Effects of Dissolved Organic Carbon on Phosphate Retention on Two Calcareous Soils

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To evaluate the effects of dissolved organic carbon (DOC) on phosphate retention (including both sorption and/or precipitation reactions) on soils, experiments were performed by using two typical calcareous soils from southeastern Spain (Calcic Regosol and Luvic Xerosol) and two different types of DOC: (1) extracts from a commercial peat (DOC-PE) and (2) high-purity tannic acid (DOC-TA). The experiments were carried out from a 0.01 M $CaCl_2$ aqueous medium at 25 °C. The results obtained show that the presence of both DOC-PE and DOC-TA, over a concentration range of 15 (DOC-15) to 100 (DOC-100) mg L^{-1}, produces in all cases a decreasing amount of phosphate retained in the soils studied, the decrease observed being higher when DOC-PE is used as source of DOC. The values of the decrease observed when DOC-PE was added ranged between 19.9% (DOC-15) and 15.6% (DOC-100) for the Calcic Regosol and between 17.3% (DOC-70, DOC-100) and 14.6% (DOC-15) for the Luvic Xerosol. The variation observed when DOC-TA was added ranged between 8.5% (DOC-100) and 0.5% (DOC-35) for the Calcic Regosol and between 7.0% (DOC-100) and 1.0% (DOC-15) for the Luvic Xerosol.

KEYWORDS: Phosphate; sorption; precipitation; calcareous soil; dissolved organic carbon

INTRODUCTION

Water quality is a matter of concern in many areas due to population growth and land use changes (*1−3*). Water pollution, which is the main cause of surface and ground water degradation today, can be categorized into (i) point and (ii) nonpoint sources. Point source pollution is a specific, large, identifiable discharge outlet. Examples include wastewater treatment plants and industrial or factory drains. Nonpoint source pollution (NSP) is defined by the U.S. Environmental Protection Agency (EPA) as being caused by diffuse sources that are not regulated as point source and normally are associated with agricultural, silvicultural, and urban runoff.

Many factors affect pollution loads from agricultural operations: soil, land use, crops, farming technology, and drainage. The major pollutants associated with agriculture include some nutrients (nitrate nitrogen and—in acidic soils—phosphorus) and pesticides (*4*).

Phosphorus (P) originating from agricultural areas has been identified as a key factor in the pollution of waters in many areas of the United States and central and northern European countries (*4*, *5*). The sources of this nutrient come from a combination of both point and nonpoint sources. However, nonpoint sources of P are considered to be dominant in most waters (*6*).

The sparingly soluble nature of most soil P compounds (*7*) makes it difficult to supply sufficient P to sustain high crop yields without the addition of inorganic P fertilizer, because most P is retained in the soil and is not available for plants. On the contrary, high P fertilizer use is undesirable not only from an economic perspective but also from an environmental one because of potential eutrophication problems. Recent soil test results have shown that the P content of most soils has increased to very high levels, sometimes higher than those that plants need (*8−10*).

Dissolved organic carbon (DOC) is a subject of interest because it has been reported to interact with chemicals, affecting their fate in soil systems. Data reveal that interaction of phosphate with DOC increases the mobility of this compound, which may affect the bioavailability of soil P (*11*, *12*).

Almería (southeastern Spain) is a farming region where the soils are arid and need to be amended and fertilized, so fertilization with organic matter and phosphorus is a common practice because of the poor quality of the native soils. Therefore, we have considered it to be useful to study the retention process (including both sorption and/or precipitation reactions) of phosphate on two calcareous soils representative

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Table 1. Physical and Chemical Characteristics of the Soils Studied

	Calcic Regosol			Luvic Xerosol		
	sand	silt	clay	sand	silt	clay
texture (%)	50.4	31.3	16.4	4.9	35.6	59.7
pH		8.7			8.2	
organic carbon (%)		1.01			0.27	
cation exchange capacity (cmol/kg)		18			16	
surface area ($m^2 g^{-1}$)		13.3			23.7	
total pore volume ($cm^3 g^{-1}$)		0.44			0.58	
total Kjeldahl nitrogen content (%)		0.11			0.04	
total $CaCO_3$ content (%)		17.8			15.5	
active Ca content (%)		22.3			31.2	

of the Almería farming region and other arid and semiarid zones of southern Europe. Then, the effect of DOC on P bioavailability was conducted by using tannic acid and a commercial peat. The DOC fraction could be a key factor to understanding the processes that govern the fate of phosphate in the soil environment, which involves two opposite aspects: the P bioavailability for plants and the potential contaminant for groundwater.

