

## Modeling the Acid–Base Surface Properties of Aquatic Sediments

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**Abstract** We propose a model that explains the acid–base surface properties of clastic sediments from two Argentinean reservoir lakes. The model uses potentiometric titration data sets and fixed parameters such as the apparent stability constants and reaction stoichiometries of acid–base equilibria involving known mineral phases. The model considers that sediments act as a set of independent sorption surfaces, such as organic matter, clay silicate, and iron (hydr)oxides, thus the acid–base equilibrium and the correspondent protolytic constants are represented by a humic acid, a Na-illite, and a poor crystalline Fe-hydr(oxide). In agreement with experimental data, the model predicts that all sediment samples show a similar charging behavior, increasing the negative charge as the pH increases. The net charge of sediments is controlled by the presence of negatively charged minerals and/or organic matter coatings. This reveals the great influence of clays and

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organic matter functional groups on the acid–base surface properties of sediments, and consequently on the surface reactivity toward contaminant transport.

**Keywords** pH-dependent charge · Clastic sediments · Potentiometric titrations · FITEQL · Multisurface approach

## 1 Introduction

The transport of contaminants in natural aquatic reservoirs mostly depends on reactions occurring at the water–sediment interface. The surface properties of oxides, clay minerals and organic matter in sediments are key factors controlling the reactivity of sediments toward contaminants and their transport in aquatic environments. In general, the acid–base properties of individual minerals, organic matter and hydr(oxides) that are usually present in sediments, as well as their adsorption properties toward different pollutants have been extensively studied (Hiemstra et al. 1989a, b; Avena and De Pauli 1998; Hiemstra and van Riemsdijk 1999; Rietra et al. 1999; Filius et al. 2000, Milne et al. 2001; Avena 2002; Antelo et al. 2005; Weng et al. 2006). However, the lack of information referred to the surface–water interface properties of heterogeneous sediments introduces some uncertainty in the models used to describe the distribution and transport of contaminants. For that reason, during the last past years, increasing research related to reactivity and surface properties of soils and sediments has been carried out (Wang et al. 1997; Davis et al. 1998; Cancès et al. 2003; Taubaso et al. 2004; Tipping et al. 2003; Fest et al. 2005; Goldberg et al. 2005; Borgnino et al. 2006; Goldberg et al. 2007; Nagy and Kónya 2007; Douch et al. 2009; Jacquat et al. 2009).

There is an array of equilibrium models that have been widely used to describe the adsorption on soil surface. The surface complexation models (SCM), which describe adsorption in terms of chemical reactions between surface functional groups and dissolved chemical species, are commonly used to explain adsorption equilibria within a general geochemical background. In the framework of SCM models, the solid surface is considered to be planar and the arrangement of charges at the interface is described according to the electrical double layer theory. From the solid–water interaction viewpoint, the SCM quantify the adsorption in terms of chemical and electrostatic interaction. The chemical term is based on thermodynamic principles of chemical equilibrium and considers reactions involving surface species, while the electrostatic term characterizes the existence of particular distribution of charges at the interface. The models most commonly used to describe the solid–liquid interface are the constant capacitance model, CCM (Schindler and Gamsjäger 1972), the diffuse layer model, DLM (Stumm et al. 1970), and the three layer models, TLM (Davis et al. 1978). Each model assumes a particular interfacial structure, resulting in the consideration of a surface reaction. It has been customary and preferred in the literature so far to assume that the surface groups react according to the following scheme:



where  $\text{SO}^-$ ,  $\text{SOH}$ , and  $\text{SOH}_2^+$  represent negative, neutral, and positive surface groups, respectively, and  $K_1$  and  $K_2$  are the intrinsic stability constants. This is the typical 2-pK model. It also exists the 1-pK model (Borkovec 1997), which just uses a single equilibrium.

More recent models are the multisite complexation (MUSIC) (Hiemstra et al. 1989a, b), and the charge distribution CD-MUSIC models (Hiemstra and van Riemsdijk 1996), which use the three plane model to describe the electrical configuration at the solid–liquid interface and requires information about the crystallographic features of the specific minerals present in the solid.

