

## EXCHANGE PROCESSES IN TWO SOILS SUBJECTED TO DIFFERENT ORGANIC TREATMENTS

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### RESUMEN

#### PROCESOS DE INTERCAMBIO EN DOS SUELOS SOMETIDOS A DIFERENTES TRATAMIENTOS ORGANICOS

Se ha estudiado el efecto que ejercen una turba y un estiércol y sus fracciones coloidales FH (ácidos fúlvicos + ácidos húmicos) en los procesos de intercambio iónico de dos suelos con diferente textura.

En un suelo franco-arenoso, la turba actuó dando lugar a una retención de iones divalentes y trivalentes, mientras que con el estiércol se obtuvo un efecto fluctuante con el tiempo. Las fracciones FH originaron generalmente un proceso de liberación de iones (debido principalmente al Al), aunque también se observó una retención de Ca.

Los procesos de intercambio iónico fueron menos acusados en el caso del suelo arcilloso. Los tratamientos de turba y estiércol mostraron con el tiempo un efecto fluctuante, debido a que los iones trivalentes y divalentes se intercambiaban alternativamente en mayor o menor proporción. La aplicación de las fracciones FH a este suelo estuvo relacionada con una liberación de Al y Fe y una retención de Ca.

Asimismo se encontró que estos procesos de intercambio dependían tanto del contenido y del tipo de arcilla presente en el suelo como de la naturaleza de la materia orgánica añadida.

Palabras clave: Intercambio iónico, turba, estiércol, montmorillonita, caolinita.

### SUMMARY

The effect of peat and manure and their colloidal FH fractions (fulvic acids + humic acids) on the ion exchange processes in two differently textured soils was studied.

In a sandy loam soil, peat had an effect of retaining trivalent and divalent ions while manure showed a fluctuating effect with time. The FH fractions basically gave rise to an ion release process, which was mainly due to Al, although a retention of Ca was also observed.

When those organic materials were added to a clay soil, the exchange processes were less marked than in sandy loam soil. Peat and manure treatments showed a fluctuating effect with time due to an alternating participation of trivalent and divalent ions, but the addition of the FH fractions was related to a release of Al and Fe and a retention of Ca.

It was also found that these exchange processes depend upon the content and type of clay present in soil as well as on the nature of the organic matter added.

Key words: Soil ion exchange, Peat, Manure, Montmorillonite, Kaolinite.

## INTRODUCTION

Interactions between humic substances and metal ions can be described as ion exchange reactions, including adsorption and desorption processes that may occur simultaneously, which are strongly influenced by the quality of the humic compounds used (Schnitzer, 1978). Thus, the effect rises as molecular size and degree of humification decreases (Fortún *et al.*, 1986, Fortún and Salas, 1988).

Therefore, it seems probable that these reactions can control the availability or accumulation of ions in the soil solution. In this sense, Fortún and Salas (1988) observed that a release of certain ions (Fe, Mn and Zn) occurred when various types of organic matter were in contact with soils. On the other hand, in a study carried out with humified organic materials and their humic

and fulvic acids fractions, Fortún *et al.* (1986) found that the ion exchange rate for Na, Mg and Ca decreased as the free groups of organic matter became more saturated, but this did not happen in the case of Zn and Fe. They also found that the exchange of some ions by others depended on the type of clay present in the soil and on the mobility of these ions.

The present study intends to determine the ion exchange processes taking place in two differently textured soils subjected to treatment with peat or manure or their humified colloidal fractions, and different periods of incubation. Also, a complementary research was carried out to establish the behaviour of two natural clays on those processes after addition of manure and its organic fraction.

## MATERIAL AND METHODS

### *Material*

The soil samples selected (0-25 cm) were sandy loam (S) and clay (C) textured calcareous fluvisols from Central Spain (Tables 1 and 2). Clay minerals present in these soils were illite, montmorillonite and kaolinite in soil "S", and montmorillonite and illite in soil "C".

The natural clay samples used in the complementary study were montmorillonite (Los Trancos, Almería, Spain) and kaolinite (Guadalajara, Spain).

