

SOIL ORGANIC MATTER–METAL INTERACTIONS IN CHILEAN VOLCANIC SOILS UNDER DIFFERENT AGRONOMIC MANAGEMENT

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ABSTRACT

The organic matter existing in volcanic soils must be investigated not only in quantity, but also in quality in order to understand its role in soils and thus ensure adequate levels of stable organic polymers contributing to soil humification.

The meaningful contribution proposed by this investigation is based on the study of the interaction of soil organic matter (SOM) in its fractions humic acid and fulvic acid with metallic elements that are macro- and micronutrients and also contaminants. The study was carried out in Chilean soils of the type Andisols and Ultisols. To this end, humic acids and fulvic acids were fractionated to determine phenolic, carboxylic and total acidity.

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In addition cation holding capacity was determined. From the knowledge of this organic matter–metal interaction, the behavior and actual contribution of organic matter to soil may be inferred in relation to storage and availability of metallic elements, both nutrients and contaminants.

The results of this study demonstrate the existence of electron-donor sites in the organic fractions of soil, which may be highly specific for heavy metals. They also confirm the possibility that metal-ion, especially micronutrient, bioavailability is affected by retention mechanisms involving the nature of SOM. Thus, the content of carboxylic groups in fulvic acid is higher than in humic acid. The number of phenolic groups is about the same in both. In addition, comparison of the maximum binding ability among the cations leads to the conclusion that the most frequent tendency is to retain cadmium (Cd) > zinc (Zn) > calcium (Ca) at the used concentrations. In wild forest, soils exhibit organic polymers with a higher content of phenolic groups and total acidity compared with the soils subjected to agronomic management and to some other use. Fulvic polymers exhibit a higher maximum cation binding ability in wild forest.

Key Words: Maximum binding ability; SOM–metal interaction; Humic polymer; Fulvic polymer; Volcanic soils

INTRODUCTION

It is a well known fact that organic matter in soil plays an essential role in nutrient availability. In the case of metallic nutrients, organic matter affects their solubilization, mobilization, and retention, acting as a whole phase. However, the specific organic fractions show higher specificity through their functional groups, such as carboxyls, hydroxyphenols, hydroxyalcohols, and carbonyls. Thus, the quantity and quality of SOM should be investigated, mainly its effect as energy and nutrient source, the microbiological ability, and its contribution of stable organic polymers to conform soil-humus pool^{1,21} Closely related to these functions, SOM is a very important soil component contributing to mobilization and retention of cationic species (macro- and micronutrients) by means of cation exchange mechanisms.

It should be remembered that SOM has stable organic fractions, i.e., humic acids and fulvic acids, which are able to form complexes with trace elements on

account of their high content of oxygen in functional groups such as carboxyls, phenolic, hydroxyls and carbonyls. Structurally, humic substances are polymeric blocks, usually complex macromolecules of a phenolic and carboxyl benzene nature, which appear bound by weak ligands, mainly hydrogen bonds. Many authors^[3-7] have determined the hypothetical structure of these compounds through the use of analytical techniques such as infrared spectrophotometry (IR), nuclear magnetic resonance, x-ray diffraction, and they deduced that humic polymers are flat lattices of condensed aromatic compounds to which functional groups and aliphatic chains linking to the polymer are bound.

Fulvic polymers possess a rather disorderly structure with a low level of aromaticity and condensation, aliphatic chains being predominant.

Due to this chemical configuration, humic polymers (humic acid and fulvic acid), separated from SOM, form metal complexes when they combine with metal solutions, where the central group is the organic molecule bound to more than one metal ion. Zunino and Martin^[8,9] and Zunino et al.^[10-12] has worked on the chemical mechanisms operating in soil to mobilize and protect essential cationic elements in soil from side reactions of hydrolysis or adsorption. His hypothesis is based on the growing affinity of elements for electron-donating sites contained in humic polymers (humic acid and fulvic acid) occurring in soil. Thus, trace element bioavailability would be regulated by the relative affinity of metal ions for the active sites in polymers and in natural complexes existing in soil solution.

For a mathematical description of the phenomenon of fixation of Zn(II), Ca(II), and Cd(II) to humic and fulvic polymers, Langmuir's and Freundlich's models have been traditionally used. In addition, new models have been proposed and tested.^[13-16] The Langmuir isothermal method is utilized by Zunino and Martin,^[8,9] since this model was and continues to be the best for the Chilean volcanic soils under study. Its principle describing gas adsorption on a solid surface is adaptable to the soil system. The Langmuir isothermal model represents a mathematical model to obtain the values required in this study. Thus, the Langmuir equation is applied to these hyperbolic functions in order to calculate a maximum (Maximum Binding Ability, MBA) and a term related to energy bonds occurring between cations and macromolecules (Relative Affinity Constant, k_2).

