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Surface properties of sediments from two Argentinean reservoirs and the rate of phosphate release

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ABSTRACT

This article reports the surface properties (electrophoretic mobility, surface charge and specific surface area (SSA)), and phosphate release rates of sediments from two Argentinean reservoirs. Even though sediments are a heterogeneous mixture of minerals with different charging behavior, electrophoresis reveals that all sediment particles are negatively charged in the pH range 3–9. Iron and aluminum oxides, which usually carry a net positive charge at low pH, seem to be forming aggregates with negatively charged minerals and/or carrying a net negative charge due to the presence of organic matter. The phosphate release rate increased by increasing pH and temperature, and depended linearly on the SSA of the sediments. These data, together with the high activation energy of the process, indicate that the rate-controlling process is a chemical reaction occurring at the solid–water interface, and not a diffusion process. The rate-controlling step seems to be the breaking of bonds between phosphate and surface groups, breaking that should be preceded by one or more deprotonation steps at the surface and favored by electrostatic repulsion between the negative charge surface and the phosphate anion.

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1. Introduction

The kinetics of phosphate release from lake sediments is a subject of increasing environmental interest. This kinetic information is required to properly characterize the phosphate supplying capacity of sediments and to develop management strategies aiming to control the eutrophic state of lakes and reservoirs. The research is usually focused on determining the factors that affect the rate of phosphate release (Koski-Vähälä et al., 2001; Kim et al., 2003; Jin et al., 2006). One of these factors is pH. Sediments where an important fraction of phosphate occurs adsorbed at the surface of metal oxides or other minerals usually show a relatively slow release in near neutral or weakly acidic media and a relatively fast release in alkaline media (Koski-Vähälä et al., 2001; Jin et al., 2006). These effects are attributed to the decreasing affinity that mineral surfaces, especially those of Fe and Al oxides, show for phosphate when the pH is increased, and to competition between hydroxyl and phosphate ions for surface sites (Lijklema, 1980; Koski-Vähälä et al., 2001; Jin et al., 2006). On the other hand, sediments where an important fraction of phosphate occurs as calcium phosphate minerals may also show an important and fast phosphate release at low pH, where these minerals preferentially dissolve (Jin et al., 2006; Golterman, 1995).

Another factor affecting the rate of phosphate release is temperature. Although very little information is available in this respect, there is experimental evidence indicating that the rate increases by increasing temperature (Holdren and Armstrong, 1980; Kim et al., 2003). This effect is easily understood in terms

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of Arrhenius-type expressions, since an activation energy (E_a) barrier needs to be overcome during the release process. The magnitude of E_a, besides providing the temperature dependence of the reaction rate, often gives relevant information regarding the mechanism of the process (Lasaga, 1997; Sparks, 2003). Although activation energies for phosphate release have been reported in the case of soils (Agbenin and van Raij, 2001), it seems that they never have been analyzed in the case of lake sediments. Other studied factors that are often considered in phosphate release studies are: dissolved oxygen concentration (Kim et al., 2003), presence of ligands competing for phosphate adsorption sites (Koski-Vähälä et al., 2001), presence of metal ions (Hansen et al., 2003) and particle size (Selig, 2003).

Besides all the mentioned factors, surface properties of sediment particles, such as surface charge density and specific surface area (SSA), can be also of significant importance for the rate of phosphate release. This is especially true for sediments where an important fraction of the total phosphate occurs at the surface of mineral particles. Surprisingly, whereas surface charge and surface area are parameters commonly considered to analyze the adsorption–desorption properties of soil materials (Sparks, 2003; Agbenin and van Raij, 2001), they were seldom considered and analyzed in the case of natural aquatic sediments (Wang et al., 1997; Ferreira et al., 1997). Changes in surface charge, for example, may be mentioned in some articles as the responsible for the changes in the release rates, but no direct measurements of this charge have been reported. In addition, in the few articles where surface charge of sediment particles was investigated, no data on phosphate release rates were reported (Wang et al., 1997; Ferreira et al., 1997). These examples indicate that research is still needed in order to evaluate the effects of surface charge on the release rate.

In this article, the surface properties of sediments from the Los Molinos and San Roque reservoirs (Argentina) are investigated. Surface charge and electrophoretic mobility data as a function of pH, phosphate release rates as a function of pH and temperature, and SSA data are reported. The aim is twofold: (i) to investigate the effects of the studied surface properties on the rate of phosphate release in order to get insights into the release mechanism, and (ii) to provide information on the behavior of sediments from South American reservoirs, from which very scarce data is available in the international literature.