Due to the heterogeneity of natural soils and sediments, the application of SCM to describe the interaction of solutes with the solid surface leads to some important uncertainties in the obtained results. In the complete review of Goldberg et al. (2007), the authors compiled two main approaches that had been traditionally applied to describe adsorption on heterogeneous materials: the Component Additivity (CA) approach (Honeyman 1984; Davis et al. 2002) and the Generalized Composite (GC) approach (Goldberg et al. 2007). The CA approach considers that total adsorption onto a natural soil or sediment is the result of adding the adsorption by their individual component minerals, and does not require the fitting of experimental data because all parameters in the model are known. By this way, sediments act as a set of independent sorption surfaces, i.e., organic matter, clay silicate, and iron (hydr)oxides. This multisurface sorption approach was used with success to evaluate the surface charge and adsorption capacity of other natural soils and sediments (Weng et al. 2001; Fest et al. 2005; Dijkstra et al. 2009; Serrano et al. 2009). In the GC approach, generic surface functional groups representing average properties of the soil or sediment are considered (Davis et al. 1998, 2002, 2004). The application of this approach implies the collection of a large set of experimental data to improve the robustness of the model, as the obtained results are only valid for the range of aqueous chemical conditions considered in the experimental data set (Goldberg et al. 2007).

In the present study, we propose a model, based on the multisurface sorption approach that describes the distribution of the pH-dependent charge of sediments that are in contact with water stored in two important midlatitude reservoir lakes in the Province of Córdoba, central Argentina. For the modeling purposes, we consider that surface charge in sediments is of two types: (1) pH-independent charge which originates from the isomorphic substitution in the lattice of minerals (mainly clay minerals) and (2) pH-dependent charge ( $\sigma_H$ ) that originates on the clay mineral edges, oxides, and organic matter, where proton adsorption occurs through equilibrium reactions, as indicated in Eqs. 1 and 2.

The obtained results may contribute with valuable information for future studies involving the adsorption/desorption dynamics of potential contaminants that may affect water quality in Córdoba city and its surroundings.

## 2 Materials and Methods

### 2.1 Sampling, Chemical and Mineralogical Analyses

Drinking water is supplied to the city of Córdoba (~1.5 million inhabitants), central Argentina, by two important reservoirs located at the foothills of Sierras Grandes de Córdoba. Los Molinos is a mesotrophic-eutrophic reservoir lake covering a surface area of 2,110 ha, with a maximum length (north–south) of 13.5 km and a maximum depth of around 50 m in regions near the dam. San Roque is an eutrophic-hypereutrophic reservoir with a surface of 1,500 ha, a maximum length (north–south) of 8.4 km, and a maximum depth of around 30 m in regions near the dam.

Six samples of clastic sediments were collected at three sampling sites in the Los Molinos and San Roque reservoirs. They were selected in order to sample representative

areas of the center, mouth of main tributaries, and the zone near the dam. Therefore, the identifying acronyms of the three samples obtained at Los Molinos are LMC, LMT, and LMD, meaning, respectively, Los Molinos Center, Los Molinos mouth of Tributary, and Los Molinos Dam. The same criterion was used to define the acronyms of the three samples obtained in San Roque, SRC, SRT, and SRD. The sediments were collected using a standard Ekman dredge, homogenized in plastic vessels and immediately placed in high-density plastic flasks and cooled to 5°C. Samples were then dried in air and gently ground in a mortar.

For textural analysis, a portion of the dried sample was dispersed by adding a 5% sodium hexametaphosphate solution. One liter of the resulting suspension was poured into a graduated cylinder, and the proportion of fine sand, silt, and clay in the sample was determined by densitometry, based on Stoke's law.

A 1:10 sediment/water suspension was prepared to measure pH following the methodology proposed by Jackson (1982). Organic matter was determined by igniting at 550°C a pre-weighted sediment portion.

The chemical analysis of sediments was performed by ICP-AES after a lithium meta-borate/tetraborate fusion.

## 2.2 Surface Characterization

The specific surface area (SSA) was determined by the methylene blue adsorption method (Avena et al. 2001). It is well known that this method seems to be more suitable for materials such as sediments, because it measures not only the external area of minerals but also the internal area of expandable clays (Avena et al. 2001).