The organic matter amendments included peat (P) and 1-year old

cattle manure (M) (Tables 1 and 2), as well as their FH fractions (humic acids + fulvic acids) (Table 2) which were obtained by repeated extractions of peat or manure with 0.1 N NaOH and purified by centrifugation and dialysis using cellophane bags.

### *Rates of organic matter used*

400 g soil samples, air dried and sieved through a 2-mm screen, were treated with solid manure or peat, ground to powder, and with the dialysed suspensions in water of FH fractions. The rates were calculated so as to increase the total content

TABLE 1

*Some characteristics of the soils and the organic matter used.*

	Soils		Organic matter	
	"S"	"C"	Manure	Peat
pH (H <sub>2</sub> O) . . . . .	8.1	7.4	8.1	7.5
% Carbonates . . . . .	7.6	8.7		
% Organic matter . . . . .	0.9	1.8	48.5	56.4
% C (oxidation) . . . . .	0.50	1.12	27.6	32.7
% Humic acids (HA) . . . . .	0.06	0.12	18.9	22.0
% Fulvic acids (FA) . . . . .	0.31	0.60	13.9	23.3
% HA + FA . . . . .	0.37	0.72	32.8	45.3
% Total N . . . . .	0.05	0.09	3.2	1.7
HA/FA . . . . .	0.2	0.2	1.4	0.9
C/N . . . . .	10.6	12.2	8.6	19.2
C. E. C. cmol <sub>c</sub> kg <sup>-1</sup> . . . . .	4.0	16.0	136.0	180.0

of soil organic matter to 1.42% in the "S" soil and to 2.07% in the "C" soil. The FH treatments received the same amount of FH as did the peat or manure treatments respectively. The amounts added to the "S" soil were 9.9 mg peat g<sup>-1</sup>, 4.5 mg peat FH g<sup>-1</sup> (FHP fraction), 11.6 mg manure g<sup>-1</sup> and 3.8 mg manure FH g<sup>-1</sup> (FHM fraction); in the soil "C" these amounts were 4.3 mg peat g<sup>-1</sup>, 1.9 mg FHP g<sup>-1</sup>, 5.0 mg manure g<sup>-1</sup> and 1.6 mg FHM g<sup>-1</sup> (FHM: fulvic + humic acids from manure, FHP: fulvic + humic acids from peat).

Complementary study was to add 1160 mg of manure or 380 mg of FHM for every 11.9 g of natural clay. These amounts were calculated on the basis of clay content in the soil "S" (100 g of soil contained 11.9 g of clay).

Experiments including treated and unamended samples were carried out in quadruplicate.

The organic solids materials and the FH fractions were gently mixed with the soil in order to have them homogeneously distributed in the soil. Samples moisture was adjusted to water-holding capacity and the samples were stored at 25 °C for 2, 4, 7, 11 and 17 weeks in the case of the soil samples, and in the case of the for 2 and 7 weeks clay samples. They were periodically sprayed with deionized water to return the moisture content to the initial value.

#### *Determination of exchanged ions*

The contents in soluble elements were determined in order to obtain those ions linked to the soil colloids by water dipoles or hydrogen bridges.

5 g of sample were shaken with 50 ml of deionized water during two hours. Successively, they were centrifuged to 3000 rpm during 15 minutes, and Fe, Mg, Al, Ca, K and Na were determined in the extracts

TABLE 2

*Total elements in the soils and organic materials.*

	mg Kg <sup>-1</sup>				mg Kg <sup>-1</sup>					
	P	K	Na	Ca	Mg	Fe	Al	Mn	Zn	Cu
S soil . . . . .	490	3770	510	28000	6350	16250	15750	215	57	101
C soil . . . . .	950	10750	670	31500	19120	33250	45000	433	138	203
Manure . . . . .	7600	27250	3000	35500	8130	7375	8000	220	155	40
FHM* . . . . .	6380	2900	770	36500	11500	8188	11500	185	1550	190
Peat . . . . .	9480	680	850	120000	4750	2075	4000	60	51	315
FHP* . . . . .	750	750	700	92500	7380	2000	5000	150	2813	163

\* FHM: FH fraction from manure, FHP: FH fraction from peat.

by ICP emission spectrophotometry (Perkin-Elmer 5500). The amount of exchanged ions ( $Q$ ) was calculated following the interpretation of Bunzl (1974) and Bunzl *et al.* (1976). According to these authors, the quantity of element obtained in the control sample plus that applied with the corresponding dose and

less that obtained after shaking, divided by the equivalent weight, is considered the exchangeable quantity (always referred to gramme of soil). Therefore, the positive sign suggests that the ion has been retained, and the negative that it has been released.