The main objectives of this paper were (i) to study the retention process of phosphate on two calcareous soils by using batch experiments and (ii) to evaluate the influence of the soluble organic fraction extracted from a commercial peat and tannic acid on the retention of phosphate on calcareous soils selected.

MATERIALS AND METHODS

Phosphate. Analytically pure KH_2PO_4 (99.9%) was obtained from Panreac, S.A. (Barcelona, Spain), and used as P source in this study.

Soil Characterization. The two calcareous soils used (Calcic Regosol and Luvic Xerosol) are the most representative soils in the studied area. Soils were sampled in the surface layer (0−20 cm) of an 8000-m^2 area from the Almería region (southeastern Spain), defined by the Universal Transverse Mercator (UTM) system coordinates, $x =$ 526.100 and $y =$ 4071.700 for the Calcic Regosol and $x =$ 524.120 and $y =$ 4068.400 for the Luvic Xerosol. Six soil samples randomly distributed in the area were mixed and stored until analysis. Triplicate air-dried <2-mm particle size samples were analyzed according to standard methods. Soil pH was determined in a 1:2.5 soil/water suspension using a glass electrode (*13*), organic matter content by the Walkley−Black method (*14*), clay content by the hydrometer method (*15*), cation exchange capacity by the barium acetate method (*16*), and total nitrogen content by the Kjeldahl method (*13*). Calcium carbonate was determined by the volumetric method (*17*). To determine the active calcium, a soil test sample is placed in a known excessive volume of titrated ammonium oxalate (*13*). Specific surface area was calculated from N_2 sorption isotherms at 77.4 K, in a volumetric adsorption system, Gemini II-2375 (Micromeritics) and using the Brunauer−Emmett−Teller (BET) equation. Soil porosity was determined by applying the Washburn equation (*18*), using an Autopore III porosimeter (Micromeritics) with a maximum pressure of 60000 psi (414 MPa) that covers spectra between 1.8 and 10000 nm. All of these soil properties are given in **Table 1**.

Dissolved Organic Carbon. Two different types of DOC were used. The first was extracted from a commercial peat (Vapo Peat A, Projar S.A. Almería, Spain), containing 36.4% of organic carbon (C) (DOC-PE). The soluble fraction solution was prepared by mixing peat (25 g) with demineralized Milli-Q quality water (1000 mL), followed by 24 h of shaking and filtration through a 0.45-mm Millipore HA filter (concentration of DOC solution was 150 mg C L^{-1}). The second type was a high-purity tannic acid (99.9%) from Fluka Chemie (Stockholm, Sweden) containing 62.5% of organic carbon, which was used as a pure chemical source of dissolved organic C (DOC-TA).

Total surface acidity (R−COOH, Ar−COOH, and Ar−OH groups) of DOC-PE and DOC-TA was determined using the Schnitzer and Gupta method (*19*), total amount of carboxylic groups according to

Table 2. Total Surface Acidity and Carboxylic and Phenolic Hydroxyl Groups of the DOC

	total surface acidity (cmol kg^{-1})	carboxylic groups (cmol kg^{-1})	phenolic hydroxyl groups (cmol kg^{-1})
DOC-PE[a]	3.76	0.05	3.71
DOC-TA[b]	11.43	1.88	9.55

[a] DOC-PE, DOC extracted from peat. [b] DOC-TA, high-purity tannic acid solution.

the method of Schnitzer and Wright (*19, 20*), and total phenolic hydroxyl groups using the method proposed by Schnitzer (*20*) as follows:

$$\text{(total surface acidity)} - \text{(carboxylic groups)} =$$
$$\text{phenolic hydroxyl groups (cmol kg}^{-1})$$

(**Table 2**).

