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## Interactions Between Ionic Pesticides and Model Systems for Soil Fractions

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### 1. Introduction

The extensive use of herbicides in agriculture and their potentially toxic effects have promoted studies investigating the physical, chemical and biological processes that determine the mobility, bioavailability and degradation of these compounds in soils (Blasioli et al., 2011). Knowledge of these processes will enable prediction of the transport and fate of herbicides in soils and aquatic systems, and thus enable measures to be taken to limit their environmental impact.

Retention is considered the main cause of the deactivation of herbicides in soils, and is important from the point of view of inhibiting the toxic properties of herbicides and of restricting their transport into aquatic systems (Jones & Bryan, 1980). Although not unique, adsorption reactions (i.e. accumulation of chemical species at the solid-solution interface) are the main cause of the retention of organic contaminants in soils, and their extent will depend on the physicochemical properties of both the adsorbent (soil) and the adsorbate (herbicide).

The chemical characteristics of organic compounds are largely responsible for their behaviour in soil, and the differences in adsorption of different herbicides in the same soil are attributed to their distinct chemical properties. Although herbicides are very diverse, two groups can be distinguished in order to interpret their interactions with soil components: those involving chemical forces and those involving physical forces. The first group comprises ionic or ionizable hydrophilic compounds, while the second group comprises non polar hydrophobic compounds.

Bipyridinium cations, such as paraquat (1,1'-dimethyl-4,4'-bipyridinium ion), are the best known members of the ionizable herbicides as they have been extensively used in agriculture and are consequently widely distributed in soils and waters. Paraquat (PQ) is applied as a dichloride or dibromide salt, which when dissolved in water releases the organic cation  $PQ^{2+}$ , which can be adsorbed on the soil surface, either by replacing inorganic cations or by an ionic interaction mechanism with negatively charged sites on the soil surface, in which the electrostatic effect will be determinant (Narine & Guy, 1982). PQ adsorbs on humic substances and the degree of adsorption increases as the pH increases, as

a result of the progressive ionization of the acid groups in the organic matter (Iglesias et al., 2009; Brigante et al., 2010). PQ shows affinity for iron oxides and clay minerals (Clausen & Fabricius, 2001; Seki & Yurdakoç, 2005; Pateiro-Moure et al., 2010). Studies of PQ adsorption to clays in the pH range 5.0-7.0 reveal surface concentrations of between 0.18 and 4  $\mu\text{mol}\cdot\text{m}^{-2}$ , depending on the type of clay. The higher adsorption of PQ on clays is explained by the ability of the planar PQ molecules to enter the lattice layers (Bromilow, 2003) and the extent of the PQ adsorption on soils is determined by the amount and type of clay minerals present in the soils (Roberts et al., 2002)

Phenoxyalkanoic acids (such as MCPA) and their derivatives constitute a large group of herbicides that are used extensively in agriculture. This type of organic pesticide has a carboxyl group that is mainly responsible for the interactions with soil components (Tunega et al., 2004). At  $\text{pH} > 4$  the acid group ( $\text{pK}_a = 3.10$ ) will be ionized giving rise to significant adsorption of the anionic form of the pesticide on mineral oxides. It is known that the adsorption of pesticides of this type on goethite is strongly dependent on pH and ionic strength, and has been suggested to be due to the favourable interaction between the sorbing anions and the positively charged surface of the iron oxides (Celis et al., 1999; Spadoto & Hornsby, 2003). It is also known that the MCPA molecule has a phenolic lipophilic structure that makes this herbicide a model substance for the study of adsorption-desorption mechanisms in soils, which may involve both polar and hydrophobic interactions.

The soil surface, which comprises organic and inorganic components, is the primary site for chemical accumulation of organic herbicides, and its reactivity depends on the number and type of accessible functional groups. In addition to their specific reactivity, the reactivity of any functional group also depends on the proximity of other functional groups, so that the ionization of an acid group is enhanced by a nearby withdrawing substituent. Another factor to be taken into account is the accessibility of the functional groups to the adsorbates, as the association between different soil minerals and natural organic matter may make some functional groups inaccessible.

Oxides and hydroxides of iron and aluminium are particularly important inorganic soil components as although they are not major components, they are responsible for many chemical processes that take place in the soil because of their high specific surface and reactivity. For example, iron oxides contribute to the variable charge of soil and are known to play an important role in the adsorption of anions and cations (Cornell & Schwermann, 1996).

The organic matter on the soil surface constitutes the main source of the variable charge of surface horizons. Humic substances are the main source of pH-dependent changes in the soil organic matter (SOM), and the functional groups that generate the charge are mainly carboxylic groups. The ionized fraction of the acid groups increases as the pH increases and the negatively charged groups formed will interact electrostatically with the cations present in the environment.

Adsorption reactions in soils have historically been described by empirical adsorption isotherm equations. An adsorption isotherm is a plot of the concentration adsorbed on to a solid surface against the concentration in aqueous solution, for different total concentrations of a chemical species. These equations are popular because they are simple to use and the adjustable parameters are easily estimated, although they do not provide information about the chemical binding mechanisms (Sposito, 1982). Although adsorption isotherm equations are excellent for describing adsorption experiments, it must be taken into account that they are numerical relationships used to fit data, so that the equation parameters obtained are valid only for the chemical conditions under which the experiments are conducted.

Various chemical complexation models have been developed to describe adsorption data at the solid-solution interface. The major advantage of the complexation models over empirical approaches is that the former have the potential to be predictive and are applicable to more than one experimental condition. However, this potential has yet to be fulfilled in a general way. The most significant benefit provided by the models is the consideration of charge on both the adsorbate and the adsorbent surface, and the insight provided into the stoichiometry and reactivity of adsorbed species. These models have been widely applied to the reference materials selected as models of soil components, but have scarcely been used for mixtures of these components or for soils.