Microelectrophoretic mobilities ( $\mu$ ) were measured in a Mark II Rank Brothers apparatus, using a thermostated 2-mm cylindrical cell, at constant temperature (25°C). An aliquot of a diluted (opalescent) dispersion, prepared by suspending a small amount of solid in 200 mL of a 0.01 M NaCl solution, was introduced into the cell. The dispersion pH was previously adjusted in the 3–9 pH range adding drops of HCl and/or NaOH as required and  $\mu$  was measured. The reported  $\mu$  values are the average of at least 20 readings.

The pH-dependent surface charge was determined by acid–base potentiometric titrations at constant temperature (25°C) under N<sub>2</sub> atmosphere. Prior to titration, sediments samples were washed with 0.01 M NaCl several times in order to remove acidic or basic impurities. Then, samples were centrifuged and dried at 40°C.

For potentiometric titrations, approximately 0.3 g of the dried samples was suspended in 50 mL of carbonate-free 0.01 M NaCl. Suspensions were continuously stirred and purged with pure N<sub>2</sub> gas during all titration and for about 1 h before the procedure begins. Titrant solutions (HCl or NaOH 0.1 M) were added and pH was recorded every 10 min until a stable potential was reached (drift 0.5 mV min<sup>-1</sup>). Short intervals (10 min) between successive increments of titrant allow dissociation equilibria to occur, and reduce the contribution of side reactions (Duc et al. 2005). Titrations were performed from pH 9 to pH 4 with a standard HCl solution. Once the dispersion reached this pH value, a measured amount of solid NaCl was added to the reaction vessel in order to increase the salt concentration by a factor of 10 and the change in pH was recorded. This salt addition helps in locating the point of zero charge (PZC, pH where the net charge of the solid surface is zero) of the sample. A NaCl solution was also titrated and used as blank. The charge of sediment particles was calculated from the difference between the amount of protons or hydroxyls taken up by the samples and the blank experiments. This is not an absolute value of the charge, but a relative value (Heil and Sposito 1993; Torn et al. 1998). Only by

knowing the PZC of the sample or by measuring independently the absolute charge at a given pH, these relative values could be corrected to obtain absolute charge versus pH curves (Avena 2002; Sposito 2004). In order to check reversibility, some additional titrations were performed in the opposite way, i.e., from native pH around 6–4, with HCl, and then from pH 4–10 with NaOH. The titrations were performed by duplicate.

All solutions were prepared using analytical grade reagents and purified water (Milli-Q system). Titrations were performed with a 665 Dosimat (Metrohm) automatic dispenser, and the pH was measured with an Orion EA 940 pH meter equipped with an Orion BN 9101 glass electrode and an Orion 163 900200 double junction Ag/AgCl/Cl<sup>-</sup>164 reference electrode.

### 2.3 Surface Modeling

We have used the potentiometric titration data sets to describe the acid–base behavior of the sediment suspensions and to estimate the distribution of the surface species in the 4–9 pH range. Modeling was performed with the nonlinear least-squares optimization program FITEQL 4.0 (Herbelin and Westall 1999), which is based on some equilibrium model reaction and titration data set. The procedure used was as follows: in a first step, we set up some equilibrium reactions for the titrated system and their corresponding protolytic constants. Then, the equilibrium model for each titration point was run. Finally, the goodness-of-fit was evaluated through the ratio WSOS/DF which is equal to the weighted sum of squares divided by degrees of freedom. Values between 0.1 and 20 are common for a reasonably good fit (Herbelin and Westall 1999).