It is known that, because of the heterogeneous nature of humic substances, trace element complexation may be considered as occurring with a great number of reactive sites with binding affinities ranging from weak attractive forces to the formation of highly stable coordinate ligands. Calcium (II) bonding, for example, may occur by (a) hydrogen bridge, (b) electrostatic attraction by the charge of the COO^- group, (c) formation of a coordinate ligand with a simple donor group, and (d) formation of a chelated structure, by combination of the sites with COOH and phenolic OH. By bonding of a trace metal, the formation of a coordinate ligand may occur. This form of complexation predominates where humic substances are abundant.

The significant contribution of this study is to learn about the interaction of organic matter in soil with metallic elements that can be classified as both essential nutrients and contaminants in Chilean volcanic soils of the Andisol and Ultisol orders. To this end, determination was done of phenolic acidity, carboxylic acidity, total acidity, and binding ability of Zn(II), Ca(II), and Cd(II). In addition, in order to demonstrate the interaction of organic polymers with the cations, infrared spectrophotometry was applied to the organic polymers extracted from SOM and to the organic polymers reacting with Zn, Ca, and Cd in the Osorno soils (nonfertilized, natural, wild prairie), Piedras Negras (wild forest), and Cudico (nonfertilized natural prairie), which enabled us to study the interaction mechanisms.

MATERIALS AND METHODS

The study of MBA and of relative affinity constant for Zn(II) and Ca(II) was carried out with the organic polymers (humic acid and fulvic acid) isolated from the selected soils (Table 1). The volcanic soils selected were: Andisols (Trumaos, Ñadis) and Ultisol (Rojo Arcillosos), corresponding to sites in southern Chile, where small extensions of land of the same soil have been

Table 1. Selected Properties of Soils

Soils	pH	% C
Andisols (Trumaos)		
Osorno Pf	4.69	8.69
Osorno P	5.04	9.40
Puerto Octay P	4.43	10.32
Puerto Octay F	4.95	10.48
Placandeps (Ñadis)		
Frutillar F	4.54	19.28
Frutillar Pf	5.16	14.92
Frutillar P	4.66	14.16
Frutillar P/B	5.35	16.44
Piedras Negras F	4.60	16.50
Piedras Negras Pf	4.20	13.51
Piedras Negras P	4.93	14.28
Ultisols (Rojo Arcillosos)		
Cudico F	5.53	10.67
Cudico P	5.40	4.96
Collipulli O	5.47	3.08

F, wild forest; P, natural prairie; Pf, fertilized prairie; O, untreated deforested soil; B, barnyard manure.

subjected to several different uses and management variables. The soils were collected and processed to obtain the respective humic and fulvic acids.

Determination of MBA and k_2 for Cd(II) was performed on the soils samples showing the highest MBA: Osorno natural prairie (Trumao Andisol), Piedras Negras wild forest (Ñadi Andisol), and Cudico natural prairie (Rojo Arcilloso Ultisol), according to Zunino and Martin.^[8,9]

Determination of Acidity in Stable Fractions of Soil Organic Matter

In theory, total acidity of humic substances is determined by using a strong base to neutralize all the acid groups present in the polymers.^[7] Acidity from carboxylic acid groups is determined by an indirect method by using a weakly acid conjugated base.^[2] Experimentally, total acidity and the number of carboxylic groups were determined by the difference of existing phenolic groups. Titration was potentiometrically performed.

Determination of MBA of Organic Polymers (Humic Acid and Fulvic Acid) with Metals Ca(II), Zn(II), and Cd(II)

The experimental methodology and the theoretical model utilized in this study were proposed and developed by Zunino and Martin.^[8,9] They permit a study of the retention properties of metal ions of polymers in colloidal solutions. For this purpose, use is made of the organic polymers humic acid and fulvic acid, previously separated from soil by the alkali extraction method.^[2] The polymers are isolated and purified by dialysis and their retention properties studied. The three elements selected are (1) Zn, a transition metal important both in plant mineral nutrition as a micronutrient and in heavy metal contamination of soils and waters. Zn interacts most frequently by coordination with the hydroxy-phenolic group of the organic polymer; (2) Ca, an important component of natural waters and soil solutions^[3] it is doubtlessly a natural competitor with other metals for the binding sites in polymeric macromolecules. It is a prototype of electrovalent element and it interacts with the carboxylic group of the organic polymer; and (3) Cd, a contaminant, is a transition metal in group IIB the same as zinc so it may be deduced that it interacts with the hydroxy-phenolic group of the organic polymer by coordination.

