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# Complexing capacity of natural waters carrying a great amount of suspended matter

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# Abstract

The cadmium binding properties of waters of the superior section of the Rio de la Plata estuarine were determined over a three-year period. Samples were collected at different hydrodynamic conditions. The complexing capacity was determined by square wave anodic stripping voltammetry (SWASV). Titration curve data were analyzed using a multivariable regression.

Suspended particulate matter (SPM) was identified by XR diffraction and FTIR. These analyses showed that SPM principal components are clays (illite, montmorillonite and chlorite). The study was applied to the untreated, filtered and centrifuged fractions of each sample at the pH of the natural waters and at pH 1.

The results show that the contribution of dissolved organic matter to the complexing capacity is negligible when compared with SPM. At natural pH, the complexing capacity of filtered and untreated fractions can be described by considering two kinds of binding sites. The associated conditional binding constants are independent of the concentration of suspended matter. Their average logarithms are ca. 6.5 and ca. 4.4. The total concentration of binding sites ( $S_T$ ) is in  $\mu$ M range, which is about three orders of magnitude higher than that reported for most of the studied estuaries. This difference is explained on the basis of the great amount of SPM. Hydrodynamic conditions produce variations in the concentration and composition of the SPM. At pH 1 samples still exhibit an important complexing capacity with only one binding site with log  $K^{cond}$  ca. 5.4. These differences could be attributed to superficial modifications that take place at very low pH.

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# 1. Introduction

Trace elements in a given aqueous environment may be present in different forms as much in the dissolved phase as in the suspended particulate matter. In the true solution the metal partitions into free hydrated ions, inorganic and organic complexes, while in the particulate matter, colloidal and suspended particles, they bind to different surface sites (Muller, 1996; Kozelka and Bruland, 1998; Velasquez et al., 2002). Strong organic complexes and suspended particulate matter, SPM, contribute to the unavailability of toxic metals for the bacteria and phytoplankton (Lead et al., 1999). However, this fact changes drastically when considering the gastro-intestinal environment of other organisms. At a very low pH, organic complexes liberate the metallic ion while SPM may still have considerable binding capacity, as it is shown in this paper.

The contribution of the SPM to the total complexing capacity of an aquatic system may be of fundamental importance. Particles that travel suspended in the river water are constantly deposited on the sedimentary bed, removed and resuspended. Floods, flows induced by winds and rains produce variation in the particle concentration (Shulkin and Bogdanova, 2003). Mechanical and physicochemical conditions, and the reactivity of the particles

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surface play a key role in the availability, transport, recycling and fate of chemicals in the aquatic environment (Turner and Millard, 2002).

From the above considerations, it arises that it is important not only to determine the amount of binding sites and their binding constants, but also to characterize the SPM.

The SPM of many rivers mainly consist in clay particles with sizes ranging from micrometers to colloidal dimensions (Lead et al., 1999; Turner and Millard, 2002). Their high specific surface area together with their concentration determine the amount of available binding sites, while their physicochemical surface properties determine their conditional binding constants.

The clay composition and concentration of SPM is related to its origin and may change under different hydrodynamic and chemical conditions, facts that make each river unique. So, comparison between different rivers or estuaries requires the consideration of the nature of the adsorptive material (Ferreira et al., 1997; Martino et al., 2004).

Some electrochemical techniques are well suited to analyze the complexing characteristics of natural waters because using them it is not necessary to modify the natural system, avoiding laboratory artifacts (Simões Gonçalves et al., 1985; Correia dos Santos et al., 2001). This is the case of the anodic stripping voltammetry (ASV) that allows to determine the concentration of the free (or weakly complexed) electroactive metals by direct electrodeposition from the sample (Wang, 1996; Lam et al., 2001).

We have studied the complexation of cadmium because its presence in natural waters is mostly due to anthropogenic activities and because its soluble compounds are highly toxic (Daher, 1995). The aim of this work is to characterize the complexing capacity of natural waters carrying a great amount of suspended matter and its correlation with the nature of them. For this purpose we have chosen the waters of the superior part of the Rio de La Plata estuary which average SPM concentration (169 mg dm<sup>-3</sup>) of which is similar to other important rivers as Orinoco (132 mg dm<sup>-3</sup>), Amazonas (162 mg dm<sup>-3</sup>) (Depetris and Paolini, 1991) and Mississippi (200 mg dm<sup>-3</sup>) (Manheim et al., 1972).