The input information to FITEQL 4.0 consisted in experimental data and known parameters taken from previous studies. The experimental potentiometric titration data, previously corrected for blank consumption, were introduced in the program as total concentration of added H<sup>+</sup> versus equilibrium pH. For the modeling purposes, we have adopted the multisurface sorption approach described in the introduction to characterize acid–base surface properties of sediment particles. Therefore, we have used known values of the protolytic constants corresponding to the following surface sites:

1. Organic matter sites: we used the protolytic constants determined by Milne et al. (2001) for humic acids, the commonest organic component in sediments.
2. Clay silicates: we considered illite to better represent the clay silicate content of the studied sediments, as it predominates in most soils and clastic sediments of the central Chacopampean plain (Camilión 2003). In illite, as well as in most clay minerals, there are two different contributions to the net surface charge of the mineral: (a) Structural permanent charge and (b) pH-dependent charge ( $\sigma_H$ ) that originates on the mineral edges. Parameters informed by Avena (2002) for a Na-illite, with cation exchange capacity (cec) = 0.21 mEq g<sup>-1</sup> and a surface area of 224 m<sup>2</sup> g<sup>-1</sup>, were used here.
3. Iron hydr(oxides): we consider amorphous iron hydroxide minerals in the proposed model because the corresponding crystalline forms were not identified in the studied sediments. Protolytic constants were obtained from Dzombak and Morel (1990).

The concentrations of all above-mentioned surface sites were optimized using the FITEQL 4.0 program. Convergence was achieved by adjusting all surface site concentrations simultaneously.

To describe the charge distribution and the potential decay on the aqueous side of the interface, we have adopted the simple Constant Capacitance Model (CCM). This model assumes the presence of a surface plane for adsorption of H<sup>+</sup>, OH<sup>-</sup>, and all specifically

adsorbed solutes. The charge-potential used in the model is  $\psi_0 = \sigma_0/C$ , where  $C$  is the capacitance of the mineral–water interface.

### 3 Results and Discussion

#### 3.1 General Characterization of Sediments

The parental rock of the studied sediments corresponds to the Achala batholith granitoids that crop-out at the top of the Sierras Grandes de Córdoba. Despite this common origin, some small differences in their mineralogical composition are observed due to natural sorting. Primary minerals consist of albite and grains of quartz, and in minor proportion, there are K-feldspar, muscovite, chlorite, and hornblende. Minerals identified in the  $<2\text{-}\mu\text{m}$  size fraction of these sediments are illite, illite/smectite, kaolinite, kaolinite/smectite, chlorite, and palygorskite (Sattler 2003).

The bulk chemical composition of the sediments is presented in Table 1, as well as the grain-size distribution, and the specific surface area. As expected, specific surface area is highest in the fine grain-size bottom lake sediments, where the silt–clay size fraction largely predominates (more than 90%), and lowest in the sand-size tributary sediments.

The chemical composition of all sediments is rather similar. The most significant difference among the analyzed sediments is the organic matter content. Sediments from lake bottoms (SRC, LMC, SRD, and LMD) showed higher concentration of organic matter, than that measured in tributary samples, probably due to predominating eutrophic conditions in the studied reservoir lakes.

#### 3.2 Surface Characterization Through Potentiometric Titrations

Figure 1 shows the electrophoretic mobilities of sediment particles in the 3–9 pH range. Despite the fact that sediments are heterogeneous mixtures of phyllosilicate clays, metal oxides, other minerals such as carbonates and sulfates, and organic matter, each one with its own charging behavior, the electrophoretic mobilities of sediment particles are always negative in the studied pH range. This behavior appears to be common for particles in aquatic systems (Ferreira et al. 1997) and is the result of one or both of the following facts: (1) each sediment particle is actually an aggregate of different minerals that carries a net negative charge and/or (2) particles that are usually positively charged in the pH range of

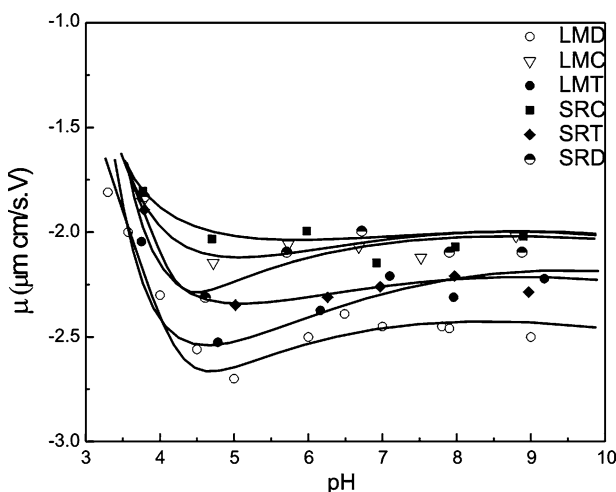
**Table 1** Chemical composition (%), grain size (%), and specific surface area (SSA) of the studied sediments