Thus, in order to determine MBA of the humic polymers obtained, and k_2 for Zn(II), Ca(II), and Cd(II) the dialyzing method described by Zunino and Martin^[8,9] was used. Calcium, Zn, and Cd determination was done by atomic absorption, in a Perkin Elmer 3110 Atomic Absorption Spectrophotometer.^[17]

Calcium, Zn, and Cd solutions were prepared with tetrahydrated calcium nitrate, hexahydrated zinc nitrate, and tetrahydrated cadmium nitrate, all the equilibrium solutions were adjusted to 0.06 ionic strength (equivalent to the solution in use with the highest concentration) by addition of the required amount of potassium nitrate that behaves as an indifferent electrolyte. pH is the same for all of the solutions. The concentrations in use were six: 4×10^{-4} , 1×10^{-3} , 2×10^{-3} , 4×10^{-3} , 8×10^{-3} , and 2×10^{-2} M.

A special dialyzing membrane (dialysis tubing, a Sigma Chemical Co. cellulose membrane) was used to make little bags containing the polymer sample. Through dialysis, the polymer becomes saturated in the metal ion by interacting with the solutions of increasing concentration of the cation under study. Dialysis was performed for 48 h to reach equilibrium, then the bag was repeatedly washed with distilled water to eliminate rebounded cations. The bag content was then drawn and ultra pure distilled water was added to volume. The appropriate dilutions were made (for calcium and cadmium) and the amount of cation fixed to the polymer was determined by atomic absorption spectrophotometry. Finally, MBA and k_2 were calculated using the Langmuir isotherm.

Zunino^[12] state that these data are valid under experimental conditions: ionic strength, pH, number of washings, etc. Although the values thus obtained are not absolute, they permit qualitative and quantitative studies of the ability of macromolecular ligands to link the metal ions.

RESULTS AND DISCUSSION

The methods used here were established and validated in previous studies.^[2,7-9] Analytical determinations were done in duplicate so that the reported values are the mean of the values obtained with fluctuations of not more than 5%.

Functional Analysis of Humic Polymers

The previously described method used to determine total, carboxylic, and phenolic acidity of humic polymers permits to find reproducible and reliable acidity values leading to a coherent analysis of these organic polymers. It should be noted that the resulting degree of acidity represents "probable" minimum values since some humic polymers might have been lost by cleavage or breakdown during extraction and purification, in spite of the application of best conditions of extraction and purification.

Table 2 shows the content levels of acidic groups of humic and fulvic fractions for Chilean volcanic soils (Andisols and Ultisols).

Table 2. Content Levels of Acidic Groups of Humic and Fulvic Fractions

Acidic Group	Humic Acid (mEq H ⁺ /g)	Fulvic Acid (mEq H ⁺ /g)
Total	2.3–15.2	5.2–16.3
Carboxylic	1.1–6.2	3.8–9.8
Phenolic	0.19–10.0	0.2–8.7

Total acidity range is 5.2 to 16.3 mEq/g for fulvic acid and 2.3 to 15.2 mEq/g for humic acid. The contents of carboxylic groups are 3.8 to 9.8 mEq/g for fulvic acid and 1.1 to 6.2 mEq/g for humic acid. Thus, total acidity and contents of carboxylic groups is higher for fulvic acid than for humic acid, which totally agrees with Schnitzer's studies.

Phenolic acidity is 0.2 to 8.7 mEq/g for fulvic acid and 0.2 to 10.0 mEq/g for humic acid, thus, both polymers contain about the same number of phenolic groups per weight unit.

Interaction of Humic Polymers with Metal Ions

The MBA values obtained for the polymers studied are similar to those found in previous studies¹²¹ for soil polymers and for models obtained by synthesis of microbial species isolated from volcanic soil (Table 3). Thus, this study leads to the following conclusions:

The narrow range of Zn-MBA goes from 4.4 to 7.9 μ Eq Zn(II)/mg for humic polymers compared with that for Zn(II) which goes from 2.1 to 7.1 μ Eq

Table 3. Range of Variation of Maximum Binding Ability (MBA) and Energy Term (k_2) of Humic and Fulvic Fractions for Zn(II), Cd(II), and Ca(II)

Cation	Humic Acid		Fulvic Acid	
	MBA (μ Eq Cation/mg Polymer)	k_2	MBA (μ Eq Cation/mg Polymer)	k_2
Zn(II)	4.4–7.9	85–260	2.1–7.1	79–346
Cd(II)	2.6–9.2	34–81	5.2–7.4	32–137
Ca(II)	0.6–3.6	645–43,170	1.2–3.2	937–6,464