## 2. Methods

#### 2.1. Description of the study area

The Río de la Plata estuary (Fig. 1) is the output of a huge drainage basin embracing an area of 3.1 millions km<sup>2</sup> partially situated in the territories of Argentina, Brazil, Bolivia, Paraguay and Uruguay. Waters and sediments are brought together from the Andes, the Mato Grosso Rain Forest and the South-east Brazilian mountains near the Atlantic Ocean. This estuary, of a total length of 317 km and a surface of 30.212 km<sup>2</sup> (Colombo et al., 1989), has caudal ca. 22000 m<sup>3</sup>/s, and carries about 80 million t/y of particulate matter from temperate and tropical regions of South America (Colombo et al., 1989; Depetris and Paolini, 1991). The samples analyzed in this work were collected in the superior part of the estuary where the low salinity of the waters (0.3%) and low depth from bottom (from 2 to 5 m) characterize this sector. The width of the estuary in this section is about 35 km. Rains increase the caudal in spring and autumn, but these donot change the river level significantly. Tides due to the oceanic influence have an amplitude that does not exceed one meter



Fig. 1. Map of Rio de la Plata Estuary. The sampling site is indicated.

but two sporadic meteorological phenomena characterized by strong winds may alter the level of this estuary's waters significantly. South-east wind between 20 and 50 km/h (known as "Sudestada") can increment the level in more than 1 m and produce strong surf, while the west wind and the north wind can produce important low tide.

#### 2.2. Sample collection and storage

The sampling site was visited four times, two times in summer 2004 (V04), 2005 (VS05) and two times in winter 2003 and 2004 (I03 and IS04). Two of these samples were collected during the phenomena called "sudestada" (IS04 and VS05). Bottles used for this purpose were carefully cleaned with sub-boiling quartz distilled HNO<sub>3</sub>, 10%.

# 2.3. Untreated, centrifuge and filtrate fraction

After transport to the laboratory, collected waters were split into three fractions: non-modified or untreated samples (U), 0.45  $\mu$ m filtered samples (F) (using Microclar® polyethersulfone membrane filters) and centrifuged samples (C) (5000 rpm for 60 min, particle size ca. 0.05  $\mu$ m).

#### 2.4. pH, major anions and electroactive metals

The pH of untreated samples was measured with Metrohm pHmeter calibrated at room temperature with Whatman buffer solutions. Chloride, sulphate, and nitrate were determined by ion Chromatography (Dionex DX 100). The determination of total electroactive metal concentration was carried out following a technique similar to that indicated by Muller (Muller, 1999). Samples and blanks were digested with hot 3 M subboiled HNO<sub>3</sub>. After adjusting the pH to 3, square wave voltammetry anodic stripping (SWASV), pre concentrating at -1.20 V vs Ag|AgCl, was applied.

## 2.5. Composition of suspended matter

Samples were centrifuged at 5000 rpm for 60 min, to collect all the remaining material. The resulting powder was dried at  $105 \,^{\circ}$ C for 24 h to assure that water was expelled.

The mineralogical composition of the suspended matter was determined by X-ray diffraction obtained using a Philips 1130 instrument with Cu K<sub> $\alpha$ </sub>, 30 mA and 40 kV.

FTIR spectra were obtained using a Nicolet 510 P FT-IR Spectrometer. The dried powder was used to make a KBr pellet for the FTIR scan. Spectra were collected for 32 scans at a resolution of  $4 \text{ cm}^{-1}$  between 400 and 4000 cm<sup>-1</sup>.

## 2.6. UV-visible spectra

UV–visible absorbance spectra were obtained from Shimadzu UV-240 from 200 to 800 nm. All the collected samples were sonicated for 1 h and divided into three fractions. One fraction was untreated, while the second was adjusted to pH 10 with NaOH solution and left overnight. The third fraction, after the same treatment of the former, was returned to pH of the sample with HCl solution. Each fraction was centrifuged for 60 min at 5000 rpm and the UV– visible spectra of the corresponding solutions were recorded. Blank spectra of the reagents had no contribution of organic compounds.

# 2.7. Reactives

All solutions were made with Milli-Q water and Merck reagents. The nitric acid used was distilled sub-boiling quartz. Cadmium titration solutions  $10^{-4}$  M were prepared from a standard of Cd(II) (concentration  $1000 \pm 2$  mg/l) provided by Merck (Merck Certipure). A Tris buffer was used to keep the titration solutions at natural pH of the sample.