Sample	Na <sub>2</sub> O	K <sub>2</sub> O	CaO	MgO	Fe <sub>2</sub> O <sub>3</sub>	SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	O.M	Grain size			pH	SSA (m <sup>2</sup> g <sup>-1</sup> )
									Sand	Silt	Clay		
SRT	1.40	2.50	2.70	1.40	6.40	62.2	13.9	9	29.7	59.7	10.6	6.50	59
LMT	1.90	1.90	2.80	0.89	5.00	67.8	11.9	7	83.9	14.2	1.9	6.20	54
SRC	0.77	2.50	1.80	1.40	6.60	54.5	12.8	15	0.4	68.6	31.0	6.20	240
LMC	0.94	2.10	1.90	1.40	6.20	57.5	11.9	14	2.0	69.0	29.0	6.13	182
SRD	0.70	2.40	1.70	1.50	7.30	52.1	13.1	15	6.4	69.7	23.9	6.10	247
LMD	0.85	2.20	1.50	1.40	6.60	55.3	12.3	14	9.4	63.6	27.0	5.70	207

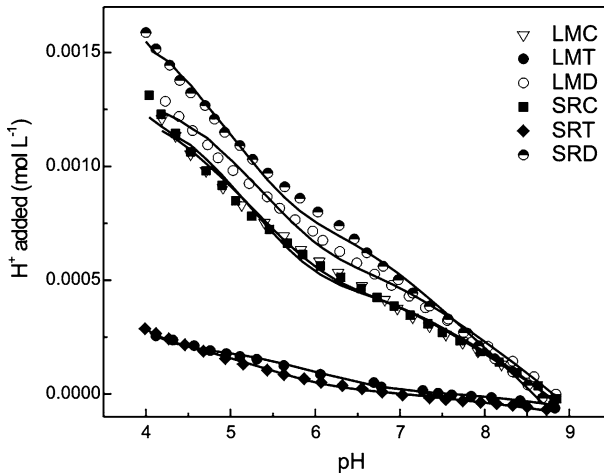
natural waters, such as metal oxides, manifest a negative charge because they are coated with organic matter, which are known to induce a net negative charge to mineral surfaces (Tipping and Cooke 1982, Beckett and Ngoe 1990).

Acid–base potentiometric titrations are usually performed in order to estimate the PZC of soils, sediments, and different synthetic materials and to evaluate the surface charge behavior of the studied sample. The PZC corresponds to the pH where titration curves performed at different electrolyte concentrations intersect (Sparks 2003). Our preliminary studies demonstrated that no intersection point was found in any case, indicating that the PZC of the sediments is outside of the investigated pH range. For the case of sediments, where typical acidic PZC minerals such as plagioclase, mica, clay minerals, and quartz (Stumm 1992; Mukhopadhyay and Walther 2001; Taubaso et al. 2004; Jara et al. 2005) occur, we considered that the PZC should correspond to a pH value lower than 4, which was the lower limit reached in our titration experiments. Salt additions at pH 4 showed that the pH decreased after increasing NaCl concentration, confirming our assumption that the PZC of the samples is below this pH value. This result indicates that the net charge of sediments is controlled by the presence of negatively charged minerals, as mentioned above. Because those minerals carry a negative structural charge that is independent of pH, potentiometric titrations only give information about the variable-charge component of the sediments, but cannot evaluate their total net charge. The presence of an important fraction of structural charge in the sediments may also contribute to the flatness of the  $\mu$  versus pH curves shown in Fig. 1.

In order to compare the proton or hydroxyl consumptions by each sediment sample, we analyzed the potentiometric titration curves carried out at 0.01 M ionic strength (Fig. 2). The curves are rather similar indicating that the variable-charge component of all samples depends on the mineralogical composition of each sample. Samples from the central part of the reservoir lakes and from areas near the dams (lake sediment samples) have much higher proton or hydroxyl consumptions than samples collected at river mouths. This is an expected result since the former have much higher SSA than the latter.