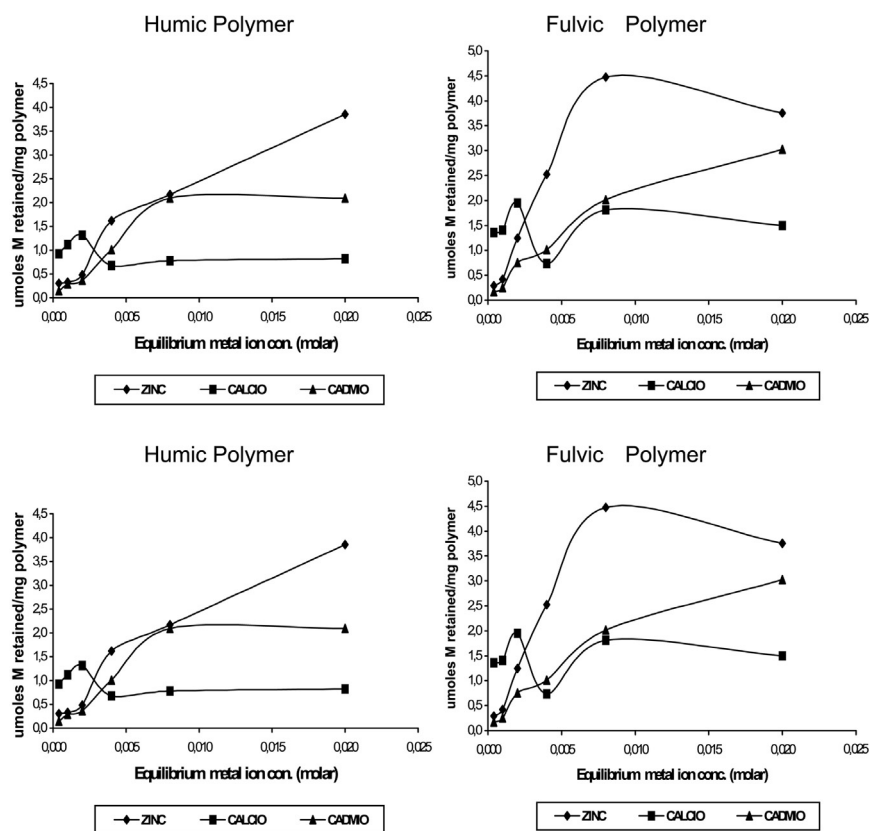


Figure 1. Adsorption isotherms for humic acid and fulvic acid of Cudico natural prairie soil and adsorption isotherms for humic and fulvic acid of Osorno natural prairie soil.

Zn(II)/mg for fulvic polymers. In addition, it may be concluded that Zn-MBA is higher for humic polymers. In order to obtain these values applying the Langmuir model, each of the data corresponding to the saturation study are selected adequately to provide the right information about the actual maximum binding ability. The Zn-MBA values reported here were analyzed with their respective plots so that the values found through the Langmuir model correspond to the saturation value observed in the plot. When this value does not correspond, the saturation value observed in the plot is reported. The same criteria are applied to determine cadmium and calcium MBA (Fig. 1).

Table 3 indicates that Cd-MBA values in the three soils under study varies from 2.6 to 9.2 μEq of Cd(II)/mg for humic polymers and from 5.2 to 7.4 μEq of

Cd(II)/mg for fulvic polymers. It may be observed that Cd-MBA varies widely and is higher for humic polymers compared to fulvic polymers.

Ca-MBA values are very similar, i.e., from 0.6 to 3.6 $\mu\text{Eq Ca(II)/mg}$ for humic polymer, and from 1.2 to 3.2 $\mu\text{Eq Ca(II)/mg}$ for fulvic polymer.

Table 3 shows the k_2 values, which are higher for the element less retained, such as in the case of most of the organic polymers in the soils under study that interact with Ca, Zn, and Cd. In general, analysis of the k_2 values leads to the conclusion that organic polymers show the largest k_2 values for Ca, followed by Zn and Cd, that is, the sequence is $\text{Ca} > \text{Zn} > \text{Cd}$. Thus, analysis of the tendency of MBA values in Table 3 show a retention sequence $\text{Cd} > \text{Zn} > \text{Ca}$. This fact confirms the meaning of the relative affinity constant in relation to MBA and it may be explained by the specificity of the polymer with the cations due to the space arrangement of the latter and to the cation accessibility to the functional groups. This is better explained by the study on calcium–zinc competition carried out,^[18] where at low concentrations the tendency is to fix calcium while the tendency to fix Zn increases with increasing concentration.