## 2.8. Voltammetric equipment

The voltammetric measurement system includes Princeton Applied Research (PAR) 203A and a PAR303A mercury drop electrode, an Ag/AgCl reference electrode (3.5 M KCl) and a platinum wire counter electrode. Samples contained in a 10 ml PAR voltammetric cell cups were deoxygenated with oxygen free nitrogen.

## 2.9. ASV titrations with metal

Samples were titrated at the original pH and at pH 1 (adding sub-boiling diluted HNO<sub>3</sub>). Cadmium titration solutions were at pH of the samples. For each titration curve, PAR cell was filled with seven milliliters sample (U, C, F) and aliquots of cadmium solution were added to reach concentrations in the range  $10^{-8}$ – $10^{-5}$  M. After an equilibration of 8 min purging with N<sub>2</sub> and stirring, Cd was electrodeposited on a hanging mercury drop electrode at -0.9 V during 60 s. After a 5 s quiescent period, the potential was ramped positive in the square wave mode (25 mV pulse amplitude, 60 Hz frequency). Peak currents of the voltammetric waves were plotted against the total cadmium concentration in the sample in order to obtain the titration curves.

## 3. Results

#### 3.1. Characterization of the samples

Due to the complexity of the aquatic systems, there are diverse definitions of the operational cutoff adopted to discriminate suspended particles and matter in the solution (Turner and Millard, 2002). For the purposes of this paper, colloids and particles are referred to collectively as the suspended particulate matter (SPM) extracted from river water by the centrifugation described in Section 2.3. Consequently, the matter remaining in water after centrifugation will be indicated as soluble fraction or solution.

## 3.1.1. The solution

The major anions were determined by ionic chromatography. The average concentrations of chloride, sulfate and nitrate are 30 mg dm<sup>-3</sup>, 20 mg dm<sup>-3</sup> and 0.3 mg dm<sup>-3</sup>, respectively. The pH of the samples varies between 7.0 and 7.8. Anodic stripping voltammetry showed that the concentrations of electroactive metals, such as  $Cd^{2+}$ ,  $Zn^{2+}$ ,  $Pb^{2+}$ and  $Cu^{2+}$ , are below the detection limit (10<sup>-8</sup> M) for our experimental conditions.

The absorbance at 254 nm, indicative of the content of organic ligands like humic or fulvic acids in the solution (Swift, 1996; Liu and Gonzalez, 1999), does not show significant differences when comparing all the samples.

# 3.1.2. The particulate material

The amount of total suspended solids depends on the hydrodynamic conditions of the estuary at the moment in which the samples were collected. Their limits were between ca.  $100 \text{ mg dm}^{-3}$  for V04 and ca.  $500 \text{ mg dm}^{-3}$  for VS05.

The XRD analysis of the particulate material shows that illite is the dominant clay, but a minor amount of Chlorite is present and discrete presence of montmorillonite is found. Other present minerals include quartz and paglioclase feldspars (Griffin and Depetris, 1968). Several modifications on the composition are observed for the treated samples: the particulate material that remains in suspension after filtering with 0.45 µm pore size filter showed a decrease in the illite proportion. On the other hand, samples obtained under different hydrodynamic conditions also show modifications on the composition: montmorillonite clay mineral proportion is higher for the samples collected during the sudestada phenomenon, in which a great agitation may remove particles from the bed. The infrared spectra from all samples confirmed the presence of the clays and minerals founded with XRD analysis (van der Martel and Beutelspacher, 1976; Hillier, 2001; Post and Borer, 2002).

#### 3.2. Complexing behaviour: titration curves

The complexing capacity of natural waters, due to the dissolved organic ligands and the particles in suspension, was characterized by metal titration (Ruzic, 1982; van den Berg, 1982; Scarponi et al., 1996). Representative titration curves of the samples are shown in Fig. 2. At the pH of the sample, significant deviations from the calibration curves show that all untreated samples have high complexing capacity. As a consequence, the titration had to be done in the micromolar scale. Titration curves curvature indicates that it is possible to determine simultaneously conditional constants and ligands concentrations with an appropriate accuracy (Scarponi et al., 1996). Filtered samples contain colloidal particles and soluble ligands. As expected due to the retention of particles by 0.45 µm filter,



Fig. 2. Representative Cd titration curves of Rio de La Plata samples at natural pH, sampled on: (a) winter, 2003 (I03); (b) winter, sudestada, 2004 (IS04).

their titration curves are indicative of a diminution of the binding capacity when compared with the untreated samples. However, except for V04 samples, they show an important remaining complexing capacity. It is to be remarked that titration curves for all the centrifuged samples lie down on the calibration curve. Titration curves for untreated samples IS04 and V04 at pH 1 and those corresponding to their natural pH are shown in Fig. 3. Comparison of titration curves for both pHs shows that samples at pH 1 have lower complexing capacity than those at natural pH. However, untreated samples at pH 1 still have a remaining capacity to adsorb cadmium.