**Fig. 1** Electrophoretic mobilities of sediment samples in 0.01 M NaCl. Lines are drawn only to serve as guides to the eyes



**Fig. 2** Potentiometric titration curves of sediments samples at 0.01 M NaCl. *Symbols* experimental data points. *Lines* calculated curves fitted with parameters listed in Table 2

In all samples, the consumption of  $H^+$  due to dissolution was negligible due to the reversibility of the titration curves in the studied pH range (Borgnino et al. 2006).

### 3.3 Modeling

As mentioned in Sect. 2.3, we have adopted the multisurface sorption approach for modeling the surface charge of the studied sediments. Table 2 summarizes the sites, acid–base reactions, and their corresponding constants included in FITEQL program. Since they are known parameters, obtained from the literature, only the concentrations of all sites were adjusted. Due to the good adjustment between modeled and experimental data (Fig. 2), the assumption that sediments act as a set of independent sorption surfaces, (i.e., organic matter, clay silicate, and iron (hydr)oxides), is considered to be correct. Values of

**Table 2** Parameters used in calculations to model the acid–base properties of sediments

Surface species	log K
Generic humic acid (Milne et al. 2001)	
Carboxylic site	3.15
Phenolic site	2.55
HFO (Dzombak and Morel 1990)	
$SOH_2^+ = SOH + H^+$	7.29
$SOH = SO^- + H^+$	8.93
Illite (Avena 2002)	
$SOH_2^+ = SOH + H^+$	3.90
$SOH = SO^- + H^+$	7.60
$X + Cat^+ = XCat^+$	1.97
$X + H^+ = XH^+$	2.28
$N_{Str} = 0.090 \text{ Cm}^{-2} = 0.21 \text{ mEq/g}$	
Capacitance, $F \text{ m}^{-2}$ : 1.00	

*X sites* represent the structural surface charge at the surface of the mineral,  $N_{Str}$  structural charge

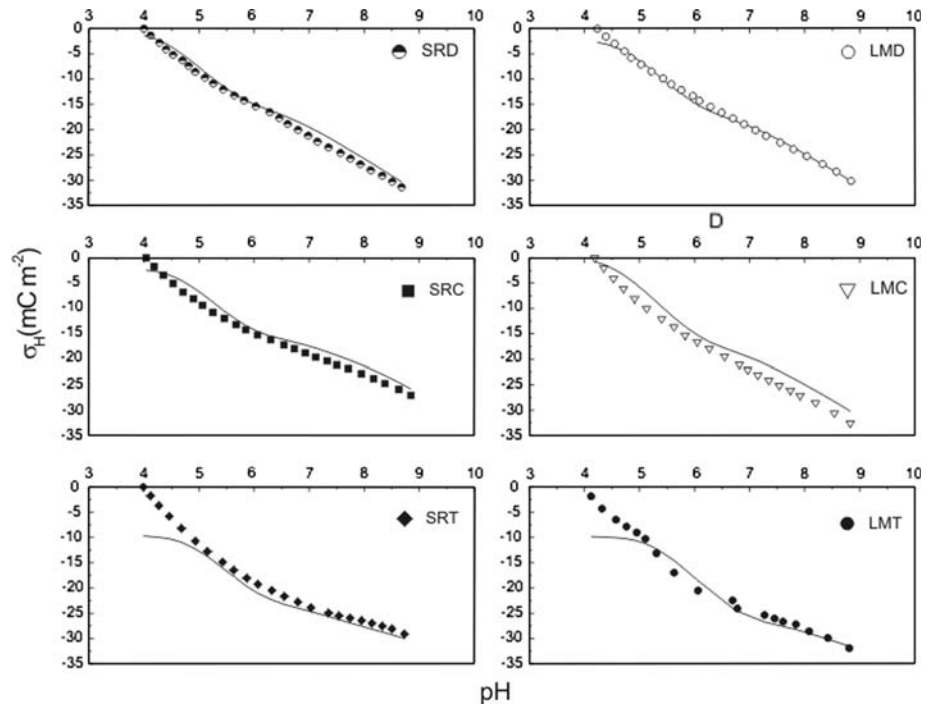


WSOS/DF (not shown here) range between 3 and 14, which also indicates the goodness-of-fit.