The different behavior of Zn and Ca in the humic and fulvic polymers of the soils under study is clearly visualized. Zn doubtlessly reacts with organic polymers according to the Langmuir model (increasing cation fixation with increasing concentration to reach saturation). Trace elements of the transition series usually participate more successfully in these adsorption processes.^[19] Their electronic configuration has been chemically demonstrated to facilitate the formation of coordination compounds with functional groups or compounds having S or N as electron donors. SOM contains just these organic groups, therefore for Zn it is easier to form coordination compounds with the electron donor group of the polymeric macromolecule. This is not the case for Ca(II).

In general, it is known that due to organic polymer heterogeneity, complexation with trace elements may occur by means of weak attracting forces, forming highly stable compounds with coordinate ligands through hydrogen bridge, formation of a coordinate ligand with a donor group, formation of a chelate at a combining site, and electrostatic attraction with a carboxyl group. Electrostatic attraction with the carboxyl group could be active in the case of Ca(II) interaction with humic and fulvic polymers. Cadmium is a transition element included in the same periodic group (IIB) as Zn. Cd behavior to interact with organic polymers differs from that of Zn though, surely due to its physical properties, such as atomic weight, ionic radius and the number of H_2O molecules coordinated.

Table 4 shows the MBA ranges for humic and fulvic polymers according to soil source. Analysis of Zn and Ca-MBA shows that in Trumaos, Ñadis, and Rojo Arcillosos soils they are similar both for humic and for fulvic polymers. The MBA-Cd values are very similar to each other, for fulvic acid. In general, behavior according to soil source does not exhibit any similarity among Trumao,

Table 4. Maximum Binding Ability (MBA, $\mu\text{Eq Cation/mg Polymer}$) Characteristics of Humic and Fulvic Polymers for the Soils Studied

	Trumaos	Ñadis	Rojo Arcillosos
Zn(II)			
Humic polymer	12.0–15.8	7.7–13.6	9.8–13.8
Fulvic polymer	9.7–13.9	4.1–14.1	11.4
Ca(II)			
Humic polymer	1.2–2.3	3.0–5.0	5.5–7.3
Fulvic polymer	2.3–3.9	2.7–6.4	3.2
Cd(II)			
Humic polymer	5.3	9.2	18.5
Fulvic polymer	13.5	14.7	10.4

Ñadi, and Rojo Arcillosos soils, and they correspond to individual behavior according to soil use or management, this is shown in Tables 5 and 6.

Tables 5 and 6 show high interaction of Zn-MBA for the Puerto Octay natural prairie (humic acid) and Frutillar wild forest (fulvic acid), while there is high Ca-MBA interaction in Cudico natural prairie (humic acid) and Piedras Negras natural prairie (fulvic acid) soils.

Tables 5 and 6 illustrate the connection between the Ca-MBA values with the carboxylic acidity found for humic and fulvic acid, and between Zn-MBA values and Cd-MBA with phenolic acidity. Comparison of phenolic acidity of organic polymers with MBA values of Zn and Cd shows that MBA values are larger than the measured phenolic groups; perhaps, cations are interacting with other functional groups present in the organic polymers containing N and S.

Comparison of carboxylic acidity of organic polymers with the Ca-MBA value shows that 20 to 60% of the carboxylic groups were occupied by the cation.

Analysis of Cd(II) interaction with phenolic groups shows that this cation occupies a greater number of functional groups than Zn, probably due to the chemical nature of Cd. It is known that wild forest soils exhibit high phenolic acidity. In the case under study a higher Zn binding ability is observed for fulvic polymers in wild forest soils compared with soils with agronomic treatments.

In fertilized soils and in soils with barnyard manure application, while no high value is observed in carboxylic acidity compared with the other agronomic treatments, Ca interacts with a larger number of carboxylic groups of the organic macromolecule. Thus, an effect might result from the agronomic use or management to which these soils have been subjected.

Table 5. Comparison of Carboxylic Acidity with Ca-MBA and Phenolic Acidity with Zn and Cd-MBA, in the Fulvic Fractions of the Soils Studied