2. Materials and methods

Sediment samples were collected from the Los Molinos and San Roque reservoirs, province of Córdoba (center of Argentina). Both reservoirs are used to supply drinking water to approximately 1.5 millions inhabitants. The general characteristics of the reservoirs, their basins and tributaries were given elsewhere (Borgnino et al., 2006). Los Molinos is a mesotrophic–eutrophic reservoir covering a surface of 2110 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 1501 ha, a maximum length (north–south) of 8.4 km and a maximum depth of around 30 m in regions near the dam.

Three sampling sites were selected in each reservoir. They were chosen in order to sample representative areas of the center, mouth of main tributaries and zone close to the dam. Therefore, the identifying acronyms of the three samples obtained in 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 plastic flasks and cooled to 5 °C. Samples were then dried in air and gently ground in a mortar.

Several relevant parameters that characterize the sediments, which were already reported and analyzed in a previous article (Borgnino et al., 2006), are given in Table 1, together with the different phosphate fractions, as determined by the EDTA sequential extraction method proposed by Golterman (1995). Most of the total phosphate in the sediments occurs as inorganic phosphate, represented by Fe-bound phosphate and as Ca-bound phosphate ($Fe(OOH)\approx P$ and $CaCO_3\approx P$, respectively, in Golterman's nomenclature). $Fe(OOH)\approx P$ corresponds to phosphate bound not only to Fe(OOH) but also to other iron oxides, aluminum oxides and perhaps other metal oxides. $CaCO_3\approx P$ corresponds to phosphate forming part of not only calcite particles but also other Ca–P-bearing minerals such as apatite, dicalcium phosphate, etc. (Borgnino et al., 2006). An important conclusion of the study of Borgnino et al. (2006) is that $CaCO_3\approx P$ is mainly

Table 1 – Some properties of the studied sediment samples

Station	Granulometry	SSA ($m^2\,g^{-1}$)	pH	Total phosphorus ($mg\,kg^{-1}$)	$Fe(OOH)\approx P$ ($mg\,kg^{-1}$)	$(CaCO_3)\approx P$ ($mg\,kg^{-1}$)	Organic matter (%)
LMD	Clay–silt	207	5.7	845	415	132	14
LMC	Clay–silt	182	6.1	777	402	139	14
LMT	Sand	54	6.2	327	43	206	7
SRD	Clay–silt	247	6.1	994	551	202	15
SRC	Clay–Silt	240	6.2	911	540	164	15
SRT	Sand–Silt	59	6.5	670	112	359	9

located within the bulk of grains or particles highly concentrated in Ca and P (mainly apatite), whereas Fe(OOH)≈P is rather homogeneously distributed in the sediments, at the particles' surface.

The SSA was measured by methylene blue adsorption. A complete description of the method and a critical analysis of it is given by Avena et al. (2001).

Surface charge was determined by acid–base potentiometric titrations at three different salt concentrations (0.001, 0.01 and 0.1 M NaCl). The method is similar to that used previously with clay minerals (Avena and De Pauli, 1998). Titrations (25 °C, under N_2 bubbling) were performed from pH around 6 to pH 10 with a standard NaOH solution, and then, to check reversibility, from pH 10 to 4 with a standard HCl solution. Once the dispersion was at this pH, 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 vs. pH curves (Sposito, 2004; Avena, 2002). Some additional titrations were performed in the opposite way, i.e. from pH around 6 to 4 with HCl and then from pH 4 to 10 with NaOH in order to check reversibility.

Electrophoretic mobilities (μ) were measured with a Rank Brothers Mark II instrument equipped with a 2 mm cylindrical cell. A very diluted (opalescent) dispersion was prepared by placing a small amount of solid in 200 mL of a 0.01 M NaCl solution. The dispersion pH was then adjusted in the range 3–9 with small drops of HCl and/or NaOH and μ was measured. The reported μ values are the average of 20 readings in most cases, and the average of 120 readings in some special cases. In these last cases, the data were also used to construct frequency distribution histograms.

For phosphate release studies, 100 mL of a 0.001 M NaCl solution were placed in a glass reaction vessel and its pH was adjusted to the desired value. Around 5 g of dry sediment were then added and the pH was readjusted if necessary. The resulting dispersion was maintained under continuous stirring. After certain selected times, aliquots of the dispersion were withdrawn, filtered through a 0.45 μm-pore filter, centrifuged at 5000 rpm, and the supernatants analyzed for phosphate content by the ascorbic acid method (Murphy and Riley, 1962). Release curves were then constructed by plotting the amount of phosphate released (P_{rel}) as a function of reaction time. Special care was taken in keeping constant temperature (~0.2 °C) and constant pH (~0.2 pH units) in the experiments. A gentle N_2 bubbling was also maintained in order to avoid significant contamination with atmospheric CO_2. This bubbling, however, did not create anoxic conditions that could lead to reduction of iron oxides during the few hours that the experiments lasted.