Since the total net charge of sediments cannot be assessed experimentally with acid–base potentiometric titrations, only the proton charge ( $\sigma_H$ ) which comes from the protonation–deprotonation of variable charge and X sites (structural surface sites) can be measured with this method. In the context of the proposed model,  $\sigma_H$  is represented by:

$$\sigma_H = F[(\text{SOH}_2^+) - (\text{SO}^-) + (\text{XH}^+)] \quad (3)$$

where  $\text{SOH}_2^+$  and  $\text{SO}^-$  represent the total moles of positive and negatively charged species present in the sediments, and  $\text{XH}^+$  represents the moles of proton-binding structural sites (see Table 2 for a description of acid–base equilibrium of each sorption surface site). The total concentrations of all species used to calculate  $\sigma_H$  with Eq. 3 were obtained from the FITEQL output file. By this way, we can obtain a modeled curve representing the variation of  $\sigma_H$  versus pH and compare it with the values of  $\sigma_H$  calculated from experimental data (Fig. 3). As we could not observe a PZC by means of acid–base potentiometric titrations, only relative data were analyzed. Therefore, the experimental curves were arbitrarily set so that the relative net proton charge was zero at pH 4 ( $\sigma_H = 0$  at pH 4). In general, the model well predicts that the negative charge increases at increasing pH in all sediment samples. The net proton charge obtained with the model closely coincides with that obtained experimentally and the pH value for which  $\sigma_H = 0$  is close or slightly lower than 4. This

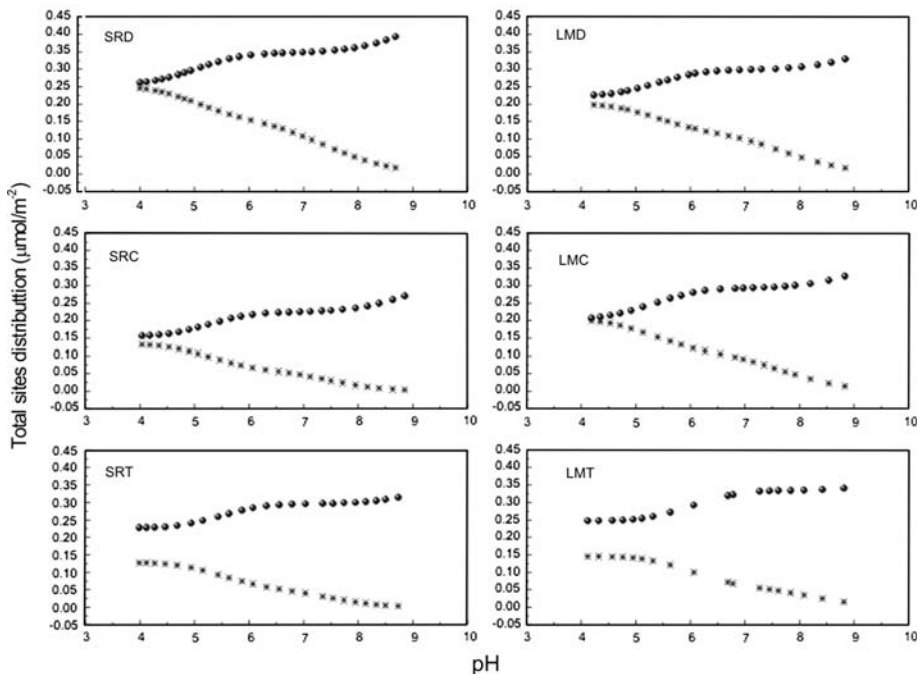


**Fig. 3** Relative net proton surface charge versus pH curves. Symbols correspond to experimental data points. Lines were calculated by replacing the total surface site concentration obtained with the FITEQL program into Eq. 3