Phosphate Retention and DOC Sorption Experiments. Retention of phosphate and sorption of DOC on the calcareous soils was performed separately. The retention experiments were carried out as follows: aqueous solutions containing initial phosphate or DOC concentrations (C_0) were prepared, ranging from 2 and 33 mg of P L^{-1} (phosphate), from 5 to 69 mg of C L^{-1} (DOC-PE), and from 3 to 66 mg of C L^{-1} (DOC-TA). Amounts of 3 g of each soil sample and 0.025 L of KH_2PO_4 or DOC solution were placed in stoppered conical flasks and shaken for 24 h in a thermostated shaker bath at 25.0 ± 0.1 °C. For the DOC sorption experiments, three drops of toluene were added to the flasks to inhibit the microbial soil activity. A time of 24 h was long enough to make quite sure that the retention equilibrium was reached (**Figure 1**). After shaking, the solutions were centrifuged and the concentration of phosphate in the supernatant liquid was determined by capillary electrophoresis (CE) using a Beckman capillary electrophoresis system (P/ACE 5000) equipped with a UV detector and data station. The CE operating conditions were as follows: The running buffer used was a mixture of 2 mM K_2CrO_7 and 2 mM diethylenetriamine (DETA) at pH 7.5. Separation was performed on a fused-silica capillary (75 μm i.d. and 67 cm in length). The separation was carried out from the negative to the positive electrode with a voltage of 30 kV and a temperature of 25 °C. Samples were injected by hydrodynamic injection for 5 s. Electropherograms were recorded with indirect UV detection at 254 nm. The concentration of DOC in the supernatant was determined by using a TOC Carbon Analyzer 5050 A (Shimadzu, Kyoto, Japan) with IR detection of CO_2 following thermal oxidation. A scheme of the experimental procedure can be seen in **Figure 2**.

The difference in phosphate or DOC concentrations between the initial and final equilibrium solutions was assumed to be due to retention or sorption, respectively, and the amount of phosphate retained or DOC sorbed per kilogram of soil was calculated. Two replicates were analyzed for each phosphate or DOC concentration. The differences between the analyses of the two replicates were always <10%. Blanks without phosphate and DOC were used for each series of experiments.

Phosphate−DOC Interaction Studies. Batch experiments were performed to study the effect of DOC on phosphate retention. Both the peat-extracted and the tannic acid studies were carried out as follows: 3 g of soil was pre-equilibrated in a thermostated shaker bath at −25.0 ± 0.1 °C and for 24 h−with 0.025 L of an aqueous solution containing a mix of phosphate ($C_0 = 10$ mg of P L^{-1}) and DOC of various concentrations ($C = 0, 15, 35, 70,$ and 100 mg of C L^{-1}) (hereafter, DOC-0, DOC-15, DOC-35, DOC-70, and DOC-100, respectively). The pH values of these solutions were measured before equilibration with the soil for both sources of DOC (DOC-PE and DOC-TA). The obtained results are given in **Table 3**.