Fulvic Acid	Carboxylic Acidity		Phenolic Acidity		
	(mEq/g)	Ca(II)-MBA	(mEq/g)	Zn(II)-MBA	Cd(II)-MBA
Andisols (Trumaos)					
Osorno Pf	4.13	*	1.04	*	*
Osorno P	4.90	3.90	4.94	11.20	13.50
Puerto Octay P	5.93	3.65	0.18	9.72	*
Puerto Octay F	7.65	2.30	8.69	13.78	*
Placandepts (Ñadis)					
Frutillar F	7.35	3.09	6.15	14.13	*
Frutillar Pf	6.42	2.71	0.24	5.76	*
Frutillar P	6.82	4.38	4.72	4.82	*
Frutillar P/B	6.86	4.27	2.11	8.32	*
Piedras Negras F	8.22	2.88	0.92	10.46	14.73
Piedras Negras Pf	9.79	2.86	0.30	9.86	*
Piedras Negras P	7.52	6.35	0.64	4.12	*
Ultisols (Rojo Arcillosos)					
Cudico F	6.08	*	5.05	*	*
Cudico P	5.87	3.17	3.54	11.38	10.44
Collipulli O	3.79	*	1.56	*	*

F, wild forest; P, natural prairie; Pf, fertilized prairie; O, untreated deforested soil; B, barnyard manure; MBA, maximum binding ability (uEq cation/mg polymer); *, not determined.

Finally, from the above discussed data it may be concluded that each type or series of soils will show its own metal binding characteristic. The bioavailability of these metals, the natural reservoir of which is humus, will represent the result of the interaction of biotic and abiotic factors, mainly composition and properties of the clay fraction and humus in soil.^[10] Evidently, fulvic and humic acids are found in soil as a part of mixed clay–humus colloids and not as a colloidal solution. The allophane–humus association in these soils is produced, of course, through the active polymer functional groups which interact physical-chemically with the active sites of the inorganic surface.

Structural Analysis

The frequencies and wavelengths of absorption depend on the relative masses of atoms, the strength constants of bonds, and the geometry of atoms.

Table 6. Comparison of Carboxylic Acidity with Ca-MBA and Phenolic Acidity with Zn and Cd-MBA, in the Humic Fractions of the Soils Studied

Humic Acid	Carboxylic Acidity		Phenolic Acidity		
	(mEq/g)	Ca(II)-MBA	(mEq/g)	Zn(II)-MBA	Cd(II)-MBA
Andisols (Trumaos)					
Osorno Pf	4.76	1.24	2.24	12.21	*
Osorno P	5.00	2.02	0.32	15.66	5.24
Puerto Octay P	4.28	2.07	0.19	15.75	*
Puerto Octay F	5.16	2.28	10.00	12.03	*
Placandeps (Ñadis)					
Frutillar F	4.12	2.96	6.76	13.32	*
Frutillar Pf	3.98	4.90	1.94	13.60	*
Frutillar P	3.74	4.12	5.18	9.20	*
Frutillar P/B	3.45	2.32	5.17	7.70	*
Piedras Negras F	4.22	4.38	1.24	8.78	9.17
Piedras Negras Pf	5.85	3.95	1.13	12.37	*
Piedras Negras P	5.05	3.90	1.38	13.49	*
Ultisols (Rojo Arcillosos)					
Cudico F	3.17	5.51	0.86	9.82	*
Cudico P	1.76	7.25	0.76	11.44	18.47
Collipulli O	1.05	6.21	1.28	13.83	*

F, wild forest; P, natural prairie; Pf, fertilized prairie; O, untreated deforested soil; B, barnyard manure; MBA, maximum binding ability ($\mu\text{Eq cation/mg polymer}$); *, not determined.

Thus, the following absorption bands are observed in the spectra of the soils under analysis.

In the spectra analyzed (Figs. 2 and 3), the vibrational lengthening frequency of the OH^- prevail both in humic and fulvic acids when there is an intermolecular hydrogen bond associated to a polymer chain (3400 to 3200 cm^{-1}).^[20]

If the spectra of pure humic and fulvic acids are compared with the spectra of humic and fulvic acids interacting with Zn and Cd, respectively, it may be observed that when organic polymers interact with these cations, the vibrational lengthening band of the carboxyl group (1720 cm^{-1})^[21] disappears; the vibrational bands of asymmetric and symmetric lengthening of the carboxylate ion are respectively near 1650 – 1550 cm^{-1} and 1420 – 1300 cm^{-1} .^[22]

In the spectra soil, a band may be observed having a vibration of lengthening of the hydroxyl group forming an intramolecular hydrogen bond as a