The kinetics of release processes are usually described as a series of first-order reactions (Lookman et al., 1995). These different processes result supposedly from the heterogeneity of soil or sediments samples, where phosphate can be present in different "pools" with different reactivity. Our release data could be well described using two pools: a pool with very fast release kinetics and a pool with slower release kinetics. Therefore, release data, as a function of time, were interpreted using the following equation:

$$P_{rel} = P_1 + P_2(1 - e^{-k_2 t}), \quad (1)$$

where P_{rel} represents the amount of phosphate released at the time t, P_1 and P_2 are two constants representing supposedly the amounts of phosphate present in pools 1 and 2, respectively, and k_2 is a rate constant. It is necessary to remark that a kinetic model such as the represented by Eq. (1) assumes that the system is far from equilibrium and that no backward reaction (i.e., readsorption or reprecipitation) takes place during the experiments. These backward reactions are likely to take place in long-term experiments, affecting long-term data and the value of P_2, which are sensitive to these data. Therefore, the value of P_2 should not be taken as indicative of a particular phosphate pool in the solid. Its value is just used here to obtain a good data fit with Eq. (1), procedure that makes it possible to accurately quantify the initial release rate (R_0). Procedures that allow to assign the value of P_2 to a particular phosphate pool were discussed and applied by Lookman et al. (1995). However, as these authors state, such procedures are not valid to estimate the initial release rate, which is one of the main aims of this article. R_0 is defined as the release rate at $t = 0$, and can be known by differentiating Eq. (1) and evaluating the resulting derivative at $t = 0$, which gives

$$R_0 = \left(\frac{dP_{rel}}{dt}\right)_{t=0} = k_2 P_2. \quad (2)$$

Apparent activation energies (E_{app}) were estimated by performing release experiments at 15, 25, 32 and 40 °C at pH 9 and 7, and using Arrhenius equation

$$R_0 = A \exp(-E_{app}/RT), \quad (3)$$

where A is the Arrhenius preexponential term.

3. Results and discussion

Although the most common method to measure the SSA of solids is N_2 adsorption, it measures the SSA of the solid–gas interface and cannot measure the internal area of expandable phyllosilicates clays such as smectites (Fontes and Weed, 1996; Sparks, 2003). For materials such as lake sediments, which are immersed in water, the methylene blue adsorption method is more suitable because it measures directly the area of the solid–water interface, even the internal area of expandable clays. In this sense, SSA values obtained by methylene blue adsorption are very similar to those obtained by adsorption of polar molecules such as ethylene glycol monoethyl ether (Avena et al., 2001). SSA values of the studied sediments are given in Table 1. Values range from 54 to 240 $m^2 g^{-1}$, and vary considerably depending on the sediment location. This variation is mainly the result of different

granulometries and clay contents. Samples taken from river mouths, which are formed by coarse-grained particles with a low clay content, have the lowest SSA (Table 1). Samples taken from the center of the reservoirs or from areas close to the dam, which are formed by fine-grained material with a higher clay content, have the highest SSA.

Table 1 indicates that there is a very good correlation between Fe(OOH)≈P and SSA. Indeed, a Fe(OOH)≈P vs. SSA plot (not shown) gives a straight line with $R^2 = 0.97$ and a slope of $2.15 \times 10^{-3}\,mg\,m^{-2}$. This good correlation is in agreement with the fact that Fe(OOH)≈P is mainly adsorbed at the surface of sediment particles (Borgnino et al., 2006), and suggests that in average the concentration of Fe(OOH)≈P at the surface of the studied sediments is $2.15 \times 10^{-3}\,mg\,m^{-2}$. A good linearity was also found in a plot organic matter vs. SSA (slope $3.85 \times 10^{-4}\,gm^{-2}$, $R^2 = 0.95$) suggesting that organic matter is mainly adsorbed at the particles surface.