After equilibration, the solutions were centrifuged and the concentration of phosphate in the supernatant liquid was determined by CE. The difference in phosphate concentration between the initial and final equilibrium solutions was assumed to be due to retention; therefore, it was possible to determine the variation of the amount of phosphate retained per kilogram of soil as a function of the concentration of DOC in solution. The pH of the supernatant was also measured to evaluate
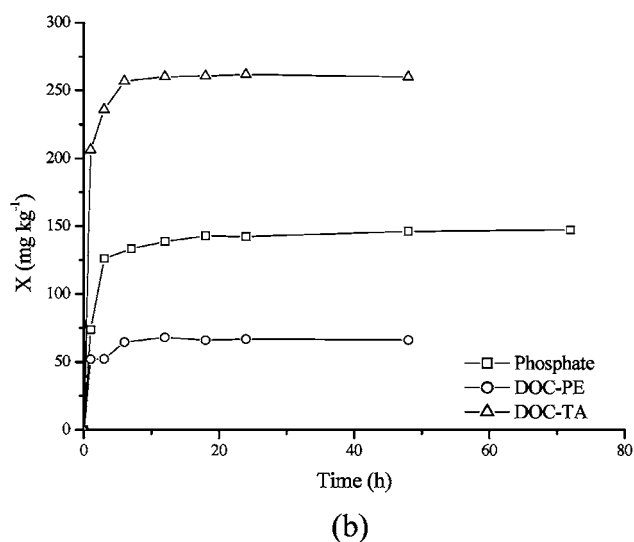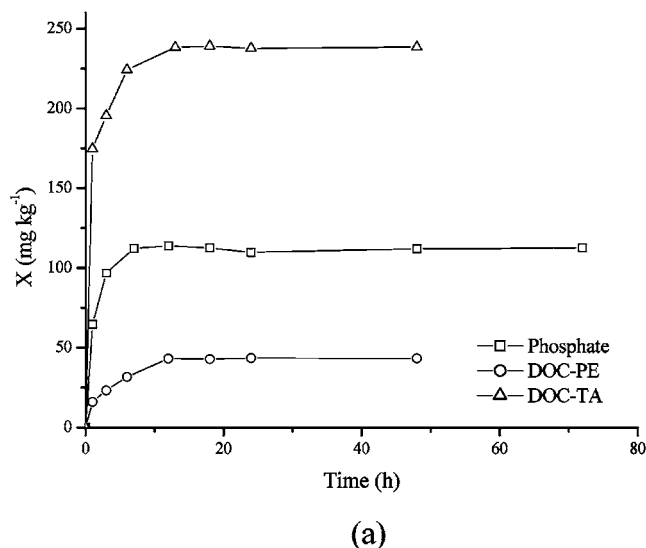
Figure 1. Retention kinetic of phosphate, DOC-PE and DOC-TA on (**a**) Calcic Regosol soil and (**b**) Luvic Xerosol soil. The initial concentrations were 20, 49, and 50 mg L^{-1} for phosphate, DOC-PE, and DOC-TA, respectively.

Table 3. pH Values of the Phosphate and DOC Mixed Solutions

| nixed solution[a]	DOC-PE	DOC-TA
DOC-0	5.7	5.7
DOC-15	4.7	5.3
DOC-35	4.4	5.0
DOC-70	4.1	4.9
DOC-100	3.9	4.3

[a] DOC-0, aqueous solution containing 10 mg of P L^{-1}; DOC-15, aqueous solution containing 10 mg of P L^{-1} + 15 mg of C L^{-1}; DOC-35, aqueous solution containing 10 mg of P L^{-1} + 35 mg of C L^{-1}; DOC-70, aqueous solution containing 10 mg of P L^{-1} + 70 mg of C L^{-1}; DOC-100, aqueous solution containing 10 mg of P L^{-1} + 100 mg of C L^{-1}.

the pH variations when DOC was added. Blanks without soil were used to check that no previous association occurs between phosphate and DOC during the pre-equilibration time of the experiments.
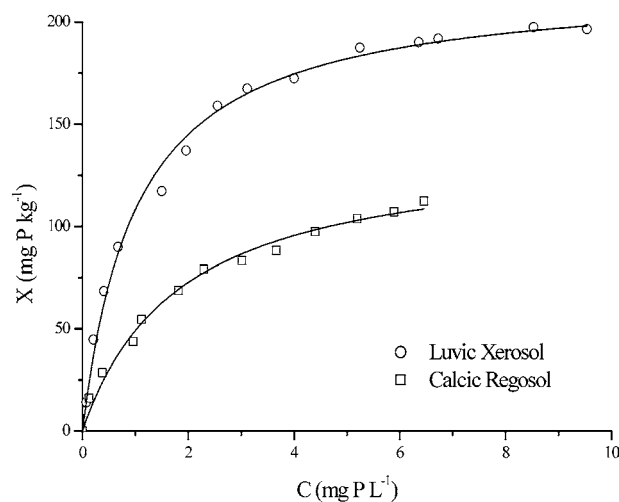
RESULTS AND DISCUSSION