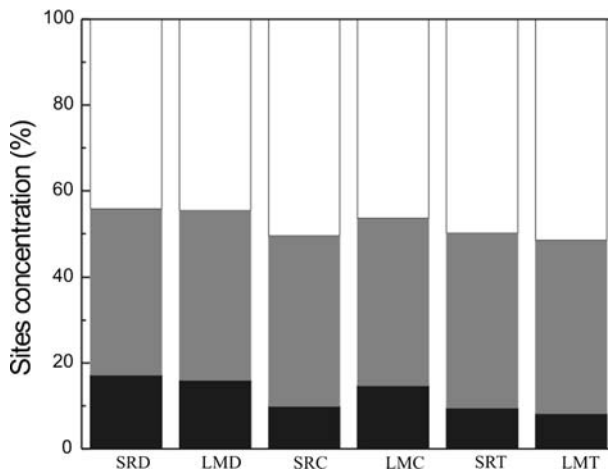
coincides with our prior assumption that the net charge of sediments is controlled by the presence of negatively charged minerals that usually carry negative structural charges, and/or by the presence of organic matter coatings.

The distribution of total surface species calculated with FITEQL program also shows the predominance of negatively charged species over the positive ones in the studied pH range, as depicted in Fig. 4. Each curve represents the sum of all positive and negative surface species, respectively. Accordingly, positive and negative curves tend to cross at pH near or below 4. Moreover, the concentration of sites assigned with the protolytic constants of a generic humic acid (Milne et al. 2001) and those characterized with the parameters fitted for a Na-illite sample (Avena 2002) explain more than 80% of the total surface sites (Fig. 5). This reveals the great influence of clays and organic matter functional groups on the acid–base surface properties of sediments, and consequently on the surface reactivity toward contaminant transport.

The proposed model can predict fairly well the acid–base behavior of sediments samples, although it fails in explaining the net surface proton charge in samples collected along tributary rivers at pH values lower than 5. At these pH values, the model overestimates the negative charges (Figs. 3, 4) probably due to the fact that we assumed that all samples had the same value of structural charges ( $N_{Str}$ ) of  $0.21 \text{ mEq g}^{-1}$ . Considering that in tributary samples, the silt–clay size fraction is lower (Table 1), the total value of  $N_{Str}$  (or cec value) introduced in the model should be also lower than that used in lake sediment samples. The



**Fig. 4** Total site concentration of positive and negative surface species in sediment samples: *Black circles*, total negative surface sites ( $\text{SO}^-$ ); *stars*, total positive surface sites ( $\text{SOH}_2^+$  and  $\text{XH}^+$ ). The concentrations were obtained from the model predictions calculated with parameters of Table 2



**Fig. 5** Sites concentration in each sediment sample, expressed as percentage of the total sites. *Black box*, sites with the Fe-hydr(oxides) constants (Dzombak and Morel 1990); *gray box*, sites characterized by humic acid parameters (Milne et al. 2001); *white box*, sites described by the parameters set for a Na-illite mineral (Avena 2002)

cec value is expressed as mEq per gram of total sample. This is not completely representative of the tributary samples, where the silt–clay size fraction is lower.

#### 4 Conclusions

We propose a model that explains the acid–base surface properties of clastic sediments collected in two reservoir lakes from the province of Córdoba, central Argentina. The model uses experimental potentiometric titration data sets and known parameters, such as the apparent stability constants and reaction stoichiometries of acid–base equilibria involving known mineral phases. Based on the mineralogical and chemical analyses of the sediments, we considered that most reactive surface sites toward proton adsorption were represented by a generic humic acid, a Na-illite, and a poorly crystalline Fe-hydr(oxide). The apparent stability constants used for each mineral acid–base reaction were obtained from previous studies.

The good adjustment between modeled and experimental data revealed the usefulness of the adopted approach to predict the development of the net surface charge in natural sediments under variable pH conditions.

Regarding the reactivity of the studied sediments toward dissolved pollutants, we may infer that they will show a high affinity for cations due to the predominance of negatively charged sites, mostly associated with clay minerals and organic matter. Depending on the extent of alteration of mineral phases (formation of Fe (hydr)oxides coatings), we may also expect increasing affinity for anions, such as phosphate, whose occurrence has been described in the studied aquatic systems.

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