Conductivity was measured at 25 °C using a ratio soil(g)/water(ml) of 5/25. Samples were heated until constant weight at 100, 400 and 900 °C in order to determine weight losses.

Total metal analysis of soils requires their total decomposition into soluble forms by acid digestion or fusion with various fluxes [21]. Since Na^+ is one of the cations under study in this work, the fusion method was rejected, as it involves the use of Na_2CO_3 . Acid digestions for metal soil determinations are commonly used involving different acid mixtures (HNO_3 , HO_4Cl , HF, H_2SO_4) in variable quantities [21–24]. We avoided using sulfuric acid because of its complex interference effects and because Ca element may be lost by inclusion in precipitated CaSO_4 in soils with high Ca (our samples are expected to be very calcareous) [25]. So, two acid digestions with no use of sulfuric acid were selected and they will be explained later. A certified reference soil (SO-3) was used in order to test the two acid digestions and to choose the most accurate one for determining the total amount of Na, K, Ca, Mg and Fe in our samples. This reference soil was purchased from the Canada Centre for Mineral and Energy Technology (Canadian Certified Reference Materials Project) and it is classified as a ludvisol with a large amount of calcite and dolomite. It was dried at 105 °C for 16 h prior to use. This reference soil was selected because its composition was the most similar one to what we expected to find in our samples (so matrix effects would be similar).

Duplicate 1 g portions of the certified soil were added to PTFE vessels and two acid digestions were carried out. In the first digestion, a HF + HNO_3 + HClO_4 acid mixture was used (A method) [26] and in the second one a HNO_3 + HClO_4 mixture was used (B method) [26]. The procedure followed in the A method consists of the addition of 10 ml of 65% HNO_3 and 10 ml of 50% HF to the soil. The solution was heated until almost complete evaporation in a sand bath. Then, 4 ml of 60% HClO_4 was added, and it was evaporated again. Finally 4 ml of 65% HNO_3 was added, and

then bidistilled water was used for necessary dilutions. The second method (B) consisted of an acid attack using 12 ml of 65% HNO₃ and 6 ml of 60% HClO₄ in a sand bath until almost complete evaporation. Then 8 ml of 65% HNO₃ was added, and it was again dried until almost complete evaporation. Finally, 4 ml of 65% HNO₃ was added and bidistilled water was used for dilution.

The analytical procedure for speciation was adapted for this study from the methods proposed by Tessier et al. [8] and Kitano and Fujiyoshi [9] and it consisted of the following consecutive steps:

1. Extraction with 1 M NH₄OAc at pH 7 (exchangeable fraction).
2. Treatment with 1 M HOAc (fraction associated with carbonates).
3. Extraction with 0.04 M NH₂OH · HCl in 25% (v/v) of HOAc at 100 °C (fraction associated with Fe and Mn oxides).
4. Treatment with H₂O₂ (30%) at pH 2 and 0.02 M HNO₃ at 85 °C followed by an extraction with 3.2 M NH₄OAc in HNO₃ (20% (v/v)) (fraction associated with organic matter and sulphurs).
5. Acid digestion. In this study, the residual fraction was determined by the difference between the total amount and the sum of the amounts extracted in the previous steps. In order to confirm the use of this subtraction method, acid digestion was applied to 12 randomly chosen samples. The differences between the results of both methods did not exceed 5%.

At each extraction step, a SBS flocculator was used for continuous agitation and, after equilibration, solid–liquid separation was achieved by centrifugation at 3500 rpm for 30 min. The supernatant was filtered through a No. 42 Whatman filter and placed in an acid cleaned tube. The solid residue was washed twice with bidistilled water for the next extraction step.

Some selective extractants considered as bioavailability predictors [27, 28] were also used:

- DTPA, according to the method proposed by Lindsay and Norvell [29].
- HCl, as the procedure followed by Xiu et al. [30].
- Na₂EDTA, as the procedure followed by Lantmann and Meuer [31].

Na was not measured when Na₂EDTA extractant was used because it is included in the extractant itself. The same applies to Ca when the DTPA procedure was used.

All measurements were performed by atomic absorption spectroscopy for Mg and Fe and emission mode for Na, K and Ca using the appropriate flame in each case (air/acetylene or nitrous oxide/acetylene flame). Matrix effects were addressed by preparing AAS standards in solution identical to the concerned extractant or acid mixture in each case.