Phosphate Retention and DOC Sorption Experiments. **Figure 3** shows the retention isotherms of phosphate on the calcareous soils selected. According to the initial portion of the
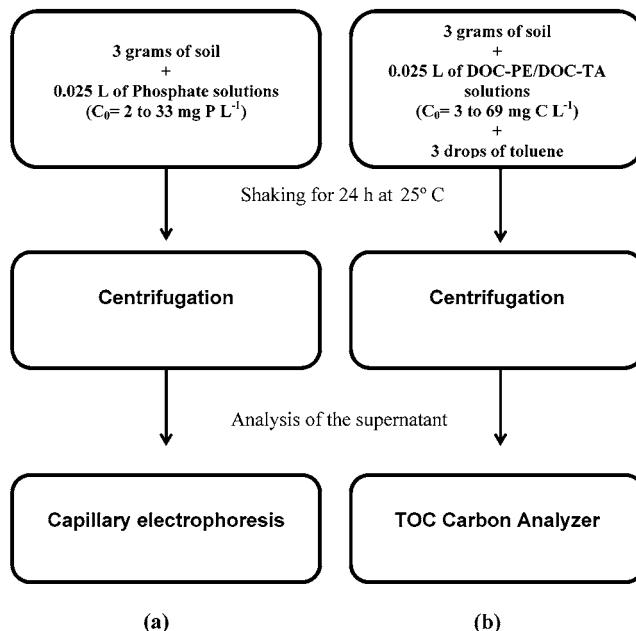
**Figure 2.** Experimental design scheme of (**a**) phosphate retention and (**b**) DOC sorption on soils.

Figure 3. Retention isotherm of phosphate on the calcareous soils

curves, these isotherms may be classified as L type of the Giles classification (*21*), which suggests both that these soils have an average affinity by the phosphate and that there is no strong competition from the solvent for retention sites. Nevertheless, the slope of the initial portion of the isotherm corresponding to the Luvic Xerosol soil is higher than that corresponding to the Calcic Regosol, which signifies, according to Giles et al. (*21*), that the Luvic Xerosol soil has a higher affinity for phosphate than the Calcic Regosol. It is also noteworthy that for a given equilibrium concentration (C_e) the amount of phosphate retained (X) on the Luvic Xerosol is much higher than that retained on the Calcic Regosol.

To identify the retention capacity of the soils, the experimental data points were fit to the Langmuir equation (*22*)

$$\frac{C}{X} = \frac{1}{(bX_m)} \times \frac{C}{X_m} \tag{1}$$

where X is milligrams of P retained per kilogram of soil, C is the equilibrium solution concentration (mg of P L^{-1}), and X_m and b are constants that characterize the retention capacity for

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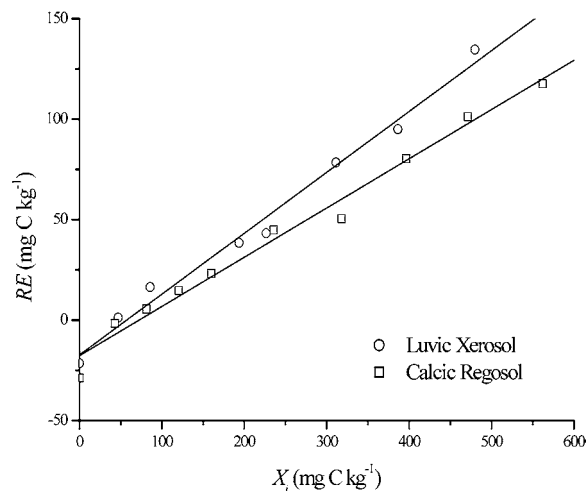
Figure 4. Initial mass isotherm corresponding to DOC-PE on the calcareous soils.