## **2. Model systems for the soil fractions**

### **2.1 Organic matter**

Humic substances constitute the largest fraction of natural organic matter, and therefore may be used as reference materials to elucidate the mechanism of interaction between ionic herbicides and SOM (Hesketh et al., 1996). The classical view (Stevenson, 1994) states that humic substances are polydisperse mixtures, and that their chemical behaviour is generally determined by two types of functional groups: carboxylic and phenolic groups. Most studies involving cation binding to humic substances have been carried out in solution (Milne et al., 2003), and the information obtained for dissolved humic substances has been used to predict the binding properties of humic substances in soils (Tipping, 2002). However, some authors question whether the parameters calculated from laboratory experiments carried out with dissolved natural organic matter can be used to provide an accurate description of the properties of the solid (soil) organic matter (Merdy et al., 2006). In order to simulate more realistic conditions, peat soils with an organic matter content higher than 90%, can be used as reference materials to study the binding properties of humic substances in the solid phase.

### **2.2 Goethite**

Iron mineral oxides and (hydr)oxides are common mineral compounds, particularly in soils. Goethite ( $\alpha$ -FeOOH) is the most widely used reference material for (oxy)hydroxides as it is the most common and stable crystalline iron oxide under the conditions existing in soil. This mineral has a relatively high surface area, is very reactive (Cornell and Schwertmann, 1996) and therefore plays an important role in the migration of cations and anions in natural environments. Its properties have been studied in great detail in recent years, and there is therefore abundant information about its structure, chemical properties and adsorption, which facilitate the study of its interactions with ionic herbicides (Cornell & Schwertmann, 1996; Antelo et al., 2005; Brigante et al., 2010). Ionic pesticides may interact with reactive sites on the mineral surface via electrostatic interactions, cation exchange reactions and surface binding reactions, so that a high degree of adsorption might take place on mineral surfaces.

### **2.3 Humic acid-coated goethite**

In soils and aquatic systems, mineral oxides are often found associated with natural organic matter and their mutual interaction will change the chemical and adsorptive properties of both the organic and the mineral fraction. Because soil colloids are multicomponent associations, to achieve a more realistic view of the behaviour of cationic and anionic pesticides in natural systems, the adsorption reactions that take place in these combined systems must be analysed. Therefore, once the adsorption of ionic herbicides on

organic and mineral fractions have been studied individually, the adsorption of herbicides on organic-mineral assemblages must be analysed. The simplest assemblage is a binary system in which the goethite particles are partially coated with humic acid, which will modify both the structural characteristics of the surface, as well as the electrostatic potential profile in the immediate surroundings (Saito et al., 2004). One approach for modeling adsorption on a complex assemblage is by component additivity (CA), which attempts to predict adsorption on the assemblage using the model parameters obtained for individual reference materials (Davis et al., 1998). One method used in the application of the component additivity approach (Weng et al., 2001, 2002) consists of using different adsorption models for different adsorbents, which may involve combining the charge distribution multisite complexation model (CD-MUSIC) (Hiemstra & van Riemsdijk, 1996) for goethite, and the non-ideal competitive adsorption (NICA) Donnan model (Benedetti et al., 1996) for humic acid.

## 2.4 Description of ion binding to soil organic matter

The negative charge on the humic molecules gives rise to a negative electrostatic potential in the immediate vicinity of the molecules and therefore to a salt dependence in the proton binding. Because of this, modelling of ion binding to humic substances requires a model that accounts for the heterogeneity of functional groups in terms of their affinity for protons, and the non-specific electrostatic interactions. The Donnan approach (Kinniburgh et al., 1999) has been used extensively and successfully in the last decade to describe ionic interactions with humic acids (Tipping, 2002; Companys et al., 2007; Vidali et al., 2009), and more recently with organic soils (Vasiliadis et al., 2007; Villaverde et al., 2009). It assumes that the surface charge,  $Q$ , is neutralized by counter-ions within a gel phase known as the Donnan volume,  $V_D$ . This requires the use of the basic equation of electrical charge balance:

$$Q / V_D + \sum Z_j (C_{Dj} - C_j) = 0 \quad (1)$$

where  $C_{Dj}$  is the concentration of component  $j$ , with charge  $Z_j$  (including sign), in the Donnan volume, and  $C_j$  is its concentration in the bulk solution. Both concentrations are related by the Boltzmann factor,  $\chi$ ,

$$C_{Dj} = C_j \exp(-Z_j F \Psi_D / RT) = C_j \chi^{Z_j} \quad (2)$$

where  $\Psi_D$  is the Donnan potential,  $F$  is the Faraday constant,  $R$  is the gas constant, and  $T$  is the temperature. The procedure used to solve the previous equations has been described in detail elsewhere (Benedetti et al., 1995). The only unknown is the Donnan volume,  $V_D$ , which varies with the ionic strength. Benedetti et al. (1996) showed that the apparent Donnan volume decreased with increasing ionic strength, in accordance with the following empirical relationship:

$$\log V_D = b(1 - \log I) - 1 \quad (3)$$

where  $I$  is the ionic strength, and  $b$  is constant.

The model enables calculation of the pH in the Donnan phase ( $pH_D$ ) by use of equation 4:

$$pH_D = pH - \log(\chi) \quad (4)$$



The effect of ionic strength due to electrostatic interactions vanishes when the Q-pH curves obtained at the various inert electrolyte concentrations are plotted as a function of  $\text{pH}_D$ , to produce a unique master curve that can also be analysed to obtain the distribution of intrinsic proton binding affinity constants.

The NICA equation (Kinniburgh et al., 1999) for a bimodal affinity distribution describes the specific binding of protons to humic substances:

$$Q = Q_1 \frac{(K_1^{\text{int}}[\text{H}_D^+])^{m_1}}{1 + (K_1^{\text{int}}[\text{H}_D^+])^{m_1}} + Q_2 \frac{(K_2^{\text{int}}[\text{H}_D^+])^{m_2}}{1 + (K_2^{\text{int}}[\text{H}_D^+])^{m_2}} \quad (5)$$

where subscripts 1 and 2, respectively, indicate the carboxylic groups and the phenolic groups,  $K_i^{\text{int}}$  represents the intrinsic proton binding constants, and  $Q_i$  is the total number of available proton binding sites of each type. The exponent  $m$  is the width of the affinity distribution. Fitting of experimental data to the NICA-Donnan model can be conducted by means of different speciation and fitting programs (Kinniburgh, 1993; Keizer & van Riemsdijk, 1998; Gustafsson, 2010).