2.3. Statistical methods

Variable classification by numerical taxonomy was used in order to establish relationships among all the measured parameters. In this multivariate method based on $(1 - r)$ distances (r being Pearson's correlation coefficient), the UPGMA method (unweighted pair group method using arithmetic averages) [32] was selected with the aim of obtaining information from the corresponding dendrograms of classification of

Table 1
Mean values and standard deviations of soil general parameters (eight samples at each sampling point)

	Point 1		Point 2		Point 3	
	Mean value	Stand. deviat.	Mean value	Stand. deviat.	Mean value	Stand. deviat.
Carbonate (%CO ₂)	1.75	1.61	6.26	6.21	2.79	3.49
OM (%C)	1.49	0.87	2.66	0.83	3.19	0.84
CEC (meq/100 g)	17.86	5.95	16.99	4.33	17.67	3.33
pH	6.75	1.40	7.73	0.31	5.86	1.16
Fe-oxide (%)	10.70	3.45	6.40	10.45	22.70	5.85
Mn-oxide (%)	60.80	9.65	42.80	18.35	33.60	5.68
Weight loss 100 °C (%)	1.04	0.31	3.25	2.89	1.56	0.29
Weight loss 100–400 °C (%)	3.48	2.59	5.17	3.75	5.86	1.62
Weight loss 400–900 °C (%)	2.95	2.51	6.06	8.11	3.45	2.22
Conductivity (μS/cm)	129	69	172	94	85	30
Sand (%)	67	15	91	4	95	3
Clay + silt (%)	31.5	14.98	5.85	4.50	3.82	3.12

variables. All the dendrograms have been obtained taking as variables metal fractions and general soil properties (shown in Table 1) except Fe-oxide and Mn-oxide. In all cases the cophenetic correlation coefficient [33] was larger than 0.876.

3. Results and discussion

Table 1 shows general characteristics of the soil samples studied. Sampling point 2 had a larger content of carbonates than the other two. The granulometric analysis showed that location 1 differed from the others, but as far as CEC was concerned no important differences were apparent. The average value of pH shown in Table 1 indicates that, according to the Blakemore classification [19], point 1 is an almost neutral soil, point 2 is slightly alkaline and point 3 is moderately acidic.

On the basis of the results shown in Table 2, the A method was chosen to be applied to the selected soils in order to determine total quantities of Na, K, Mg, Fe and Ca. The use of HF in the selected method indicates that for soil macroconstituents it is necessary to dissolve the silica matrix. Table 3 shows mean values and standard deviations for the total amounts of the major cations studied, determined by using the A method.

The use of the sequential extraction procedure gives an idea of the binding strength of the analyzed elements, but it does not accurately describe the metal geochemistry [7]. The speciation method used in this study showed the distribution of Na, K, Ca, Mg and Fe in different soil fractions (Figs. 1–5). From these figures, it was concluded that Na, K, Mg and Fe elements were mainly accumulated in the residual fraction as constituents of aluminosilicates, which is in agreement with Elejalde et al. [2], and shows that they come from natural sources.

Table 2

Comparison of results for the certified reference soil when applying the A and B acid digestion methods.

Element (%)	Certified value	A method	B method
Na	0.74 ± 0.04	0.76 ± 0.01	0.39 ± 0.01
K	1.16 ± 0.05	1.08 ± 0.02	0.60 ± 0.00
Ca	14.63 ± 0.40	14.55 ± 0.20	16.25 ± 0.37
Mg	4.98 ± 0.10	4.00 ± 0.20	8.15 ± 0.13
Fe	1.51 ± 0.06	1.37 ± 0.08	0.95 ± 0.06

Data represent average values in a 95% confidence interval, the number of measures being higher than four in all the cases.

Table 3

Mean values and standard deviations for total amounts of macroconstituents in the three sampling points

Element (%)	Point 1		Point 2		Point 3	
	Mean value	Stand. deviat.	Mean value	Stand. deviat.	Mean value	Stand. deviat.
Na	0.219	0.052	0.148	0.024	0.164	0.078
K	0.081	0.019	0.067	0.007	0.046	0.020
Ca	2.735	1.044	6.230	3.839	2.787	1.888
Mg	0.193	0.051	0.291	0.138	0.171	0.140
Fe	1.617	0.227	2.637	1.030	0.933	0.132

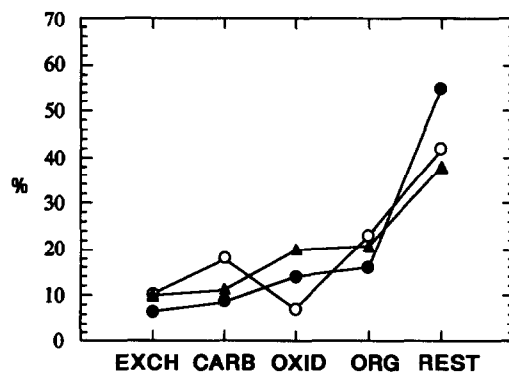


Fig. 1. Speciation of Na (● point 1; ○ point 2; ▲ point 3).