Figure 5. Initial mass isotherm corresponding to DOC-TA on the calcareous soils.

the phosphate. The constant X_m is the maximum amount retained for the soil, and b is a measurement of the intensity of retention (*23*, *24*). The X_m and b values were calculated from the least-squares method applied to the linear form of the Langmuir equation, the resulting values being $X_m = 133.33$ mg of P kg^{-1} and $b = 0.64$ for the Calcic Regosol and $X_m = 212.76$ mg of P kg^{-1} and $b = 1.20$ for the Luvic Xerosol. The correlation coefficients were 0.991 and 0.996, respectively, being significant at the 0.01 probability level according to the statistical F test. The X_m and b values for the Luvic Xerosol are, respectively, 1.5 and 1.9 times higher than those obtained for the Calcic Regosol. This fact might be due to the higher active Ca content of the Luvic Xerosol, because for calcareous soils as those are, the precipitation reaction as calcium phosphate seems to be the main mechanism in the global retention process of phosphate (*25*, *26*).

The X_m and b values obtained for the soils here used are of the same order as those obtained for retention of phosphate ions on different soils from the Almería region (southeastern Spain) (*27*).

The Langmuir equation was also applied to the sorption data of DOC on the soils used. The result obtained showed that sorption of DOC on the soils did not fit at all to the Langmuir equation. Therefore, the initial mass isotherm was used to measure the sorption capacity of DOC-PE and DOC-TA and the soils studied (*28*). For those systems in which the solute to be sorbed is present in the sorbent, such as for the sorption of organic carbon on soils, it is necessary to apply the initial mass isotherm [proposed by Nodvin et al. (*28*)] to correct the amount of organic carbon released from soil and to have reliable data about the amount of organic carbon sorbed. The amount of DOC-PE and DOC-TA sorbed on the soils during the experiment was plotted as a function of the concentration of DOC-PE and DOC-TA added to the soil system (**Figures 4** and **5**). These linear isotherms are described by the relationship

$$RE = mX_i - b \qquad (2)$$

where RE is the amount of DOC-PE and DOC-TA released or sorbed per kilogram of soil (mg kg^{-1}), m is the slope of the straight lines obtained, equal to the fraction of DOC-PE and DOC-TA sorbed by the soil, X_i is the initial concentration of DOC in solution, expressed as mg kg^{-1} of soil, b is the DOC released from the soil when X_i is zero (mg kg^{-1}).

The values of m (0.23 for DOC-PE and 0.92 for DOC-TA) were used to calculate the distribution coefficient (C_d), which
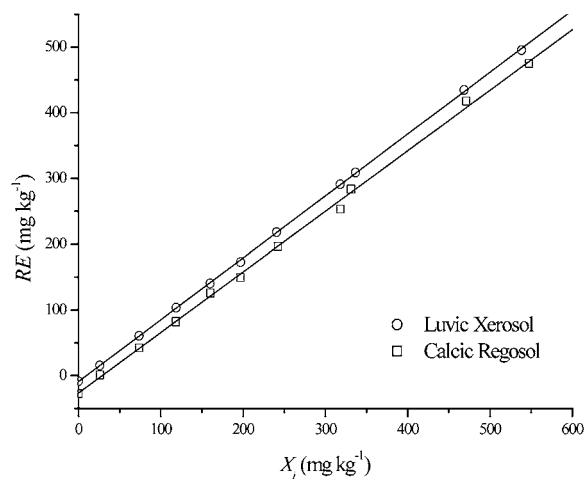
Table 4. C_d Values Corresponding to the Sorption of DOC-PE, DOC-TA, and Phosphate on the Calcic Regosol and Luvic Xerosol

	C_d (L kg^{-1})	
	Calcic Regosol	Luvic Xerosol
DOC-PE	2.5	3.4
DOC-TA	95.8	130.6
phosphate	16.9	23.5

was used to compare the sorption of DOC on the soils studied (*3*); the results obtained are given in **Table 4**

$$C_d = \frac{m}{(1 - m)} \times \frac{V}{M} \qquad (3)$$

where V is the volume of solution (0.025 L) and M is the mass of soil (0.003 kg).