As in the case of the protons, modelling of the interaction between organic cations and SOM must take into account electrostatic and specific binding contributions. Interpretation of the effects of pH and ionic strength on cation binding is carried out with the previously described Donnan model. For this purpose, some electrostatic parameters derived from acid-base studies are required: (i) the magnitude of the negative charge of the organic matter sample at the values of pH and ionic strength corresponding to the experimental binding isotherms, and (ii) the optimized parameter  $b$ , which determines the Donnan volume for a given ionic strength. From these parameters, the electrostatic potential due to the negative charge on the natural organic matter can be calculated, and thus the concentration of cation within the Donnan phase,  $C_D$ , can be determined from equation 2. Once the electrostatic effect is accounted for, the Langmuir-Freundlich equation (6) enables us to obtain binding parameters under different experimental conditions:

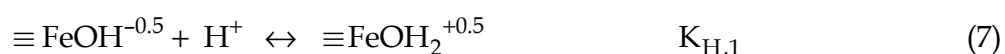
$$M = M_{\text{max}} \frac{(K^{\text{int}}C_D)^m}{1 + (K^{\text{int}}C_D)^m} \quad (6)$$

here  $M$  is the concentration of bound cation,  $M_{\text{max}}$  is the maximum concentration of the cation that can be bound,  $K^{\text{int}}$  is the intrinsic binding constant and  $m$  is the width of the affinity distribution. The advantage of the correction for the electrostatic effect arises from the fact that a unique set of binding parameters ( $K^{\text{int}}$ ,  $M_{\text{max}}$  and  $m$ ) enables prediction of the cation binding to SOM over a range of pH and ionic strengths. Note that equation 6 is restricted to a unique distribution of binding sites. This simplification was included since most of the cation binding experiments are conducted in experimental conditions ( $\text{pH} < 8$ ) under which only carboxylic groups of the organic matter are ionized. Therefore, it is assumed that only these types of groups are involved in electrostatic interactions between SOM and cationic species.

## 2.5 CD-MUSIC model for description of adsorption processes on goethite

Surface complexation models (SCMs) are applied in order to understand and predict the reactivity at the solid-solution interface of mineral surfaces. SCMs describe the adsorption of cations, anions and small organic molecules on mineral surfaces by formation reactions for surface species on well defined coordination sites, in combination with an electrostatic model accounting for the influence of the electrostatic mean field potential of the charged surface. These models are usually divided into two main parts: one describing the solid surface, the type and reactivity of surface sites, the adsorbed species, the surface charge, etc, and the other describing the charge distribution and potential decay in the electrical double layer.

Among many SCMs that have been applied so far, the CD-MUSIC model has become one of the most popular models for describing the charging and adsorptive behaviour of goethite and other well crystallized mineral oxides. A complete description of the model has been published by Hiemstra & van Riemsdijk (1996, 2006), but a brief description is also given here, in which the surface equilibrium reactions considered are presented together with some remarks that help understand the main features of the model. This model describes the mineral surface populated with different surface groups, which can undergo protonation and can bind ions or molecules from the solution. In accordance with Hiemstra & van Riemsdijk (1996) within a pH interval 1-11, the charging behaviour of the goethite depends on the protonation/deprotonation reactions of singly,  $\equiv\text{FeOH}^{-0.5}$ , and triply coordinated,  $\equiv\text{Fe}_3\text{O}^{-0.5}$ , surface groups. On the other hand, doubly coordinated surface groups,  $\equiv\text{Fe}_2\text{OH}^0$ , are not reactive against protons and remain uncharged in this pH range. Protonation of the goethite surface can therefore be described by the following reactions:



According to Venema et al. (1998) the proton affinity,  $\log K_{\text{H}}$ , of the singly and triply coordinated surface groups present in the goethite are close to 8.0 and 11.7, respectively, suggesting that singly coordinated groups are more acidic. Nevertheless, for practical reasons, both  $\log K_{\text{H},1}$  and  $\log K_{\text{H},3}$  are made equal to the point of zero charge (PZC) of the goethite surface (Hiemstra & van Riemsdijk, 1996; Antelo et al., 2005). At sufficiently high pH, the goethite surface is mainly populated with  $\equiv\text{FeOH}^{-0.5}$  and  $\equiv\text{Fe}_3\text{O}^{-0.5}$  groups, resulting in a net negative surface charge, whereas at sufficiently low pH, the mineral surface is mainly populated with  $\equiv\text{FeOH}_2^{+0.5}$  and  $\equiv\text{Fe}_3\text{OH}^{+0.5}$  groups, resulting in a net positive surface charge.

The salt dependency effect can only be described if ion pair formation is considered, and it is therefore necessary to include the equilibria between surface charged groups and electrolyte ions, as described extensively in the relevant literature (Tadanier & Eick, 2002; Antelo et al., 2005). In addition, charged surface groups may interact with ions or molecules to form inner- or outer-sphere complexes. These surface complexes are located differently in the electrical double layer. The effect of the ionic strength can be used to distinguish between inner- and outer-sphere complexes (Hayes et al., 1988; Sparks, 2003). Adsorption via outer-sphere complexes may be sensitive to changes in the ionic strength because: (i) the background electrolyte ion may compete for the available binding sites at the surface, and (ii) the activity of the adsorbing species may be influenced by the variation in the interfacial

potential due to changes in the ionic strength. Outer-sphere complexes are located on the same electrostatic plane in the solid-solution interface as the adsorbed background electrolyte ions. Inner-sphere complexation occurs in an electrostatic plane closer to the surface than the plane where the background electrolyte ions are located, and therefore is generally not affected by ionic strength.

The extended Stern model is used by the CD-MUSIC model to describe the solid-solution interface of the goethite particles and the location of the ionic charge in this electrostatic double layer is of great importance for calculating the energy involved in the electrostatic interaction. Protonated surface groups are located on the 0-plane, the charge of specific adsorbed ions or molecules is distributed between the 0-plane and the 1-plane, and supporting electrolyte ions are assumed to be single point charges located on the 1-plane or on the 2-plane. The diffuse layer starts at the 2-plane and extends toward the bulk solution. A schematic representation of the goethite-water interface and its double layer structure is shown in Figure 1.