# 4. Discussion

Apart from a great amount of particulated material, waters of the Rio de La Plata estuary also carry natural and anthropogenic organic ligands. Then a large number of different binding sites may be available for binding metals and distribution values for the conditional binding constants may be expected.



Fig. 3. Comparison between untreated samples at pH 1 and at the pH of the sample: (a) winter, sudestada, 2004 (IS04); (b) summer, 2004 (V04). Calibration curve is also plotted for comparison. C, F and U letters after the sample's names correspond to the centrifuged, filtered and untreated fractions, respectively.

#### 4.1. Equilibriums and displacements

Models of discrete or of continuously changing binding strengths can be used to interpret experimental data (Ruzic, 1996). These models consider that metal ions interact with each kind of surface active sites,  $\equiv S_i$ , or an organic ligand,  $O_j$ , with a binding strength that can be expressed in terms of a conditional stability constant,  $K_{S_i}$  or  $K_{O_i}$ .

The complexation processes taking place during titration with a metal M, Cd(II) in our case, at constant pH related to the particulate material can be described as:

$$\equiv \mathbf{S}_i + \mathbf{M} \rightleftharpoons \equiv \mathbf{S}_i \mathbf{M} \tag{1}$$

while that corresponding to the natural organic ligands can be described as:

$$O_j + M \rightleftharpoons MO_j$$
 (2)

where M is the free trace Cd(II) concentration consisting of labile complexes, and  $\equiv S_iM$  and MO<sub>j</sub> represent a surface and soluble complex, respectively.

This is a simplified vision of a more complex system where organic substances, majority ions and even electroactive trace ions may compete in others adsorption and displacement equilibriums. Organic substances may have a major role in the complexing behaviour, not only because of the process represented by Eq. (2), but also due to their adsorption at the surface of the particles. Consequently the following equilibrium should be taken into account:

$$\mathbf{O}_i + \equiv \mathbf{S}_i \rightleftharpoons \equiv \mathbf{S}_i \mathbf{O}_j \tag{3}$$

where  $\equiv S_i O_j$  are the organic adsorbed species (Stumm, 1992).

Considering that some organic substances, like humic acids, have more than one adsorption site, then, a binary complex may be formed after adding the metal to the solution:

$$\equiv \mathbf{S}_i \mathbf{O}_j + \mathbf{M} \rightleftharpoons \equiv \mathbf{S}_i \mathbf{O}_j \mathbf{M} \tag{4}$$

where  $\equiv S_i O_j M$  are the metal-organic adsorbed complex (Stumm, 1992; Bradl, 2004).

Displacements equilibriums are represented by

$$\equiv \mathbf{S}_i \mathbf{M}_{\mathrm{E}} + \mathbf{M} \rightleftharpoons \equiv \mathbf{S}_i \mathbf{M} + \mathbf{M}_{\mathrm{E}} \tag{5}$$

$$\mathbf{M}_{\mathrm{E}}\mathbf{O}_{j} + \mathbf{M} \rightleftharpoons \mathbf{M}\mathbf{O}_{j} + \mathbf{M}_{\mathrm{E}} \tag{6}$$

$$\equiv \mathbf{S}_i \mathbf{O}_j + \mathbf{M} \rightleftharpoons \equiv \mathbf{S}_i \mathbf{M} + \mathbf{O}_j \tag{7}$$

where  $M_E$  is a majority ion or an electroactive trace ion.