As can be seen from **Table 4**, the C_d values for DOC-TA are much higher (38 times) than those for DOC-PE, considering both soils studied. Likewise, the C_d values for the Luvic Xerosol are higher (1.36 times) than those for the Calcic Xerosol, now considering the two types of DOC used. These facts could be explained according to the mechanism proposed by Greenland (*29*), for which the sorption of organic matter takes place by anionic exchange between the carboxylic and phenolic groups (responsible for the total surface acidity of the organic matter) and the Al and Fe ions present in the soil clay fraction. The higher total surface acidity would justify the higher sorption of DOC-TA on both soils, and the higher clay content of Luvic Xerosol would justify the higher sorption of both DOC types on this soil.

To compare the results obtained when using phosphate and DOC, the retention data of phosphate were also plotted as the initial mass isotherm form (**Figure 6**), and the resulting values for C_d are also given in **Table 4**.

As can be seen from **Table 4**, the C_d values for phosphate are 1.4 times higher for the Luvic Xerosol soil than for the Calcic Regosol soil. This result is the same as that obtained when the X_m values were compared in both soils. In addition, the C_d values for phosphate in both soils are about 7 times higher and 5.5 times lower than those corresponding to DOC-PE and DOC-TA, respectively.
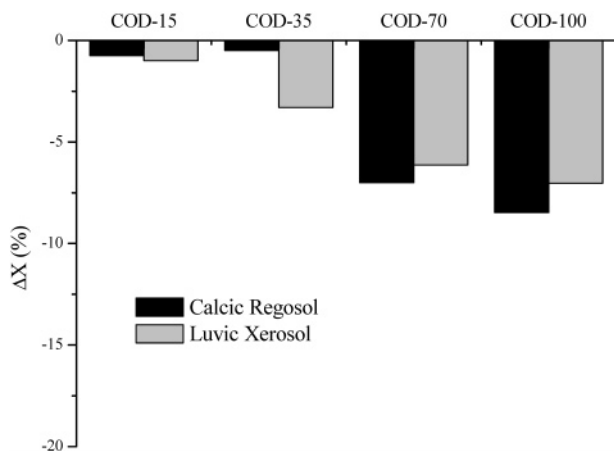
Figures 7 and **8** show—in terms of percentage—the variation of the amount of phosphate retained in the presence of DOC-PE and DOC-TA relating to the amount retained when no DOC
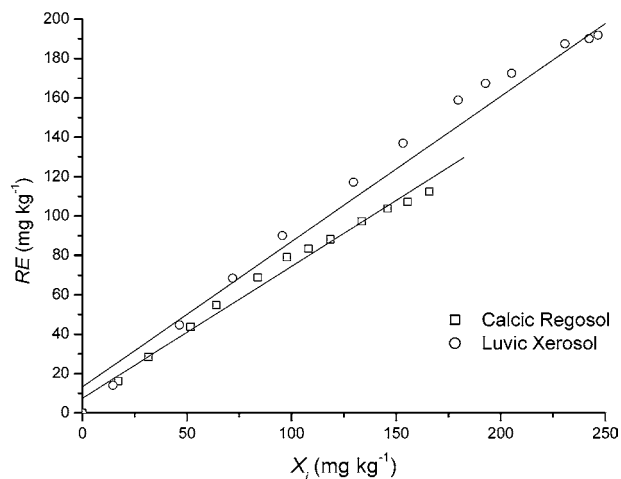
Figure 6. Initial mass isotherm corresponding to phosphate on the calcareous soils.
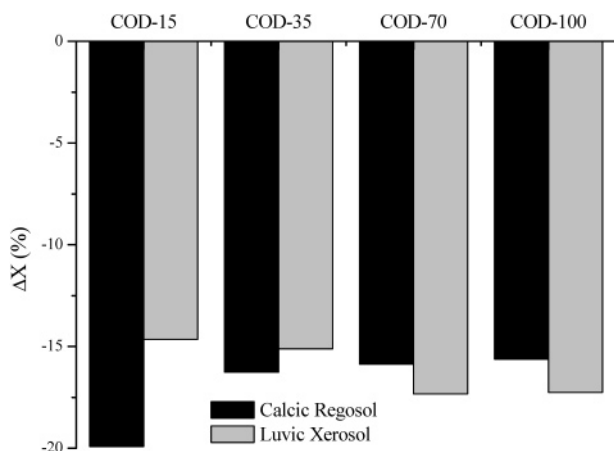
Figure 7. Percentage variation of the amount of phosphate retained in the presence of DOC-PE relative to the amount retained when no DOC is present.