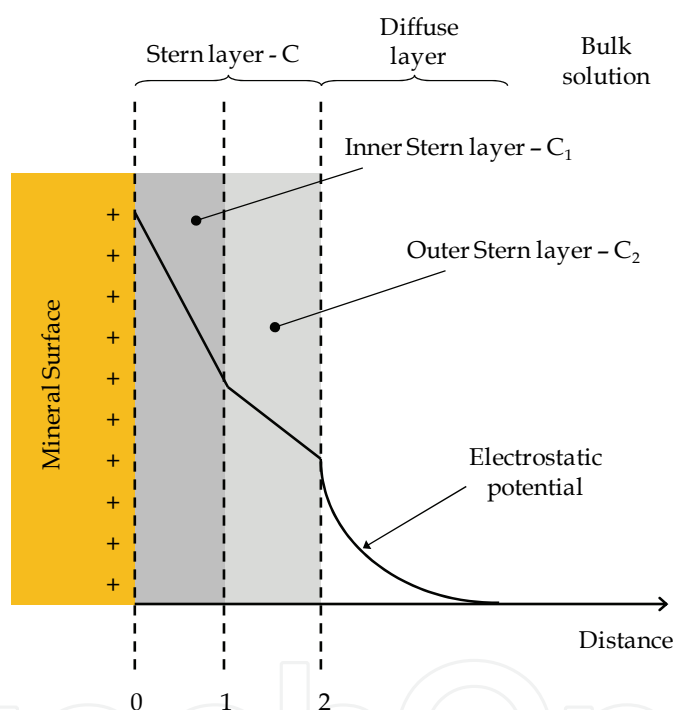


Fig. 1. Scheme of the extended Stern model for the solid-solution interface.

### 3. Case study: interaction between pesticides (Paraquat and MCPA) and model systems for soil fractions

#### 3.1 Paraquat and MCPA interaction with soil organic matter

This section focuses on the interactions between SOM and ionic pesticides, PQ and MCPA, and presents binding results obtained with a dissolved humic acid sample and a peat soil. Humic acids (HA) constitute one of the most reactive fractions in the SOM. Binding studies on dissolved humic acid may be considered as representative of the processes occurring in the soil solution, in which dissolved organic matter molecules exhibit a less aggregated conformation. In contrast, a peat soil may be used as a reference material for the solid SOM comprising a complex aggregated mixture of diverse fractions.



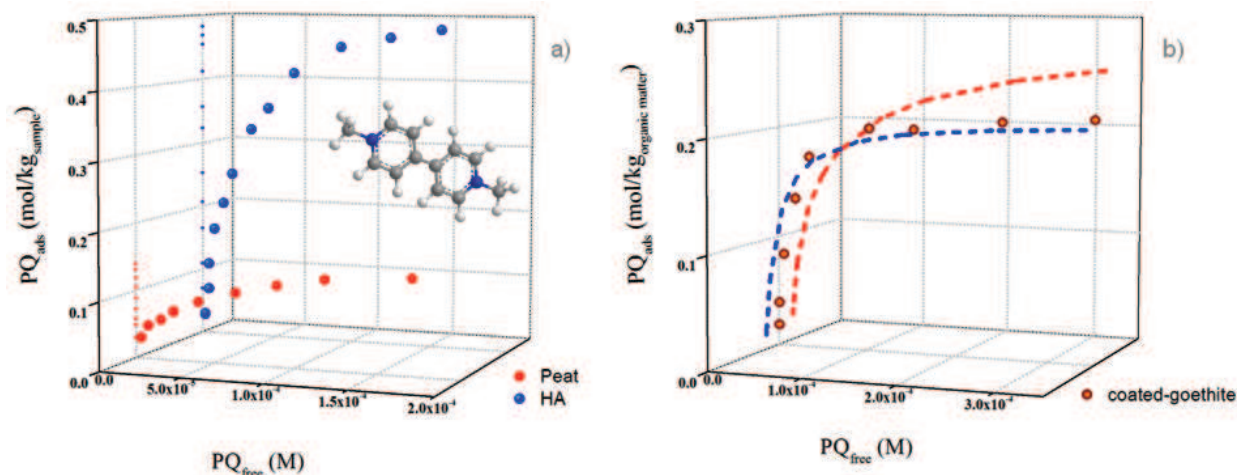


Fig. 2. a) Comparison of PQ bound to HA and peat soil samples. b) Simulation of PQ adsorbed on HA-coated goethite. Symbols: experimental data; blue dashed line: simulation with HA parameters; red dashed line: simulation with peat parameters.

The amount of MCPA bound to dissolved HA has been found to be almost negligible, even at the most favourable pH (Iglesias et al., 2009). In contrast, experimental studies of the interaction between PQ and dissolved HA (Iglesias et al., 2009) and with a peat soil (Gondar et al., unpublished results) have shown the high affinity of this cationic pesticide for the SOM, together with a significant effect of the pH and the ionic strength. This behaviour is indicative of the predominant role of the electrostatic interaction between SOM and ionic pesticides. The increase in PQ binding with pH is produced by the increase in the negative charge on the SOM resulting from the ionization of its acid groups. At the same time, the decrease in PQ binding produced as the ionic strength increases is a consequence of the screening effect produced by the inert electrolyte on the electrostatic interaction between species of opposite charge. Similar results have previously been reported (Narine and Guy, 1982; Pacheco et al., 2003; Brigante et al., 2010), suggesting that the binding of PQ to SOM samples may be explained by an electrostatic interaction.

A comparison of the behaviour of HA and peat soil as regards PQ binding is shown in Figure 2a. Under the same conditions of pH and ionic strength, the amount of PQ bound by dissolved HA is approximately four times greater than the amount bound by the peat soil. This can be explained by taking into account the electrostatic nature of the interaction and the charging properties of both sorbents in terms of the acid groups content (Table 1). The proton binding parameters show that the humic acid is richer in acid groups than the peat soil, and the content of carboxylic groups is approximately four times higher in HA than in the peat soil, whereas the content of phenolic groups is almost the same in both samples. Under acidic conditions the charge on the SOM is determined by the ionization of carboxylic groups, so that the HA will have a significantly higher charge than the peat, which will favour adsorption of the cationic herbicide.