Equilibriums 1, 2, 5 and 6 may be described using the apparent binding constants at constant solution composition:

$$K_{\mathbf{S}_i} = \frac{[\mathbf{MS}_i]}{[\mathbf{M}][\mathbf{S}_i]} \tag{8a}$$

and

$$K_{\mathbf{O}_j} = \frac{[\mathbf{M}\mathbf{O}_j]}{[\mathbf{M}][\mathbf{O}_j]} \tag{8b}$$

The mass balances for Cd(II) and ligands are:

$$M_{\mathrm{T}} = [\mathbf{M}] + \sum_{i} [\equiv S_{i}\mathbf{M}] + \sum_{j} [\mathbf{M}\mathbf{O}_{j}] + \sum_{i,j} [\equiv S_{i}\mathbf{O}_{j}\mathbf{M}] \quad (9a)$$
$$S_{\mathrm{T}} = \sum_{i} [\equiv S_{i}] + \sum_{i} [\equiv S_{i}\mathbf{M}] + \sum_{i,j} [\equiv S_{i}\mathbf{O}_{j}\mathbf{M}] + \sum_{i,j} [\equiv S_{i}\mathbf{O}_{j}]$$

$$\mathbf{O}_{\mathrm{T}} = \sum_{j} [\mathbf{O}_{j}] + \sum_{j} [\mathbf{M}\mathbf{O}_{j}] + \sum_{j,i} [\equiv \mathbf{S}_{i}\mathbf{O}_{j}\mathbf{M}] + \sum_{i,j} [\equiv \mathbf{S}_{i}\mathbf{O}_{j}]$$
(9c)

where  $M_T$  is total metal concentration,  $S_T$  the total amount of binding sites per dm<sup>3</sup> and  $O_T$  is the concentration of total organic ligands.

Finally, the binding capacity due to all the different kinds of ligands present in the aquatic system is given by considering the six different terms in Eqs. (9b) and (9c).

The relative weight of each term of Eqs. (9) can only be obtained from the experimental results.

## 4.2. Contribution of the organic matter

Titrations curves of centrifuged fraction (solution) are coincident with calibration curve in the micromolar scale. As a consequence the contribution of the soluble organic ligands,  $L_T$ , may be neglected even though natural organic matter is present. The speciation of Cd(II) by these compounds should be studied at nanomolar scale.

In order to investigate whether humic acids are adsorbed at the particles surface, UV–visible spectra of the centrifuged of the untreated sample and ASO (kept overnight at pH 10) samples were compared. No differences between them were observed. The same result is observed if the pH of centrifuged ASO is returned to 7. Considering that at pH 10, humic acids should desorb from the surface particles and remain in the solution (Swift, 1996; Liu and Gonzalez, 1999), the previous results indicate that desorption of humic acids from the particulate material, if any, is negligible. Even more, the coincidence between titration curves of centrifuged ASO returned to pH 7 and the calibration curve points to the same conclusion.

The previous analysis indicates that the contribution of  $O_T$  may also be neglected in our working scale ( $\mu$ M). Thus, the complexing capacity of the studied waters is determined by the surface binding sites of the suspended particulate material.

## 4.3. Contribution of the particulate matter

Under the previous considerations, the relationship between  $M_T$  and (M) is obtained by combining Eqs. (8) and (9):

$$\mathbf{M}_{\mathrm{T}} = [\mathbf{M}] + \sum_{i} \frac{K_{i}[\equiv \mathbf{S}_{i}]_{\mathrm{t}}[\mathbf{M}]}{1 + K_{i}[\mathbf{M}]}$$
(10)

where  $[= S_i]_t$  represents the total binding site concentration of a site *i*.

In order to determine the heterogeneity of the binding sites and consequently the number of constants relevant to characterize the titration curves, we have used the Scatchard transformation (Scatchard, 1949), i.e., the representation of  $(M_T - [M])/[M]$  as a function of  $\sum_i [\equiv S_i M]$ :

$$\frac{\mathbf{M}_{\mathrm{T}} - [\mathbf{M}]}{[\mathbf{M}]} = \sum_{i} K_{i} ([\equiv \mathbf{S}_{i}]_{\mathrm{t}} - [\equiv \mathbf{S}_{i}\mathbf{M}])$$
(11)