The distribution of Ca species (Fig. 3) shows that this element was mainly associated with carbonates in the selected soils. The relatively small amount of Ca associated with organic matter + sulphurs could be explained by the small affinity of this element to form complexes with the organic matter in natural environments [34].

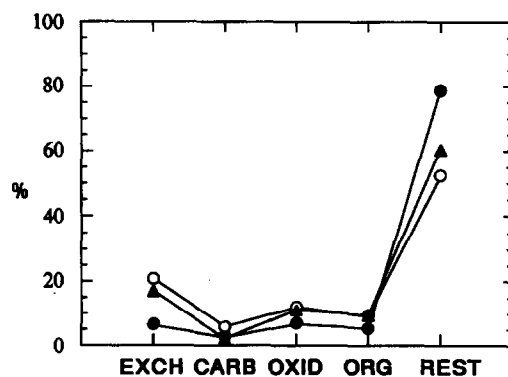


Fig. 2. Speciation of K (● point 1; ○ point 2; ▲ point 3).

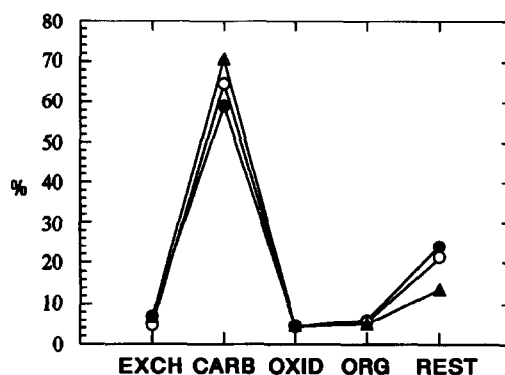


Fig. 3. Speciation of Ca (● point 1; ○ point 2; ▲ point 3).

However, some authors [35] indicated that a non-biogenic association of organic matter with particles of calcium carbonate is possible, which could explain the small percentage that appears in the organic fraction.

The percentage distribution of K and Ca fractions for the three sampling points was similar. In the case of Mg (Fig. 4), the fraction associated with carbonates for point 2 appeared to be larger than the exchangeable fraction, which is just the contrary for points 1 and 3. This fact can be explained by the presence of a greater amount of dolomite ($\text{Ca, Mg}(\text{CO}_3)_2$), which frequently appears associated with calcite. The percentage amount of Na associated with oxides in point 2 (Fig. 1) showed a different behavior with respect to other fractions and to the other sampling points, which could be related to the different amounts of Fe and Mn associated with oxides shown in Table 1. It can be concluded that Na was preferentially associated with Fe-oxides, which explains the different behavior in sampling point 2.

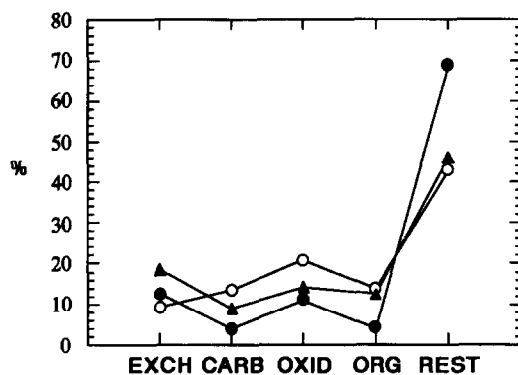


Fig. 4. Speciation of Mg (● point 1; ○ point 2; ▲ point 3).

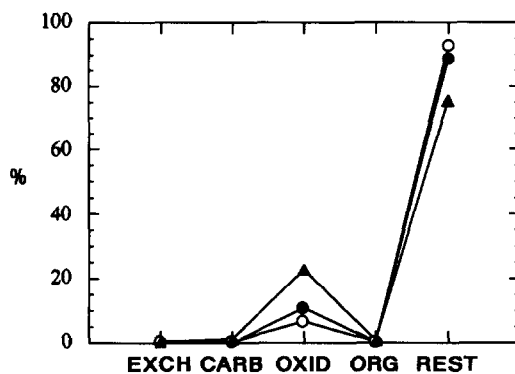


Fig. 5. Speciation of Fe (● point 1; ○ point 2; ▲ point 3).