Application of the Donnan model has enabled interpretation of the effect of pH and ionic strength on the PQ-HA interactions, so that the isotherms for experimental adsorption have been reproduced calculating the electrostatic effect with the parameters used to describe the proton binding of the dissolved HA (Iglesias et al., 2009).

ORGANIC FRACTION		
	Carboxylic groups (mol kg <sup>-1</sup> )	Phenolic groups (mol kg <sup>-1</sup> )
Humic acid (dissolved organic matter)	4.22	0.99
Peat (solid organic matter)	0.97	1.02
MINERAL FRACTION		
	Surface site density (sites nm <sup>-2</sup> )	Specific surface area (m <sup>2</sup> g <sup>-1</sup> )
Goethite	Singly coordinated: 3.45 Triply coordinated: 2.70	67.90

Table 1. General properties of the reference materials used for the soil fractions

It has recently been observed that the effect of the ionic strength on the ionization of acid groups is different for dissolved HA and for aggregated (solid) HA (Smith et al., 2001; Gustafsson & Kleja, 2005). Notably, the variation in the ionic strength of the medium has a much greater effect on the charge of the dissolved HA. Some authors (Smith et al., 2001) have proposed a modification of the Donnan model for solid SOM consisting of the use of fixed Donnan volume that is not dependent on the ionic strength. In order to interpret the contribution of the electrostatic effect on the PQ-peat interaction, we considered a value of 0.1 for parameter b (equation 3), obtained in a study of proton binding in peat soils of similar origin (Vasiliadis et al., 2007).

With the aim of comparing the affinity of both SOM samples for the cationic pesticide, and taking into account the difference in the amount adsorbed, the binding parameters were optimized, which enabled interpretation of the adsorption of PQ on the peat soil within a wide range of conditions (pH and ionic strength). Of the results obtained, the value of log  $K^{int}$  (0.36) was noteworthy as it was higher than previously observed for HA in solution (log  $K^{int}$  = -0.10), showing that the reference substances for the SOM behave differently in their interactions with PQ, as regards both the contribution of the electrostatic effect, and the nature of the groups involved in the adsorption.

3.2 Adsorption of Paraquat and MCPA on goethite

The herbicide MCPA (a phenoxyalkanoic acid herbicide) possesses a carboxylic group that is responsible for its high pH-dependent reactivity (Tunega et al., 2004) against humic substances or mineral oxides, due to changes in the percentage of ionization. Ionization of this weakly acid site on the molecule makes electrostatic interactions of great importance in describing the mechanism of adsorption.

As regards the negative charge of ionized MCPA molecules in solution, interaction with the goethite is only expected to be effective at pH values below PZC=9.4, at which the surface of the mineral oxide is positively charged. Experimental results (Iglesias et al., 2010a) indicate that the adsorption of MCPA on goethite decreases as the pH increases. At pH 4 there is a strong electrostatic interaction between both substances, but the adsorption decreases linearly with increasing pH because of the decrease in the positive surface charge of the goethite, so that at pH values close to the PZC, there is little interaction between the organic anions and the surface. This response is similar to that observed by Filius et al. (1997, 2001), who studied the adsorption of small organic acids on goethite and attributed the decrease in

adsorption at increasing pH to the fact that the sorbent-sorbate interaction is usually dominated by electrostatic effects. The present experiments involving MCPA adsorption on goethite did not show any significant adsorption of the herbicide at pH 7.0 or higher, at which the surface charge on the goethite is less positive or even negative. On the other hand, the adsorption of MCPA increased as the ionic strength of the system decreased (Figure 3a), an effect that is usually attributed to competition between the pesticide ions and the supporting electrolyte for adsorption sites.

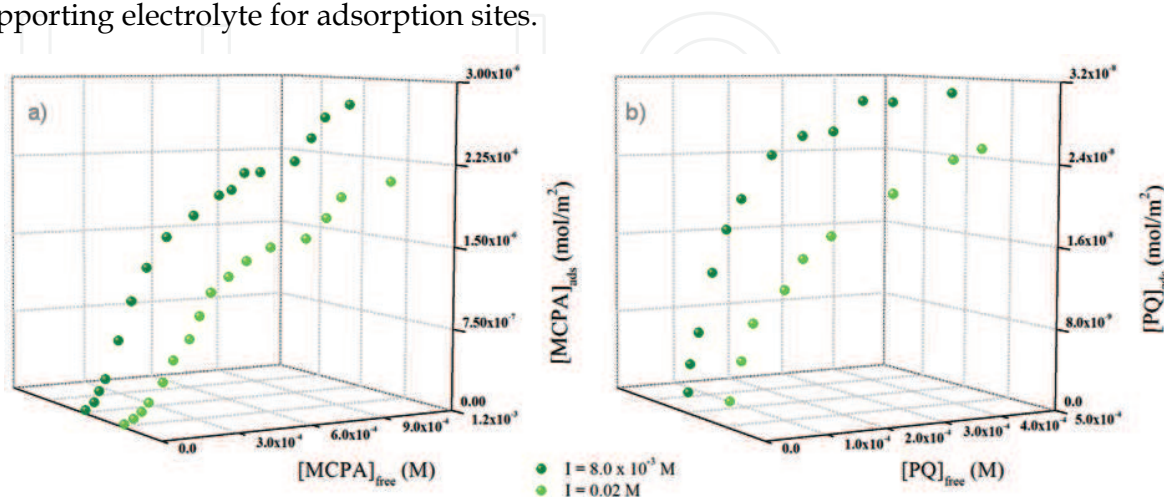


Fig. 3. Effect of ionic strength on the adsorption of ionic pesticides on goethite. a) MCPA at pH = 4.0 and b) PQ at pH = 10.5.