Figure 8. Percentage variation of the amount of phosphate retained in the presence of DOC-TA relative to the amount retained when no DOC is present.

is present (ΔX). As can be seen from **Figures 7** and **8**, and according to the negative values of ΔX, the presence of DOC-PE and DOC-TA produces a decreasing phosphate retention in the two soils studied. A similar behavior has been reported for acid soils by other authors (30, 31). The values of the decrease observed when the DOC-PE was added ranged between 19.9% (DOC-15) and 15.6% (DOC-100) for the Calcic Regosol and

between 17.3% (DOC-70, DOC-100) and 14.6% (DOC-15) for the Luvic Xerosol. The variation observed when DOC-TA was added ranged between 8.5% (DOC-100) and 0.5% (DOC-35) for the Calcic Regosol and between 7.0% (DOC-100) and 1.0% (DOC-15) for the Luvic Xerosol.

The main features of the above results are the following:

(1) The decrease of the phosphate-retained amount is more important for DOC-PE than for DOC-TA.

(2) The decrease produced in the phosphate retention (ΔX) is, in general, higher as the DOC concentration increases.

The reason for which the presence of DOC produces a decrease in the amount of P retained for the calcareous soils here used seems to be related with the decreasing pH values of the phosphate solutions (pH 5.7) when DOC is added (12). As can be seen in **Table 3**, this decrease goes from 4.7 (DOC-15) to 3.9 (DOC-100) for DOC-PE and from 5.3 (DOC-15) to 4.3 (DOC-100) for DOC-TA. Taking into account that for calcareous soils the main mechanism in relation to the P retention is the precipitation as calcium phosphate (26, 32), the decrease in the pH values above indicated would explain the observed behavior. The fact for which the decrease of P retention is much higher when DOC-PE is used could be justified according to the higher sorption of DOC-TA on the soils studied (C_d values are ~38 times higher than for DOC-PE). The DOC-TA sorbed on the soil surface could create new retention sites for phosphate, so compensating the retention inhibition owing to the pH decrease.

Conclusions. Considering the above and taking into account that retention of P as calcium phosphate is a serious problem of P bioavailability in arid region soils of southeastern Europe, the addition of organic matter to those soils could be used to have a high growth response owing to the lower P retention as calcium phosphate. However, and taking into account the possible ground water contamination due to the increased leaching processes of phosphate when DOC is present, the addition of organic matter in soil amendments must be carefully studied to find an optimum amount that leads to a higher crop production, together with a minimum environmental impact.

Thus, and according to the results shown in this paper, for high-permeability calcareous soils in which leaching is an expected process, it would be recommendable to amend such soils with organic molecules similar to tannic acid such as those present in the soluble fraction of humic acids. On the other hand, for low-permeability calcareous soils, it would be more suitable, due to the lower risk of P leaching, to carry out the amendment of the soil with peat, which leads to a better P bioavailability for the plant.

ABBREVIATIONS USED

DOC-PE, DOC extracts from peat; DOC-TA, high-purity tannic acid solution (99.9%); CE, capillary electrophoresis

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