As far as Fe distribution is concerned (Fig. 5), only two fractions were important: the fraction associated with oxides and the residual one. Because of the fact that only a small quantity of soil Fe is relatively soluble (oxide fraction), this element is considered as a macroconstituent in soils but as a microconstituent in bioavailability studies [36].

The first four fractions are considered to be more easily released to the soil solution than the residual fraction; thus, the sequence from the most easily released element to the most retained one in the soils is: $\text{Ca} > \text{Na} \approx \text{Mg} > \text{K} > \text{Fe}$.

The results obtained for selective extractants are shown in Table 4. It was not possible to determine Ca extracted with DTPA or Na with EDTA because both were present in the extractants used according to the selected methods. Quantities extracted by using HCl are the largest ones, except for Fe which basically agrees with Norvell [37].

The possible associations among all the parameters studied have been determined from the analysis of the individual dendrograms for each element (UPGMA method)

Table 4
Average quantities extracted using HCl, EDTA and DTPA ($\mu\text{g/g}$ soil dw)

		Point 1	Point 2	Point 3
Na	HCl	48.16	87.43	85.9
	DTPA	36.28	33.22	55.83
K	HCl	63.21	269.7	90.49
	EDTA	36.44	86.69	72.01
	DTPA	43.13	67.71	180
Ca	HCl	5756	21 570	7559
	EDTA	5689	12 480	5359
Mg	HCl	135	543.8	173.9
	EDTA	83.38	321	100.1
	DTPA	79.30	117	118.7
Fe	HCl	226.6	414.2	773.9
	EDTA	197.9	1035	484.2
	DTPA	383.7	238.9	1011

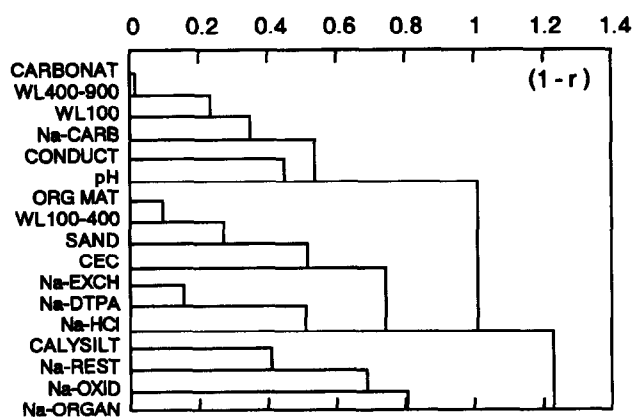


Fig. 6. Dendrogram for Na.

obtained by means of classification by numerical taxonomy. In this study, the critical value of the correlation coefficient was 0.404 for 24 samples, or observations at 95% confidence level, so distances shorter than 0.596 become significant.

The dendrogram of Na (Fig. 6) reveals that the fraction associated with carbonates is related to carbonate content, conductivity and soil pH. The exchangeable fraction shows relationships with DTPA and HCl extractions. The other species are mainly related to clay + silt content in the soils.

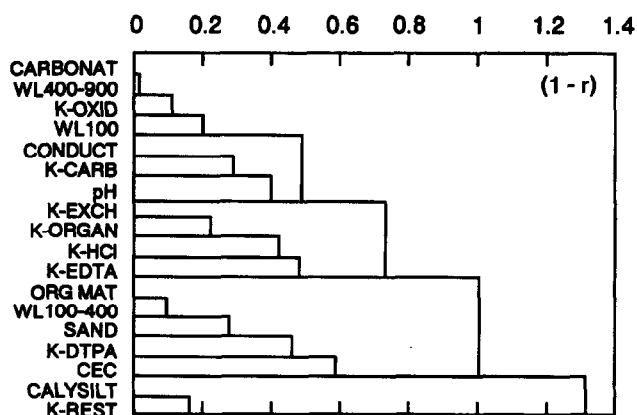


Fig. 7. Dendrogram for K.