This transformation applied to untreated and filtered I03, IS04 and VS05 titration data yields plots with two apparent linear regions (see the inset of Fig. 3). Even though distribution values for the apparent constants could be necessary to describe natural waters, Scatchard representation suggests that it is possible to describe the complexing behaviour of our system assuming the presence of two kinds of ligands or surface binding sites,  $[=S_1]$  and  $[=S_2]$  (Mantoura and Riley, 1975; Kozelka and Bruland, 1998). The binding constants could be quantified from the slopes of this representation, however it is difficult to

accurately assess the binding parameters from experimental results since they are obtained by extrapolating to  $M_T = 0$ . Binding constants could also be quantified using Ruzic representation for two ligands (Ruzic, 1996):

$$\frac{[\mathbf{M}]}{\mathbf{M}_{\mathrm{T}} - [\mathbf{M}]} = \frac{1 + (K_2 + K_1)[\mathbf{M}] + K_1 K_2 [\mathbf{M}]^2}{K_1 [\equiv \mathbf{S}_1]_t + K_2 [\equiv \mathbf{S}_2]_t + K_2 K_1 ([\equiv \mathbf{S}_1]_t + [\equiv \mathbf{S}_2]_t) [\mathbf{M}]}$$
(12)

When the labile metal concentration, (M), is high enough, Eq. (12) may be rewritten as the van den Berg approach:

$$\left(\frac{[\mathbf{M}]}{\mathbf{M}_{\mathrm{T}} - [\mathbf{M}]}\right)_{[\mathbf{M}] \to \infty} = \frac{[\Xi \mathbf{S}_{2}]_{\mathrm{t}}}{K_{2}([\Xi \mathbf{S}_{1}]_{\mathrm{t}} + [\Xi \mathbf{S}_{2}]_{\mathrm{t}})^{2}} + \frac{[\mathbf{M}]}{[\Xi \mathbf{S}_{1}]_{\mathrm{t}} + [\Xi \mathbf{S}_{2}]_{\mathrm{t}}}$$
(13)

Then  $S_T = [\blacksquare S_1]_t + [\blacksquare S_2]_t$  may be obtained from the slope of the asymptotic straight line to the extreme experimental points ( $[M] \rightarrow \infty$ ) in this Ruzic/ van den Berg representation. However, results depend on the reliability of  $[M] \rightarrow \infty$  condition (Ruzic, 1982; Scarponi et al., 1996). At the pH of the sample, titration curves cannot reach high [M] values because of the precipitation of cadmium hydroxide compounds, not only in the solution but even at the surface particles (Echeverria et al., 2002). Consequently, Ruzic representation yields a higher slope than that corresponding to the limit condition  $[M] \rightarrow \infty$ , underestimating  $S_T$ .

Even though the representations analyzed above are not appropriate to obtain conditional constants and the total concentration of binding sites of our system, it becomes clear that two binding sites are necessary and sufficient to describe it. In other words, it is necessary to obtain two conditional binding constants,  $K_1$  and  $K_2$ , and the total concentration of the two binding sites,  $[=]S_1]_t$  and  $[=]S_2]_t$ . These four parameters can be obtained rearranging Eq. (10) to obtain

$$\frac{[\mathbf{M}]_{t} - [\mathbf{M}]}{[\mathbf{M}]} = \frac{K_{1}[\Xi\mathbf{S}_{1}]_{t}}{1 + K_{1}[\mathbf{M}]} + \frac{K_{2}[\Xi\mathbf{S}_{2}]_{t}}{1 + K_{2}[\mathbf{M}]}$$
(14)

and applying a multivariable regression. M concentration is obtained from titration curve and no other assumption is made afterward.

The best fit of Eq. (14) is shown in Fig. 4. The corresponding conditional constants and  $[=]S_1]_t$ ,  $[=]S_2]_t$  and  $S_T$  values are given in Table 1. These values were also tested fitting Ruzic–van den Berg and Scratchard representations (insets of Fig. 4), and the titration curves (Figs. 2 and 3).

The comparison of  $S_T$  values for different samples shows that hydrodynamic conditions determine the amount of SPM. This is an expected result because water agitation removes particles from the bed. Thus  $S_T$  value for quiet water (V04U) is lower than that obtained for "sudestada" phenomenon (IS04U and VS05U). I03U sample, also collected under quiet conditions, seems not to follow this trend; in fact its  $S_T$  value is as high as IS04U  $S_T$  value. The reason for this fact is that I03U sample was collected after a flood of the Salado river, an important affluent of Y.S. Minaberry, G.J. Gordillo / Chemosphere 69 (2007) 1465-1473



Fig. 4. Examples of multivariable regression plot of Cd titration data. The ratio of  $[\equiv$ SCd] to [Cd] is plotted versus [Cd]. Rio de la Plata water sampled on winter sudestada, 2004 IS04: (a) untreated fraction, U. (b) Filtered fraction, F. Upper inserted graph: Scatchard transformation; the ratio  $[\equiv$ SCd] to [Cd] is plotted versus  $[\equiv$ SCd]. Lower inserted graph: Ruzic–van den Berg transformation; the ratio of [Cd] to  $[\equiv$ SCd].

the Paraná river, that carries clays from the northwest mountains of the Andes.