Fig. 1 shows the electrophoretic mobility of sediment particles obtained in the SRD station, and exemplifies the behavior of all the studied sediments. The frequency histogram corresponds to measurements performed at pH 5. The mobility of the sediment particles ranges between −1.5 and $-5.5\,\mu m\,cm\,V^{-1}\,s^{-1}$, with a peak between −2 and $-3\,\mu m\,cm\,V^{-1}\,s^{-1}$. It is interesting to observe that all sediment particles have negative mobilities, in spite of the fact that the solid phase of sediments is a heterogeneous mix of phyllosilicate clays, metal oxides, other minerals such as carbonates, sulfates, etc., and organic matter, each one with its own charging behavior. This high heterogeneity in composition does not seem to be reflected in the histogram. In fact, even though pure aluminum and iron oxides are positively charged at pH 5 (Sparks, 2003) and are important constituent of sediments, no particles with a net positive charge were detected at this pH. This relatively low heterogeneity in μ values may be the result of one or both of the following two facts: (i) each sediment "particle" observed in electrophoresis experiments is actually an aggregate of different minerals that carries a net negative charge, and (ii) iron and aluminum oxides particles are negatively charged because of the presence of organic matter (Table 1), such as humic substances at their surfaces, which are known to induce a net negative charge to mineral surfaces even at very low concentrations (Tipping and Cooke, 1982).

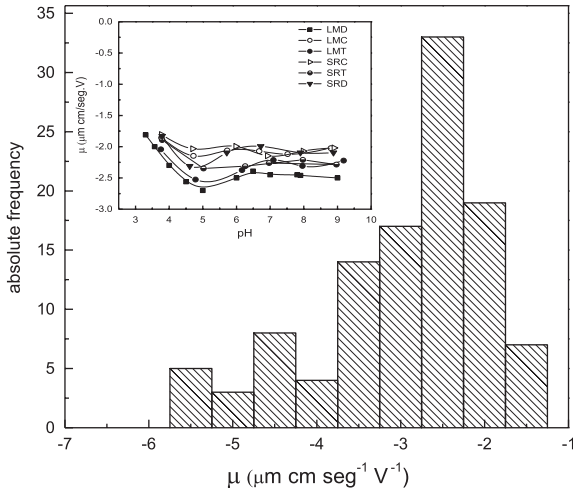

Fig. 1 – Electrophoretic mobilities of the studied sediment particles. The frequency histogram shows data performed to sample SRD at pH 5 in 0.01 M NaCl. The inset shows μ vs. pH curves for all the studied samples.

The inset of Fig. 1 shows the μ vs. pH curves for all the studied samples. The mobility is negative in the pH range 3–9, indicating that all sediment "particles" have a net negative charge in this pH range. This behavior appears to be common for particles in aquatic systems (Ferreira et al., 1997). It is also interesting to note a slight but consistent decrease in the negative mobility at pH above 5 for most samples. This is an unusual behavior when compared to that of metal oxides with a pH-dependent surface charge. In these oxides the electrophoresis vs. pH curves are rather flat at pH values that are 2 or 3 pH units above the isoelectric point (Sparks, 2003) but they do not show a decrease in the negative mobility. The slight decrease seen in Fig. 1 may be due to some phosphate desorption, which does take place at pH above 6 (see below), and perhaps to some desorption of adsorbed organic matter.

Acid–base potentiometric titrations are usually performed on minerals, synthetic materials and soils in order to quantify the charges that the solid surface develops at different pH and to evaluate the PZC. The PZC corresponds (or is close) to the pH where titrations curves performed at different electrolyte concentrations intersect (Sparks, 2003). No intersection point was found in any case, indicating that the PZC of the sediments is outside the investigated pH range 4–9. Salt additions at pH 4 showed that the pH decreased after increasing NaCl concentration, suggesting that the PZC of the samples is below this pH value, and that sediments carry a net negative charge in the pH range investigated, in agreement with electrophoresis and with previously reported data for river sediments (Wang et al., 1997). The results indicate that the net charge of the studied sediments is controlled by the presence of negatively charged minerals such as SiO_2 or smectites. These last minerals usually carry a great deal of negative structural charges, which are independent of pH. Therefore, it is possible that a very important fraction of the sediment charge arises from structural charges in smectites. As a result, potentiometric titrations are giving information about the variable-charge component of the sediments, but cannot evaluate their total net charge. The presence of an important fraction of structural charges in the sediments may also contribute to the flatness of the μ vs. pH curves shown in Fig. 1.