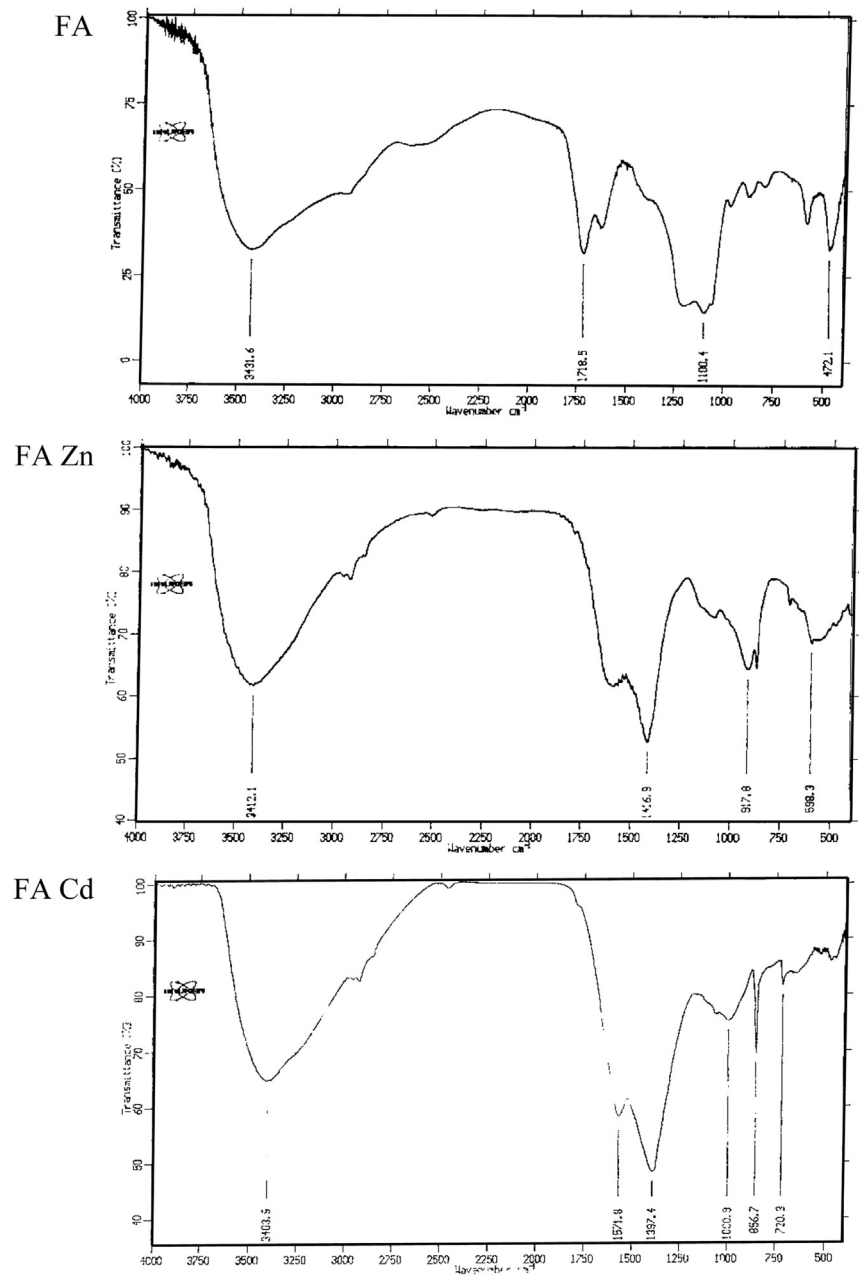


Figure 2. IR-spectra of fulvic acid before and after interacting with Zn(II) and Cd(II) solutions.