The adsorption isotherms for MCPA on goethite consist of two different regions (Figure 4a). The first corresponds to an S-shaped isotherm (Giles et al., 1960; Celis et al., 1999; Inacio et al., 2001; Iglesias et al., 2010a), which presents an initial region of low affinity between the solid surface and the herbicide, so that adsorption of a certain amount of adsorbate will be necessary to facilitate the adsorption process (Grant et al., 1998) and after this initial section, a Langmuir-shaped portion is observed in the isotherm. At acidic pH, MCPA may be sorbed through its  $\text{-COO}^-$  groups oriented toward the positively charged iron oxide surface, which favours lateral van der Waals interactions between the aromatic rings of the MCPA in the first adsorption layer (Celis et al., 1999). Pesticide-pesticide interaction can also be established between the first layer of adsorbed MCPA and the subsequent molecules of pesticide added, so that a second adsorption layer may be formed.

Among the experimental results that correspond to the interaction between the pesticide and the surface groups of goethite, the part of the isotherm which displays Langmuir behaviour (Figure 4b) has been interpreted with the CD-MUSIC model (Iglesias et al., 2010a). It can be assumed, as for other simple organic acids (Filius et al., 1997), that the carboxylic groups of the organic molecules can form inner-sphere and outer-sphere surface complexes with the singly coordinated surface groups ( $\equiv\text{FeOH}^{-0.5}$ ), and that the triply coordinated surface groups ( $\equiv\text{Fe}_3\text{O}^{-0.5}$ ) do not take part in the MCPA binding (Figure 5). In the inner-sphere complexes, one oxygen atom of the carboxylate group is exchanged for a surface water group. We can assume that the overall charge on the carboxylate group is equally divided over both carboxylate oxygens. One carboxylate oxygen, and its corresponding charge, is located on the surface plane (0-plane), and the charge on the second carboxylate oxygen is located on the 1-plane. On the other hand, outer-sphere complexes are linked to the protonated surface site by an H bond. The charge of the organic group is equally distributed between the 1-plane and the 2-plane, and the charge on the

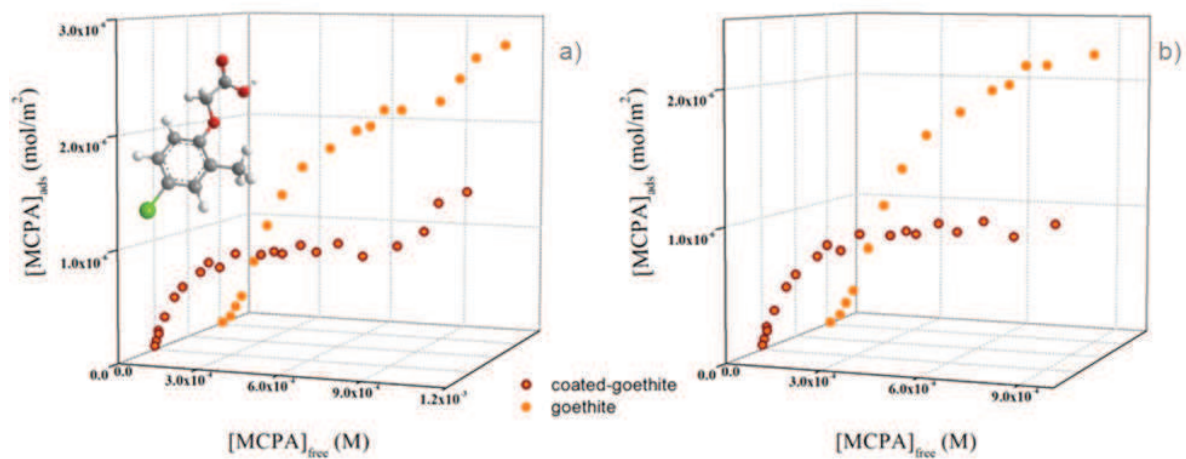


Fig. 4. a) Comparison of adsorption of MCPA on goethite and on HA-coated goethite. b) Section of the isotherms corresponding to the first adsorption layer (surface-pesticide interaction).

proton is distributed over the 0- and 1-planes. The affinity constants obtained for the formation of outer-sphere complexes are significantly larger than for inner sphere complexes, in accordance with the results obtained by Boily et al. (2000) and Filius et al. (2001) for the binding of benzenecarboxylates by goethite. Both authors indicated that carboxylates are predominantly adsorbed as hydrogen-bound outer-sphere complexes on mineral oxides. The assumption of the existence of these two types of complexes is consistent with the previously described effect of the ionic strength on adsorption of MCPA (Figure 3a).

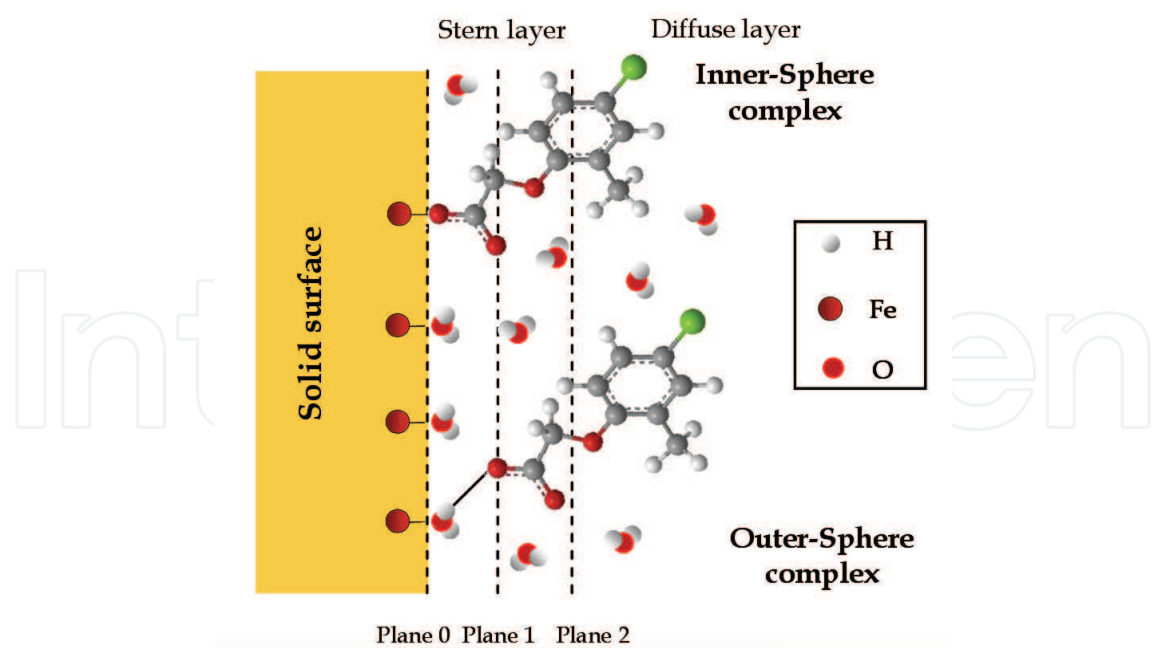


Fig. 5. Scheme of the solid-solution interface including inner- and outer-sphere surface complexes for MCPA