Since no PZC could be detected with acid–base potentiometric titrations, only relative data can be analyzed. Fig. 2 shows relative charge vs. pH curves obtained in 0.01 M NaCl solution for all studied samples. The curves were arbitrarily set so that the relative charge is zero at pH 4. The variable-charge component of all samples show a similar behavior, increasing the negative charge as the pH increases. Actually, in a per gram basis, samples from central areas or regions near the dam have much higher proton or hydroxyl consumptions than samples from the river mouths. However, since the former have SSA that are much higher than the latter, all relative surface charge vs. pH curves become nearly coincident in a per area basis. This interesting result indicates

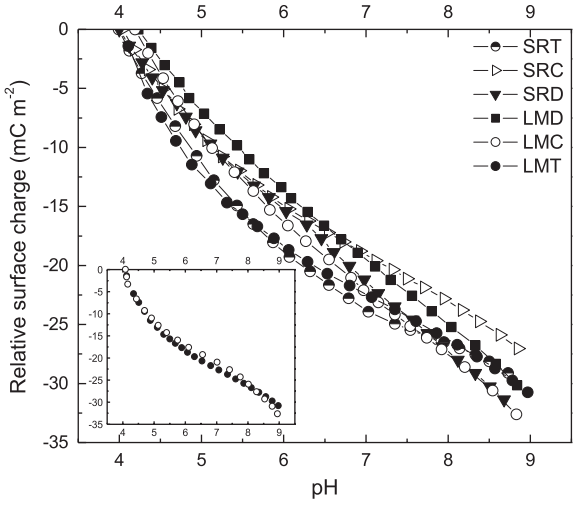

Fig. 2 – Relative surface charge vs. pH curves obtained in 0.01 M NaCl. The inset shows two titrations performed to sample LMT to check reversibility. Solid symbols, titration from pH 9 to 4. Open symbols, titration from pH 4 to 9.

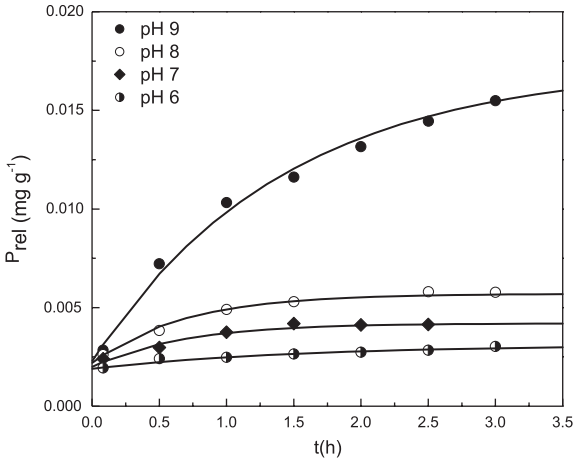

Fig. 3 – P_{rel} vs. t curves at different pH values for sample SRD. Symbols: experimental data; lines: predictions of Eq. (1) with parameters in Table 2.

that the reactivity of surface groups toward proton or hydroxyl consumption is very similar in all sediments, irrespective of the granulometry and the SSA value. Moreover, derivative of the surface charge vs. pH curves (not shown here) were all similar giving a broad band with a maximum at pH around 7, indicating that apparent protonation constants are similar in all cases.

It must be noted that titration curves of a very complex mixture of minerals and organic matter such as a lake sediment may be affected by dissolution of one or more of its constituents. Dissolution of small carbonate or apatite contents would surely affect the titration results and data analysis. However, titration curves were rather reversible in the studied pH range (see Fig. 2), suggesting that no significant dissolution of carbonate and/or apatite took place. Moreover, if important carbonate or apatite dissolution had occurred at low pH (below pH 5 for example), an important and unusual proton consumption would have been detected in the titration curves, fact that is not observed in Fig. 2.

Fig. 3 shows the release of phosphate as a function of time at different pH for sample SRD. All curves start with phosphate released values of around $0.002\,mg\,g^{-1}$. This means that this amount of phosphate is quickly released to the solution and is independent on the pH. This phosphate is believed to represent a pool of soluble phosphate salts that are not interacting with mineral particles of sediments, thus it rapidly dissolves once the solid is placed in contact with the aqueous solutions. After this initial process, phosphate is released at a lower rate, which depends on pH. The experimental results could be well fitted with Eq. (1); examples of this fit are given by lines in the figure and the corresponding parameters in Table 2. Although not shown here, all the studied sediments showed the same kind of behavior, with an increased release rate as the pH increased. The results for all samples at all pH are resumed by their respective fitting parameters in Table 2. Except for sample LMD that shows a significant variability in the value of P_1, the value of this parameter oscillate randomly with pH for each sample, and thus it seems to represent the mentioned pool of rapidly dissolved phosphate. The values of P_2 and k_2 are more difficult to analyze. Even though P_2 clearly increases as the pH increases in all the studied samples, its value cannot be taken as indicative of a particular phosphate pool as stressed above. In spite of this, the sum P_1+P_2 represents the total phosphate released at long times (see Eq. (1)). It could then be interpreted as an apparent equilibrium value for phosphate in solution. P_1+P_2 increases as the pH increases for all samples, in agreement with the fact that oxide and mineral surfaces usually show a decreased affinity for phosphate when the pH increases. On the other hand, k_2 does not show a particular trend with pH. Its value is linked to the value of P_2 and can only be interpreted as a fitting parameter that allows to evaluate R_0 through Eq. (2).