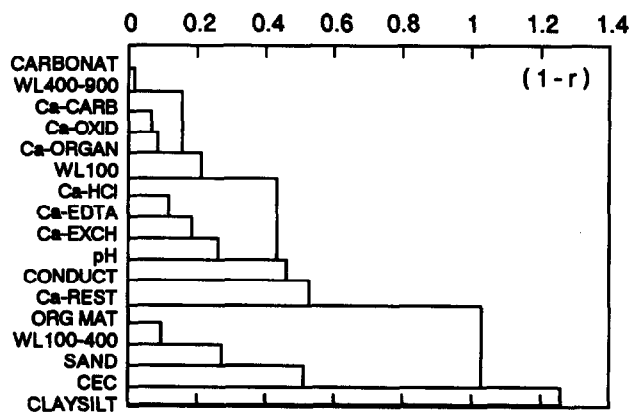


Fig. 8. Dendrogram for Ca.

In general terms, the dendrogram for K (Fig. 7) shows that residual K is related to clay + silt fraction of the soil which indicated that this element is present in the silicated soil constituents. Most of the K species were related to carbonate content. As far as selective extractants were concerned, EDTA and HCl extractions were associated with carbonate content whereas DTPA extractant did not show this relationship and was related to soil organic matter.

In Fig. 8 associations for Ca are shown. It appeared that all species, even selective extractants, were related to the carbonate content. The less significant association is observed for residual Ca (Ca-REST), although it was higher than the critical value. A second group included several soil parameters such as organic matter, weight losses between 100–400 °C, sand content and cationic exchange capacity.

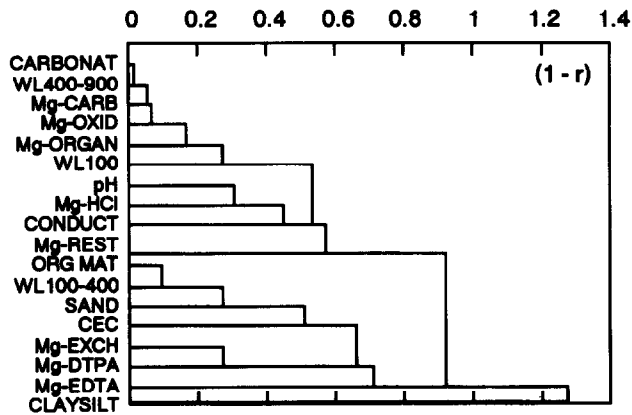


Fig. 9. Dendrogram for Mg.

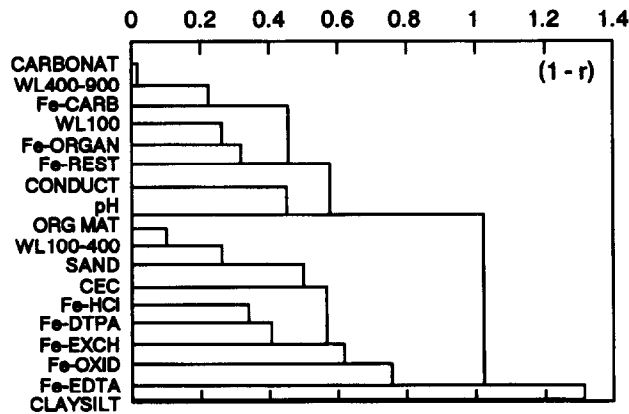


Fig. 10. Dendrogram for Fe.

The dendrogram for Mg is shown in Fig. 9. Most Mg species were also associated with carbonate content, but the exchangeable fraction stands apart from the others and was related to DTPA and EDTA extractions. This fact suggests that those two selective extractants could be more readily used as biodisposable Mg predictors.

As shown in Fig. 5, the most important species in Fe speciation were the fraction associated to oxides and the residual fraction, so in the analysis of the dendrogram (Fig. 10) only these fractions were taken into account. The residual Fe seemed to be associated with the carbonate content, but the oxide fraction was related to certain selective extractants (DTPA, HCl) and certain soil parameters (CEC and organic matter).

Carbonate content and weight losses between 400–900°C logically have a large correlation coefficient in all dendrograms because of the thermal degradation of

carbonates within that temperature range [38]. A similar conclusion was obtained from the fact that in all the dendrograms the organic carbon content and weight losses between 100–400 °C had a very large correlation coefficient.

4. Conclusions

In spite of their different origin, the distribution of major soil cations was very similar in the three sampling locations. For four of them (K, Na, Mg and Fe) the greatest fraction was the residual one but in the case of Ca the fraction associated with carbonates was the most important one. In an attempt to relate general soil properties and metal fractions, variable classification by numerical taxonomy was applied. Individual studies for each element showed that carbonate content was related to a large amount of macroconstituent fractions. The selective extractants were not specifically related to any fraction.

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