The comparison of  $S_T$  for untreated and filtered samples indicates that small particles are the major contributor to the complexing capacity, due to the increment of the area–volume ratio when the particle size diminishes.

X-ray results show that the proportion of illite and montmorillionite in the SPM depends on hydrodynamic collection conditions. However, it is remarkable that conditional binding constants remain nearly the same.

Our results are congruent with proposed mechanisms for the adsorption on Cd(II) in the different clays present in the particulate material. Outer and inner sphere coordination complexes have been proposed for illite (Lackovic et al., 2003) and montmorillonite (Barbier et al., 2000) from the results of adsorption isotherms at the pH of the samples. Inner sphere coordination complexes ( $\equiv$ S– O–CdOH<sub>2</sub><sup>+</sup>) have higher binding constant values, in our case pK<sub>1</sub>  $\approx$  6.5 (at the pH and ionic strength of the sample). They are involved in the equilibrium between surface hydroxyl groups ( $\equiv$ S–OH) and the metal (Lackovic et al., 2003, 2004), that depending on the clay surface composition and the pH of the solution may be described as:

$$\equiv S-OH + Cd^{2+} \rightleftharpoons \equiv S-O-Cd^{+} + H^{+}$$
(15)

or

$$\equiv S - O^{-} + Cd^{2+} \rightleftharpoons \equiv S - O - Cd^{+}$$
(16)

Other sites, dominant in illite-montmorillinite speciation diagrams, are related to outer sphere coordination complex. This complex is originated by binding Cd(II) at surface hydroxyl groups

$$\equiv S-OH + Cd^{2+} \rightleftharpoons \equiv S-O-H \cdots Cd^{2+}$$
(17)

or at permanent negatively charged sites

$$2X^{-} + Cd^{2+} \rightleftharpoons X_{2}^{2-} - Cd^{2+}$$
(18)

where X represents a permanent negatively charged site on the crystal face resulting from an isomorphous substitution (Bradl, 2004). They correspond to a labile binding site with the lower apparent binding constant, in our case  $pK_2 \approx 4.5$ .

We can describe the contribution of these sites to the binding capacity  $[=]S_2]_t$ , using only one apparent binding constant. The main reason for this is found in the speciation diagrams; they show that at the pH of the sample the concentration of =SOH sites is about 30 times lower than the concentration of X<sup>-</sup> related species (Barbier et al., 2000).

Speciation diagrams for Cd(II)–illite (Lackovic et al., 2003) and Cd(II)–montmorillinite (Barbier et al., 2000) show that, at the sample pH, the concentration of the inner sphere coordination complexes is very low in comparison to that of outer sphere coordination complexes. In fact, the reported proportion in this case is ca. 1–200. Thus, in concordance with what we report, the contribution of the inner sphere coordination complexes to the total binding capacity  $S_T$  is quite low.

At pH 1, only one binding site is observed for the untreated samples (Fig. 5). Binding capacities and apparent constants are reported in Table 1.

It has been reported that at pH values lower than 3, surface hydroxyl groups protonated at low pH ( $\equiv$ S-OH<sub>2</sub><sup>+</sup>) are not able to bind cadmium. Then, only X sites are available to form outer sphere complexes, X<sub>2</sub><sup>2-</sup>-Cd<sup>2+</sup>(Lothenbach et al., 1999; Barbier et al., 2000; Echeverria et al., 2002; Lackovic et al., 2003, 2004). The diminution of the binding capacity in acidic condition has been attributed to the protonation of these sites. Our results are in accordance with the reported trend. However, it is striking that the binding capacity is still within the micromolar scale.