Fig. 4A presents R_0 vs. pH data for all the studied sediments. Even though all samples show an increased R_0 by increasing pH, some samples are more active in releasing phosphate than others. At most investigated pH, for example, samples from the center of the reservoirs or from zones close to the dam release phosphate several times faster than samples from the mouths of tributaries. However, when the rate of phosphate release is normalized by the SSA, all curves become nearly coincident (Fig. 4B). This is an important result that confirms that the release process under the investigated conditions is mainly a surface process, and that released phosphate proceeds mainly from adsorbed phosphate. In agreement with other reports (Koski-Vähälä et al., 2001; Jin et al., 2006), an analysis of the content of total phosphate and its fractions suggests that $Fe(OOH) \approx P$ is the main phosphate fraction that is being released in our experiments, since this phosphate is located at the particles surface. $CaCO_3 \approx P$, which is located within the bulk of grains or particles highly concentrated in Ca and P (mainly apatite-like minerals and perhaps some carbonate minerals) only should be significantly released at relatively low pH, where these mineral dissolve. A combined analysis of Figs. 2 and 4

Table 2 – P_1, P_2 and k_2 values for the studied samples

	LMD	LMT	LMC	SRD	SRT	SRC
			pH 9			
P_1 (mg g^{-1})	0.0147	0.0025	0.0018	0.0023	0.0019	0.0060
P_2 (mg g^{-1})	0.0205	0.0053	0.0131	0.0150	0.0073	0.0124
k_2 (h^{-1})	0.5050	0.5300	0.7000	0.7000	0.4000	0.9000
R_0 (mg g^{-1} h^{-1})	0.0103	0.0028	0.0092	0.0105	0.0029	0.0111
			pH 8			
P_1 (mg g^{-1})	0.0041	0.0013	0.0028	0.0022	0.0012	0.0021
P_2 (mg g^{-1})	0.0093	0.0022	0.0054	0.0035	0.0082	0.0045
k_2 (h^{-1})	0.500	0.600	0.8000	1.4900	1.4800	1.1050
R_0 (mg g^{-1} h^{-1})	0.0047	0.0013	0.0043	0.0052	0.0012	0.0050
			pH 7			
P_1 (mg g^{-1})	0.0012	0.0009	0.0016	0.0022	0.0015	0.0017
P_2 (mg g^{-1})	0.0013	0.0006	0.0015	0.0020	0.0007	0.0015
k_2 (h^{-1})	1.7000	1.000	1.4500	1.5000	0.9300	1.7000
R_0 (mg g^{-1} h^{-1})	0.0023	0.0006	0.0021	0.0029	0.0007	0.0026
			pH 6			
P_1 (mg g^{-1})	0.0016	0.0012	0.0025	0.0019	0.0024	0.0029
P_2 (mg g^{-1})	0.0008	0.0006	0.0006	0.0012	0.0011	0.0020
k_2 (h^{-1})	0.8000	0.3000	1.0000	0.6617	0.2000	0.4000
R_0 (mg g^{-1} h^{-1})	0.0007	0.0002	0.0006	0.0008	0.0002	0.0008
			pH 9			
SRD (°C)	15	25	32	40		
P_1 (mg g^{-1})	0.0035	0.0023	0.0054	0.0055		
P_2 (mg g^{-1})	0.0065	0.0150	0.0280	0.0373		
k_2 (h^{-1})	0.7500	0.7000	0.9600	1.1800		
R_0 (mg g^{-1} h^{-1})	0.0049	0.0105	0.0269	0.0440		
			pH 7			
SRD (°C)	15	25	32	40		
P_1 (mg g^{-1})	0.0015	0.0022	0.0017	0.0023		
P_2 (mg g^{-1})	0.0007	0.0020	0.0023	0.0052		
k_2 (h^{-1})	0.7200	1.5000	1.5000	1.1000		
R_0 (mg g^{-1} h^{-1})	0.0007	0.0029	0.0034	0.0057		

indicates that the release rate is correlated to the relative charge. Indeed, a plot R_0/SSA vs. relative charge (not shown) can be fitted with a straight line with $R^2 = 0.815$. Even though the net charge of the solid could not be evaluated, these results show that the release rate increases when surface deprotonation increases.