Adsorption of PQ on goethite occurred at pH values at which the mineral surface is negatively charged, i.e. above the PZC. On the other hand, no adsorption was observed on



goethite at any pH values below the PZC (Iglesias et al., 2010b). Electrostatic effects therefore play an important role in the interaction between PQ and the charged mineral surface. At pH below PZC, pesticide cations would be repelled, thus preventing their adsorption on the oxide. In contrast, at pH 10.5 some 90% of the surface groups would be ionized, thus favouring the adsorption process. Even under these most favourable conditions, the surface concentration of adsorbed PQ is rather low,  $0.03 \mu\text{mol m}^{-2}$  at pH 10. The results for PQ adsorption on goethite show that the contribution of this iron oxide is negligible for retention of the pesticide. Nevertheless, Pateiro-Moure et al. (2010) recently found that quartz particles coated with fresh and aged iron oxide precipitates have a larger adsorption capacity for cationic pesticides like paraquat and diquat. In the latter study both adsorption surfaces showed lower PZC (around 8.0) than goethite particles (around 9.3). This again indicates the importance of the electrostatic interactions on the adsorption of cationic pesticides, since mineral surfaces with lower PZC will have a higher amount of negatively charged surface groups and therefore will favour interactions between the mineral surface and the pesticide molecules. On the other hand, the crystallinity of the mineral surface also has an important effect on the reactivity of iron oxides against cationic pesticides, with the most amorphous forms being the most reactive.

The adsorption of PQ depends on the ionic strength (Figure 3b) in the same way as MCPA, i.e. the cationic pesticide adsorption decreases as the electrolyte concentration increases. This effect indicates that outer-sphere surface complexes are involved in the adsorption of PQ onto goethite (Hayes et al., 1988; Sparks, 2003). So far, different types of surface complexes have been postulated for PQ adsorption on different clay mineral surfaces (Rytwo et al., 2002; Draoui et al., 1999), but there is not much data for adsorption on goethite or other types of iron oxides.

The PQ-goethite binding behaviour can be described with the CD-MUSIC model (Iglesias et al., 2010b), which considers the general charging parameters of goethite (Table 1), assuming that only singly coordinated surface groups,  $\equiv\text{FeOH}^{-0.5}$ , are responsible for PQ complexation. After considering the dimensions of a PQ molecule,  $0.45 \text{ nm}^2$ , its planar structure, and the density of the adsorption sites on the goethite surface (Table 1), it was assumed that the PQ forms surface complexes in a flat conformation by the interaction with two negative sites on the goethite surface, and that the charge of the organic cation is located on the 1-plane of the solid-solution interface. Previous simulations showed that each adsorbed PQ molecule interacts with two surface sites and at the same time, several other surface groups become blocked and unavailable for further interactions with other PQ molecules. Therefore good agreement between experimental isotherms and model predictions can be achieved considering the surface complexation constant as well as the density of singly coordinated surface groups bound to the molecules of adsorbed pesticide as adjustable parameters.

### 3.3 Adsorption of Paraquat and MCPA on HA-coated goethite

The interactions between anionic and cationic pesticides and well defined systems, i.e. HA, peat soil, and goethite, have been shown in previous sections. However, it is well known that in natural complex systems, associations between soil constituents occur, which may be particularly relevant in the highly reactive colloidal soil fraction. The interactions between SOM and mineral oxide particles may alter the chemical properties and the reactivity of each isolated fraction. In order to elucidate the effect of mineral oxide-SOM associations on the interaction with ionic pesticides, the adsorption of PQ and MCPA on HA-coated goethite was investigated (Iglesias et al., 2010a,b).



Previously discussed results have shown that significant adsorption of anionic pesticides on goethite takes place at acidic pH, when the net charge on the oxide surface is positive, while no adsorption was observed for cationic pesticides. Also, MCPA binding to dissolved HA is negligible under these conditions. It is therefore expected that at acidic pH, adsorption of PQ on HA-coated goethite is produced through the reactive sites of the adsorbed HA, while the adsorption of MCPA occurs through the available reactive sites at the goethite surface.

The MCPA adsorption isotherms on bare and coated goethite are compared in Figure 4. The adsorption isotherm for MCPA on HA-coated goethite also shows two plateaus, as already observed for the bare goethite (Figure 4a). However, there was a notable difference in the adsorption of MCPA on both surfaces, as reflected by the shape of the isotherms at low concentrations of MCPA. Unlike in the bare goethite, the adsorption isotherm for MCPA on HA-coated goethite does not exhibit an initial section of shallow slope, which suggests that the presence of HA on the goethite surface favours or activates MCPA adsorption at low concentrations of pesticide. Except at this lowest range of concentration of MCPA, the adsorption of MCPA on HA-coated goethite is significantly lower than on bare goethite. The adsorption of HA on goethite implies the formation of chemical bonds between reactive groups of HA and the mineral surface, so that it may be expected that there will be fewer goethite reactive sites available for the interaction with MCPA after HA adsorption. Weng et al. (2007) found that, under similar conditions of pH and ionic strength, less than 3% of the singly coordinated surface groups present in the goethite form inner-sphere surface complexes with HA. This small percentage of goethite sites that are specifically bound to HA, and thus, not available to MCPA, is not sufficient to explain the magnitude of the experimentally observed decrease in the adsorption of MCPA on HA-coated goethite. However, because of the relatively large size of HA molecules, more goethite surface reactive sites than those specifically bound to HA may become inaccessible. This screening effect produced by adsorbed HA molecules in the vicinity of the bound surface sites may hinder the adsorption of MCPA. In addition, the electrostatic properties of the mineral surface are expected to change after being coated by HA. Since the adsorption of negatively charged HA molecules on goethite surface reduces the magnitude of the positive charge on the oxide surface, and decreases the negative electrostatic potential near the goethite surface (van Riemsdijk et al. 2006), the presence of HA will make the electrostatic interaction between anionic pesticide and the mineral surface less favourable. According to the above, the interaction between MCPA and HA-coated goethite will occur via the available surface sites at the mineral oxide and the electrostatic properties of this coated surface.