## RESULTS AND DISCUSSION

When soil "S" was treated with peat (Table 3), it was found that the total amount of exchanged ions ( $Q_t$ ) was positive for the different incubation periods, with a minimum of ion retention after the 7-week period. The greater participation was due to the trivalent ions (mainly Al) followed by the divalent ions. When the FHP fraction was used, a release of trivalent ions and a retention of divalent ions (especially Ca) were the predominant processes. Dyanand and Sinha (1980) showed that certain retention processes might be the consequence of some ions displacing others and they specifically described the case of Fe displaced by Ca. In the studied soil, this did not always occur. Adsorption and desorption processes took place alternately (although Ca was always released and K was always retained), when this soil was treated with manure (Table 3), but when FHM was added, basically an ion release, which decreased after 7-weeks of treatment, was observed. Trivalent ions (especially Al) were the mainly exchanged ions after both treatments.

Hayes (1986) pointed out that there was a greater probability to

join two or more particles together by cation bridges when the weight of the involved organic molecule increased. This may explain the fact that there is always a retention phenomenon in presence of peat, which is not the case of manure because it is a less polymerized material. This was confirmed by Fortún and Salas (1988) who found that the most humified and polymerized material acted by preventing the release of Fe, Mn and Zn in the soil.

FHM showed a similar behaviour to FHP giving rise to an ion release after 2, 4 and 17 weeks of contact. This might be because both fractions were constituted of fulvic acids having a greater capacity for ion complexation in soil, which would allow trivalent ions to be soluble after a short contact period (Fortún *et al.*, 1986).

The amount of exchanged ions after organic amendments in the soil "C" (Table 4) was noticeably lower than those in the soil "S", especially for the trivalent ions. This may be due either to the lower amount of organic matter applied to this soil or to the influence of

TABLE 3

*Amount of ions exchanged (Q) per gramme of sandy loam soil after the organic treatments (meq 10<sup>-3</sup>).*

Treatment*		Fe	Mg	Al	Ca	K	Na	Q <sub>t</sub>	Q <sup>3+</sup>	Q <sup>2+</sup>	Q <sup>+</sup>
P	2	2.9	2.7	7.9	1.5	0.6	0.5	16.1	10.8	4.2	1.1
	4	1.5	1.7	5.8	3.1	0.2	0.0	12.3	7.3	4.8	0.2
	7	0.9	1.2	3.6	0.2	0.0	0.1	6.0	4.5	1.4	0.1
	11	1.8	1.8	6.2	1.6	0.2	0.2	11.8	8.0	3.4	0.4
	17	3.5	2.7	11.1	1.1	0.5	0.1	19.0	14.6	3.8	0.6
FHP	2	-1.2	0.1	-5.4	0.6	0.7	0.5	-4.7	-6.6	0.7	1.2
	4	-1.6	-0.1	-7.6	6.5	-0.4	-0.1	-3.3	-9.2	6.4	-0.5
	7	-0.2	0.7	0.3	5.2	-0.1	0.1	6.0	0.1	5.9	0.0
	11	0.9	1.1	4.0	5.5	0.1	0.2	11.8	4.9	6.6	0.3
	17	-2.4	0.6	-10.3	4.6	-0.5	-0.1	-8.1	-12.7	5.2	-0.6
M	2	1.1	0.8	4.0	-1.3	3.0	0.0	7.6	5.1	-0.5	3.0
	4	1.3	0.3	3.3	-0.4	2.3	0.0	6.8	4.6	-0.1	2.3
	7	-2.9	-1.5	-9.7	-0.7	2.1	-0.1	-12.8	-12.6	-2.2	2.0
	11	3.8	1.3	14.9	-1.0	1.3	-0.3	20.0	18.7	0.3	1.0
	17	-7.0	-2.0	-19.2	-3.8	2.5	-0.2	-29.7	-26.2	-5.8	2.3
FHM	2	-1.3	-0.2	-6.8	-2.5	0.3	0.2	-10.3	-8.1	-2.7	0.5
	4	-2.4	-0.7	-12.2	2.4	-1.1	-0.2	-14.2	-14.6	1.7	-1.3
	7	-0.9	-0.1	-0.8	1.9	-0.3	0.1	-0.1	-1.7	1.8	-0.2
	11	2.9	1.5	10.8	2.9	0.4	0.2	18.7	13.7	4.4	0.6
	17	-0.9	0.6	-1.7	0.7	-0.3	-0.1	-1.7	-2.6	1.3	-0.4