Fig. 5 shows the effect of the temperature on the rate of phosphate release at pH 9 for one selected sample. The rate significantly increases as the temperature increases, and a value of 71 kJ mol^{-1} was estimated for E_{app} (inset of Fig. 5). The same kind of experiment, but at pH 7, yielded a value of 65 kJ mol^{-1} for E_{app}. Sparks (2003) indicates that typical values of E_{app} are 8–25 kJ mol^{-1} for physical processes, <21 kJ mol^{-1} for diffusion-controlled processes in water, 20–40 kJ mol^{-1} for diffusion-controlled processes in pores, 42–84 kJ mol^{-1} for surfaces processes controlled by chemical reactions at mineral surfaces and 84–503 kJ mol^{-1} for solid-state diffusion in minerals. Therefore, the relatively high value of E_{app} found here suggests that diffusion is not actually important in the release rate of phosphate, and that the rate-controlling step is a chemical reaction at the surface. Solid-state diffusion can be in principle discarded here because the released phosphate is mainly located at the particles surfaces. In addition, the similarity in E_{app} values at pH 7 and 9 suggests that the same release mechanism is operating in alkaline and neutral conditions.

The increase in the release rate by increasing pH is usually explained in the literature by a decreased affinity of the solid surface for phosphate anions and/or by ligand exchange with OH^- ions. However, since the affinity is conceptually the ΔG of adsorption, and the exchange is directly related to a ligand exchange constant (i.e. a ΔG of ligand exchange), the connection between overall reaction rates and equilibrium parameters such as ΔG may not be straightforward (Lasaga, 1997; Sposito, 2004) and does not provide mechanistic information on the release process. The factors influencing the release rate should be better understood in terms of a rate-controlling step and factors influencing it. Although there is no definitive information about the identity of the rate-controlling step, the following evidences from this article must be taken into account in order to propose a controlling step: (a) The rate-controlling step is a reaction occurring at the surface of the particles, (b) the high values of E_{app} suggest that a chemical bond is broken during this step, and (c)

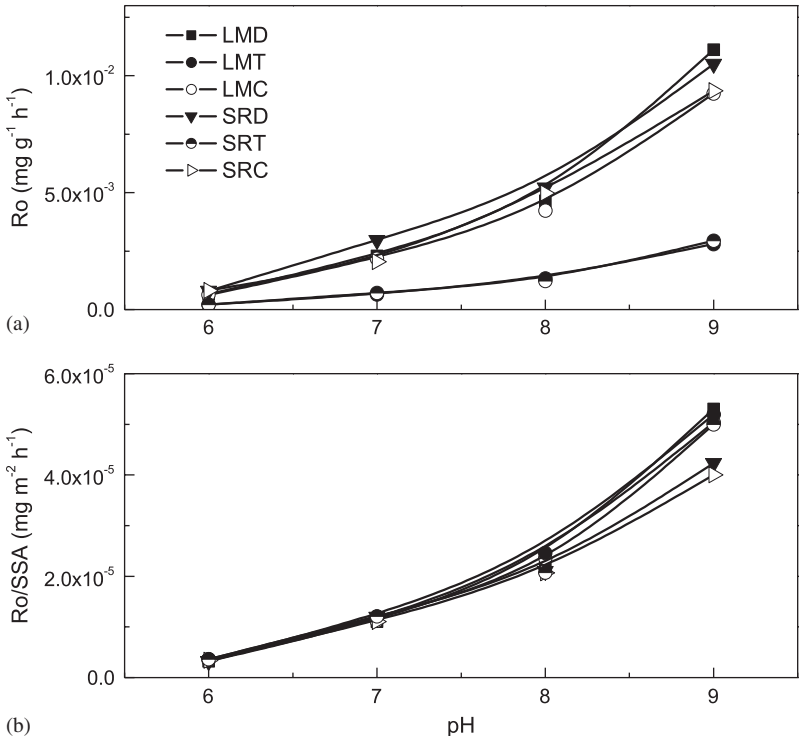

Fig. 4 – Effects of pH on the initial rate of phosphate release for all the studied samples. (A) R_0 vs. pH curves; (B) idem but with R_0 normalized by SSA.