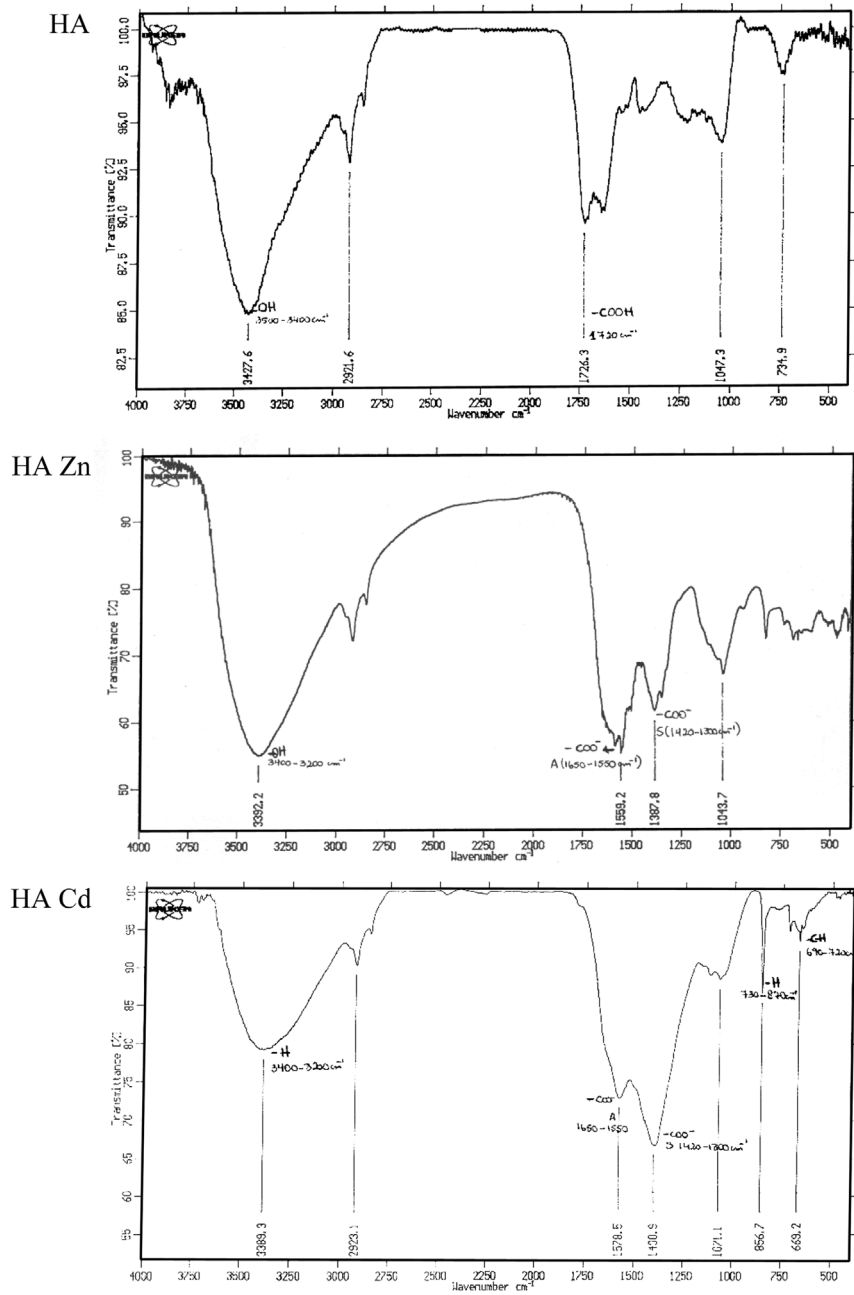


Figure 3. IR-spectra of humic acid before and after interacting with Zn(II) and Cd(II) solutions.

chelate compound ($3200\text{--}2500\text{ cm}^{-1}$).^[23] In general, this band disappears when these organic polymers interact with Zn or Cd. In the spectra under analysis, low frequencies ($730\text{ to }870\text{ cm}^{-1}$) are observed, corresponding to the vibration of lengthening of hydrogen atoms adjacent to the functional group in the aromatic ring, such as 4 adjacent hydrogen atoms ($770\text{--}735\text{ cm}^{-1}$), 2 adjacent hydrogen atoms ($860\text{--}800\text{ cm}^{-1}$).^[24]

In the spectra of fulvic acids of the three soils under study, bands are observed indicating the flexing vibration C—H out of plane in di-substituted aromatic compounds ($690\text{--}720\text{ cm}^{-1}$) and ($860\text{--}900\text{ cm}^{-1}$).^[24]

Summing up, nutrient availability and storage together with heavy metal soil contamination may be analyzed in relation to the reactions that may occur between metal ions and the stable organic fraction of organic matter in soil. The results of this study suggest that there are sites of donor electrons in the organic fractions of soil, which can be highly specific for heavy metals. They also confirm the possibility that metal ion bioavailability, specifically micronutrients, may be affected by retention mechanisms involving the nature of organic matter in soil.

Our contribution to a better knowledge of the interactions between organic macromolecules and metal ions will help chemists to propose recommendations to deal with soil contamination by heavy metals and to account for the role of organic matter in heavy metal translocation.

CONCLUSIONS

1. Total acidity and the content of carboxylic groups on fulvic acid is higher than in humic acid. The number of phenolic groups per weight unit is approximately the same for both polymers. Thus, fulvic acid has a lower molecular weight and a greater number of carboxylic groups than humic acid.
2. The behavior of soil in relation to cations according to soil origin does not show similarities in Trumao, Ñadi, and Rojo Arcillosos. These rather show individual behavior according to the use or management of land.
3. Soils from “wild forest” have organic polymers with a higher content of phenolic groups and total acidity compared with soils subjected to other use or agronomic management. Thus, fulvic polymers in soils with wild forest have a higher cation-binding ability.
4. Comparison of the maximum binding ability of the cations under study leads to the conclusion that the most frequent tendency is to retain $\text{Cd} > \text{Zn} > \text{Ca}$ at the offered concentrations. This encourages future research in soil-contaminating elements.

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