The conditional stability constant obtained at pH 1 is higher than that obtained for outer sphere complexes at the pH of the natural water. It is to be remarked that both conditional constants are not comparable since the ionic strength and composition of the aqueous solution are drastically changed when pH is adjusted to 1 with HNO<sub>3</sub>. The new conditional stability constant value may be attributed

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Table 1

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		pH of the sample					pH 1	
		$Log K_1^{g}$	$[\equiv S_1]^g$	$\log K_2^{g}$	$[\equiv S_2]^g$	$S_T^g$	$Log K_1^g$	$S_T^g$
I03 <sup>a</sup>	U <sup>e</sup> F <sup>f</sup>	$\begin{array}{c} 6.2\pm0.3\\ 6.3\pm0.3\end{array}$	$\begin{array}{c} 0.6\pm0.1\\ 0.3\pm0.1 \end{array}$	$\begin{array}{c} 4.16\pm0.05\\ 4.2\pm0.1\end{array}$	$\begin{array}{c} 11.7 \pm 0.3 \\ 10.3 \pm 0.9 \end{array}$	$\begin{array}{c} 12\pm0.4\\ 11\pm1 \end{array}$	5.1 ± 0.4 -	9.0 ± 0.1 -
V04 <sup>b</sup>	U F	$6.8\pm0.2$	$\begin{array}{c} 0.96 \pm 0.05 \\ \mathrm{CC^{h}} \end{array}$	$4.2\pm0.1$	$\begin{array}{c} 3.0\pm0.7\\ \mathrm{CC^{h}} \end{array}$	$4\pm0.8$	$5.73\pm0.06$	$\begin{array}{c} 1.35\pm0.05\\-\end{array}$
IS04 <sup>c</sup>	U F	$\begin{array}{c} 6.2\pm0.1\\ 6.7\pm0.2\end{array}$	$\begin{array}{c} 1.5\pm0.3\\ 0.10\pm0.05\end{array}$	$\begin{array}{c} 4.63\pm0.08\\ 4.60\pm0.05\end{array}$	$\begin{array}{c} 8.8\pm0.2\\ 5.3\pm0.2\end{array}$	$\begin{array}{c} 10.3\pm0.5\\ 5.4\pm0.3\end{array}$	$5.62\pm0.09$	$\begin{array}{c} 0.6\pm0.3\\-\end{array}$
VS05 <sup>d</sup>	U F	$\begin{array}{c} 7.2\pm0.4\\ 7.2\pm0.4\end{array}$	$\begin{array}{c} 0.63 \pm 0.05 \\ 0.31 \pm 0.05 \end{array}$	$\begin{array}{c} 4.5\pm0.05\\ 4.9\pm0.05\end{array}$	$\begin{array}{c} 28.3\pm0.9\\ 23.9\pm0.9\end{array}$	$\begin{array}{c} 29.6\pm1\\ 24.2\pm1\end{array}$	$\begin{array}{c} 6.00\pm0.05\\-\end{array}$	$\begin{array}{c} 1.22\pm0.05\\-\end{array}$

Binding site concentration and conditional stability constant from multivariable regression of Rio de La Plata samples

<sup>a</sup> I03: winter, 2003.

<sup>b</sup> V04: summer, 2004.

<sup>c</sup> IS04: winter, sudestada, 2004.

<sup>d</sup> VS05: summer, sudestada, 2005.

<sup>e</sup> U: untreated.

<sup>f</sup> F: filtered.

 $^{g}$  Concentration of Binding sites ( $\equiv$ S<sub>1</sub>,  $\equiv$ S<sub>2</sub> and S<sub>T</sub>), in  $\mu$ M scale, and conditional stability constants, and their respective standard deviation, determined by multivariable regression.

<sup>h</sup> CC: Titration points lie on the calibration curve.



Fig. 5. Ruzic-van den Berg linearization of Cd titration curves at pH 1 of Rio de la Plata waters sampled on summer, 2004 (V04) and winter, sudestada, 2004 (IS04).

to a modification of the surface composition. Acid treatments of clay minerals can often replace exchangeable cations with protons and release cations out of both tetrahedral and octahedral sites, but leaving the silicate groups largely intact (Beena et al., 2006; Bhattacharyya and Susmita, 2006).

# 5. Conclusions

As far as we know, this work is the first study about the complexing capacity of an aquatic system carrying a great amount of naturally suspended particulate matter.

In the present work, we have identified the most relevant complexing agents that happen to be the constitutive clays of the suspended particulate matter, while the contribution of organic ligands turns out to be negligible. At natural pH, the complexing capacity can be described by considering a minimum of two kinds of binding sites. Conditional binding constants for active surface sites have shown to be consistent with those reported for individual purified clays in model systems. Analysis of samples collected over a three year period has shown practically the same conditional binding constants even though hydrodynamic conditions and temperatures were different.

This study indicates that in the case of rivers with high concentration of particulate suspended matter, the former may play a major role in complexing metals, reducing their bioavailability and contributing to their transport and auto-depuration of the natural water.

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