\* P: peat, FHP: FH fraction from peat, M: manure, FHM: FH fraction from manure.  
2, 4, 7, 11 and 17: weeks of incubation with the organic materials.

Q<sub>t</sub>: total amount of exchanged ions, Q<sup>3+</sup>: amount of exchanged trivalent ions,

Q<sup>2+</sup>: amount of exchanged divalent ions, Q<sup>+</sup>: amount of exchanged monovalent ions.

TABLE 4

*Amount of ions exchanged (Q) per gramme of clay soil after the organic treatments (meq 10<sup>-3</sup>).*

Treatment*		Fe	Mg	Al	Ca	K	Na	Q <sub>t</sub>	Q <sup>3+</sup>	Q <sup>2+</sup>	Q <sup>+</sup>
P	2	-0.2	0.1	-0.6	0.6	-0.2	-0.3	-0.6	-0.8	0.7	-0.5
	4	0.5	0.2	1.8	1.1	0.1	-0.5	3.2	2.3	1.3	-0.4
	7	0.1	-0.2	0.2	-1.0	-0.1	-1.0	-2.0	0.3	-1.2	-1.1
	11	-0.4	1.0	-1.4	2.7	0.1	1.3	3.3	-1.8	3.7	1.4
	17	0.6	0.4	2.1	-0.8	-0.2	-0.5	1.6	2.7	-0.4	-0.7
FHP	2	-0.5	-0.4	-1.5	0.6	-0.2	-0.1	-2.1	-2.0	0.2	-0.3
	4	-1.2	-1.5	-4.5	3.4	-0.1	0.5	-3.4	-5.7	1.9	0.4
	7	0.0	0.4	-0.3	3.0	0.0	-0.2	2.9	-0.3	3.4	-0.2
	11	-0.3	-0.1	-0.8	6.3	0.3	1.2	6.6	-1.1	6.2	1.5
	17	-0.1	0.2	-0.5	6.4	0.3	-0.2	6.1	-0.6	6.6	0.1
M	2	-0.2	-0.3	-0.5	-2.5	3.0	0.2	-0.3	-0.7	-2.8	3.2
	4	0.1	0.2	0.0	-0.5	2.5	-0.7	1.6	0.1	-0.3	1.8
	7	0.1	0.3	0.2	-3.1	2.0	-1.4	-1.9	0.3	-2.8	0.6
	11	-0.8	-1.2	-2.6	2.9	2.3	1.0	1.6	-3.4	1.7	3.3
	17	0.0	0.0	0.2	4.0	2.3	-0.2	6.3	0.2	4.0	2.1
FHM	2	-0.9	-1.1	-2.9	0.6	0.4	-0.4	-4.3	-3.8	-0.5	0.0
	4	-0.8	-1.1	-3.0	1.4	-0.2	0.4	-3.3	-3.8	0.3	0.2
	7	-0.6	-0.8	-2.4	2.6	0.0	0.4	-0.8	-3.0	1.8	0.4
	11	-0.4	-0.4	-1.5	3.2	0.2	0.8	1.9	-1.9	2.8	1.0
	17	-0.1	0.1	-0.1	4.6	0.0	-0.4	4.1	-0.2	4.7	-0.4

\* P: peat, FHP: FH fraction from peat, M: manure, FHM: FH fraction from manure.