A rigorous interpretation of this interaction, using the CD-MUSIC model, requires knowledge about the parameters that determine the electrostatic potential at the solid-solution interface of HA-coated goethite. Since this information is not available, interpretation of the adsorption of MCPA onto HA-coated goethite was based on parameters previously obtained for bare goethite, with some modifications (Iglesias et al., 2010a). As in the case of the bare goethite, the formation of inner- and outer-sphere complexes between MCPA and singly coordinated groups of the coated mineral surface was assumed for the modelling calculations. The main modification is that, together with the surface complexation constants, the site density of singly and triply coordinated surface groups were treated as adjustable parameters. Modelling results show that an adequate description of MCPA adsorption on HA-coated goethite can be achieved with surface complexation constants similar to those corresponding to bare goethite, along with a significant reduction in the density of surface sites (1.14 and 0.8 sites nm<sup>-2</sup> for singly and

triply coordinated groups, respectively). Although there is a lack of experimental evidence for the availability of surface sites on the coated mineral oxide to support these results, it appears that the SOM coating on the goethite particles produces a significant reduction in the number of surface sites available to interact with MCPA.

As already mentioned, the interaction between PQ and bare goethite at acidic pH is almost negligible, whereas significant adsorption is observed on HA-coated goethite (Figure 2b), which is also consistent with the results reported by Brigante et al. (2010). Taking into account the favourable electrostatic interactions between SOM and cationic pesticides, the adsorption of PQ on HA-coated goethite appears to take place by direct binding to the HA molecules adsorbed onto goethite particles. Although the shape of the PQ adsorption isotherm on the HA-coated goethite is similar to that obtained for PQ binding on dissolved HA (Figure 2), the magnitude of the PQ adsorption, expressed in mol of adsorbed PQ per kg of organic matter adsorbed on mineral surface, is approximately 2.5 times lower. The HA-goethite association is produced by interactions between the negatively charged functional groups of HA and the positively charged goethite surface groups. The acid groups of HA are also involved in the PQ binding, and therefore a significant fraction of the ionized acid groups of the HA adsorbed on goethite become occupied and/or inaccessible for binding PQ.

The amount of PQ adsorbed by the HA covering the surface of the goethite was similar to the amount adsorbed by the same amount of organic matter in the peat soil. However, it is not known if changes in the distribution and/or conformation of the functional groups of the organic fraction occur during the process of formation of the goethite-HA aggregate, which would confer a more similar nature to that of the solid SOM represented by the peat soil.

In order to analyse whether the behaviour of the HA adsorbed on the goethite is more similar to that of the dissolved HA or of that of the peat soil, the amount of PQ adsorbed on the covered goethite was estimated from the individual behaviour of each of the reference SOM. The binding parameters corresponding to the HA and the peat soil were used for this purpose, and only a different concentration of the carboxylic groups accessible to the PQ was assumed. The results obtained in this simulation (Figure 2b) show how the form of the experimental isotherm for PQ-HA coated goethite was better represented by the behaviour of the dissolved HA. It is therefore possible to explain the adsorption of PQ on the goethite-HA aggregate by only taking into account a reduction in the available reactive sites on the HA, relative to the same amount of HA in solution.

However, as already indicated, rigorous interpretation of the interaction between PQ and the covered surface is more complex, and requires a more detailed knowledge of the properties of the surface, beyond the individual contributions of the component fractions. Given the electrostatic nature of the interaction between the ionic pesticides and binary goethite-HA systems, it is essential to know how the charge on the mineral surface is modified by the adsorption of negatively charged HA molecules.

#### 4. Conclusions

An overall view of how PQ and MCPA interact with the HA and peat soil samples reveals the electrostatic nature of the interaction between ionic pesticides and SOM. The partial ionization of the acid groups in the SOM explains the high affinity of SOM for cationic species, such as PQ, and its low affinity for anionic compounds like MCPA. The difference in the amount of PQ bound to both types of SOM samples also appears to be directly related to their respective carboxylic group contents.

As a result of their anionic character, the MCPA molecules only interact with goethite at pH values below the PZC, at which the net surface charge of the goethite is positive. Adsorption of cationic pesticides on bare goethite was negligible at pH values below PZC, and was only observed at pH values at which the goethite particles are negatively charged. The experimental results observed for the interaction between pesticides and goethite revealed that these interactions are electrostatically controlled.

Adsorption of natural organic matter on the surface of goethite produces a clearly opposite effect on the subsequent interactions with anionic and cationic pesticides. While the interaction with PQ is significant under acidic conditions, and no interaction was observed on bare goethite, the adsorption of MCPA onto goethite was significantly lower when the goethite surface was coated with HA. In general, acceptable qualitative interpretation of the adsorption of cationic and anionic pesticides on these combined and complex systems can be achieved by taking into account the reduction in reactive sites on the fraction involved in the interaction.

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## **Pesticides in the Modern World - Risks and Benefits**

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This book is a compilation of 29 chapters focused on: pesticides and food production, environmental effects of pesticides, and pesticides mobility, transport and fate. The first book section addresses the benefits of the pest control for crop protection and food supply increasing, and the associated risks of food contamination. The second book section is dedicated to the effects of pesticides on the non-target organisms and the environment such as: effects involving pollinators, effects on nutrient cycling in ecosystems, effects on soil erosion, structure and fertility, effects on water quality, and pesticides resistance development. The third book section furnishes numerous data contributing to the better understanding of the pesticides mobility, transport and fate. The addressed in this book issues should attract the public concern to support rational decisions to pesticides use.

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