2, 4, 7, 11 and 17: weeks of incubation with the organic materials.

Q<sub>t</sub>: total amount of exchanged ions, Q<sup>3+</sup>: amount of exchanged trivalent ions.Q<sup>2+</sup>: amount of exchanged divalent ions, Q<sup>+</sup>: amount of exchanged monovalent ions.

amount and type of the clay present in the soils.

Release and retention processes took place alternately when peat or manure were added to the clay soil (Table 4). In either treatment, trivalent as well as divalent ions participated.

When FHP was added to this soil, an ion retention after 17-weeks was obtained, which was an opposite effect to that observed in the soil "S". However, this fraction generally caused a release of trivalent ions and especially a retention of Ca, which was in accordance with the results obtained in the soil "S".

FHM treatment (Table 4) mainly acted giving rise to an ion release process ( $Q$  was negative), although a decreasing release of trivalent ions (especially Al) and an increasing retention of Ca with time was also found. This process decreased as time goes showing an ion retention after 17-weeks of contact.

Participation of fulvic acids may again be taken into account, which would be in accordance with the theories of several authors (Martín, 1969, Mortland, 1970, Schnitzer and Kodama, 1977), who pointed out that fulvic acids penetrate into the clay interlayer sites where they are initially associated by water dipoles or hydrogen bindings.

Therefore, the effect of organic matter on the processes retention and release varies depending on the soil texture and the nature of organic material.

A more detailed study about the above mentioned aspects was carried out by treating two natural clays present in the "S" soil with manure and FHM fraction. This soil was the

selected one because the exchanged ion amounts here obtained were higher than those in the "C" soil.

The addition of manure to montmorillonite (Table 5) gave rise to a release of Na, Mg and Ca, and a great retention of Al and K (Fe was slightly retained). However, when this clay was amended with FHM, Ca and Al were the mainly retained ions. The total amounts of exchanged ions ( $Q_t$ ) indicate that both organic materials in contact with montmorillonite exert an ion retaining effect (mainly due to Al) which increases with time. Manure treatment showed higher  $Q_t$  values than FHM treatment.

When these organic materials were added to kaolinite (Table 5), it was found that manure caused a great initial release of Al which considerably increased with the time of incubation; only Ca was retained. FHM fraction also gave rise to a release of Al and a retention of Ca, but these processes hardly varied with time. The total amounts of exchanged ions ( $Q_t$ ) show that addition of these organic materials to kaolinite cause an ion release process (mainly due to Al) which noticeably increases after 7-weeks of contact in the case of manure treatment, but when FHM is used the ion release slightly decreased with time. Again, manure treatment resulted in the highest  $Q_t$  values.

When these results are compared to those obtained in the "S" soil after 2 and 7 weeks of incubation (Table 3), it can be suggested that the processes of initial ion retention turning into ion release after 7-weeks, which took place in "S" soil after



TABLE 5

*Amount of ions exchanged (Q) per gramme of montmorillonite and kaolinite after organic treatments (meq 10<sup>-3</sup>).*

	MONTMORILLONITE				KAOLINITE			
	M		FHM		M		FHM	
	2	7	2	7	2	7	2	7
Fe .....	4.2	3.8	0.6	-0.2	0.4	-0.2	-0.4	-0.1
Mg .....	-16.2	-12.8	-0.5	1.3	-0.2	-0.2	3.3	3.3
Al .....	62.9	70.7	14.8	28.7	-47.0	-107.0	-38.0	-32.0
Ca .....	-7.3	-6.3	24.4	24.9	3.1	2.0	18.4	18.3
K .....	49.1	50.3	-0.4	-0.4	-5.6	-10.2	-0.2	-0.2
Na .....	-30.7	-29.1	-7.3	-9.4	-3.5	-4.0	0.0	-0.3
Q <sub>t</sub> .....	62.0	76.6	31.6	44.9	-53.6	-119.6	-16.9	-11.0

M: manure, FHM: FH fraction from manure.

2 and 7: weeks of incubation with the organic materials.

Q<sub>t</sub>: total amount of exchanged ions.

amendment with manure, were affected by the interaction of this organic material with montmorillonite and kaolinite together. The predominant process was an ion retention after 2-weeks and an ion release after 17-weeks.

However, kaolinite seems to exert a greater action on the ion release process taking place after adding

FHM to this soil, although montmorillonite is also probable to interact but only after 7-weeks of contact which is manifest by a decrease in the ion release.

Consequently, the type of clay present in soils has a direct bearing on the ion exchange processes that occur when they are treated with organic matter.

## CONCLUSIONS

— In a sandy loam soil, the most humified material (peat) has a retaining effect of mainly trivalent and divalent ions, while release and retention processes take place alternately when this soil is treated with manure. Al is mainly involved in both treatments.

Fluctuating release and retention processes occur when peat or manure are added to the clay soil. In either treatment, trivalent as well as divalent ions participate.

— FHP and FHM treatments show a similar behaviour and they give rise to a release of trivalent ions (mainly

Al) and a retention of divalent ions (especially Ca). After 17 weeks, these fractions differently act depending on the soil used.

— When the original organic matter is added to the sandy loam soil, ion exchange processes are as a consequence of simultaneous interactions with montmorillonite and kaolinite.

Therefore, under the conditions studied, Al and Ca are exchanged and the predominant process depends on the content and type of clay and on the nature of the organic matter used.

## BIBLIOGRAFIA

- BUNZL, K., 1974a. Kinetics of ion exchange in soil organic matter II. Ion exchange during continuous addition of  $Pb^{2+}$  ions to humic acid and peat. *J. Soil Sci.*, 25: 343-356.
- BUNZL, K., 1974b. Kinetics of ion exchange in soil organic matter III. Differential ion exchange reactions  $Pb^{2+}$  ions in humic acid and peat. *J. Soil Sci.*, 25: 517-532.
- BUNZL, K., WOLF, A. and SANSONI, B., 1976. Kinetics of ion exchange in soil organic matter. V. Differential ion exchange reactions of  $Cu^{2+}$ ,  $Zn^{2+}$  and  $Ca^{2+}$  ions in humic acid. *Z. Pflanz. Bodenk.*, 139: 475-481.
- DYANAND, S. and SINHA, M. K., 1980. The kinetics of reaction of Fe-DTPA and Fe-fulvate in calcareous soils. *J. Ind. Soc. Soil Sci.*, 28: 429-436.

- FORTUN, C., ORTEGA, B. C. y FORTUN, A., 1986. Selectividad de las sustancias húmicas por los elementos Na, K, Ca, Mg, Zn y Fe. *Agrochimica*, 30: 93-103.
- FORTUN, C. y SALAS, M. L., 1988. Estudio del poder de adsorción de Fe, Mn y Zn por diferentes materiales orgánicos: incidencia en la producción vegetal. *Ag. Med.*, 118: 261-265.
- HAYES, M. H. B., 1986. Soil organic matter extraction, fractionation, structure and effects on soil structure. In: *The role of organic matter in modern agriculture*. Y. Chen and Y. Avnimelech (eds.), 25, 183-208. *Developments in Plant and Soil Sciences*. Dordrecht.
- MARTIN, W. E., 1969. Interlamellar adsorption of a black earth humic acid on Na-montmorillonite. *Z. Pflanz. Bodenk.*, 124: 52-57.
- MORTLAND, M. M., 1970. Clay organic complexes and interactions. *Adv. Agron.*, 22: 75-117.
- SCHNITZER, M. and KODAMA, H., 1977. Reactions of minerals with soil humic substances. In: *Minerals in soil environments*. J. B. Dixon and S. B. Weed (eds.), 741-770. *Soil Sci. Soc. Amer. Madison*.
- SCHNITZER, M., 1978. Humic substances: chemistry and reactions. In: *Soil organic matter*. M. Schnitzer and S. U. Khan (eds.), 1-64. Elsevier Publishing Co. Amsterdam.

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