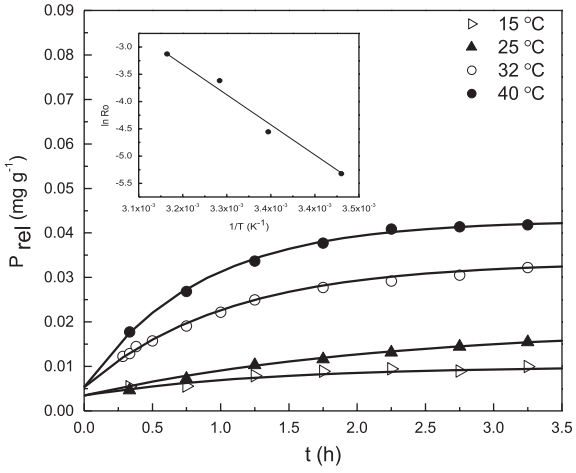

Fig. 5 – P_{rel} vs. t curves at different temperatures and pH 9 for sample SRD Symbols: experimental data; lines: predictions of Eq. (1) with parameters in Table 2. The inset shows the Arrhenius plot of the data.

deprotonation reactions at the surface are needed before this step proceeds. In the case of kinetics of mineral weathering, the rate-controlling step for mineral dissolution is the breaking of bonds at the surface (Casey, 2002; Stumm, 1992). By analogy, a slow breaking of the chemical bonds between adsorbed phosphate species and surface groups could be possibly the controlling step for phosphate release. As it occurs with mineral dissolution in alkaline media (Stumm, 1992), this breaking should be preceded by one or more fast deprotonation steps that weaken the linkages, and this is why the rate depends on the surface charge. Additionally, the increase in the negative surface charge and negative surface potential will enhance the repulsion of attached phosphate species at high pH, favoring them to overcome the high activation energy and to quickly leave the surface. According to Strauss et al. (1997), electrostatics plays an important role on the adsorption–desorption kinetics of phosphate on goethite. It also seems to play a role in the release rate of phosphate from lake sediment particles.

4. Conclusions

- The surface charging behavior of all the sediments is very similar in a per area basis, indicating that pH-dependent charges are developed mainly at the particles' surface and that the reactivity of surface groups is very similar in all cases.
- Data consistently indicate that the release of phosphate between pH 6 and 9 is mainly a desorption process. The fact that Fe(OOH)≈P is located at the surface of the solid particles, the very good correlation between release rates and SSA, and values of E_{app} that are common for surface processes support this conclusion.
- Changes in the rate of phosphate release with pH seem to be directly related to deprotonation reactions at the particles surface. These deprotonation reactions should precede the breaking of bonds between phosphate and surface groups. Deprotonation reactions, on the other hand, increase the negative surface charge and the negative surface potential and thus an increased electrostatic repulsion between the

surface and sorbed phosphate by increasing the pH may also increase the release rate.

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REFERENCES

Agbenin, J.O., van Raij, B., 2001. Kinetics and energetics of phosphate release from tropical soils determined by mixed ion-exchange resins. Soil Sci. Soc. Am J. 65, 1108–1114.

Avena, M.J., 2002. Acid–base behavior of clay surfaces in aqueous media. In: Hubbard, A. (Ed.), Encyclopedia of Surface and Colloid Science. Marcel Dekker, New York, pp. 37–63.

Avena, M.J., De Pauli, C.P., 1998. Proton adsorption and electrokinetics of an Argentinean montmorillonite. J. Colloid Interface Sci. 202, 195–204.

Avena, M.J., Valenti, L., Pfaffen, V., De Pauli, C.P., 2001. Methylene blue dimerization does not interference in surface-area measurements of kaolinite and soils. Clays Clay Min. 49, 168–173.

Borgnino, L., Orona, C., Avena, M., Maine, A., Rodríguez, A., De Pauli, C.P., 2006. Phosphate concentration an association as revealed by sequential extraction and microprobe analysis: the case of sediments from two Argentinean Reservoirs. Water Resour. Res. 42, W01414, doi:10.1029/2005WR004031.

Casey, W.H., 2002. Dissolution of mineral oxides. In: Hubbard, A. (Ed.), Encyclopedia of Surface and Colloid Science. Marcel Dekker, New York, pp. 1486–1495.

Ferreira, J.R., Lawlor, A.J., Bates, J.M., Clarke, K.J., Tipping, E., 1997. Chemistry of riverine and estuarine suspended articles from the Ouse-Trent system, UK. Coll. Surf. A 120, 183–198.

Fontes, M.P.F., Weed, S.B., 1996. Phosphate adsorption by clays from Brazilian oxisols: relationships with surface area and mineralogy. Geoderma 72, 37–51.

Golterman, H.L., 1995. The labyrinth of nutrients cycles and buffers in wetlands: results based on research in the Camargue (southern France). Hydrobiologia 315, 39–58.

Hansen, J., Reitzel, K., Jensen, H.S., Andersen, F., 2003. Effects of aluminum, iron, oxygen and nitrate additions on phosphorus release from the sediments of a Danish softwater lake. Hydrobiologia 492, 139–149.

Heil, D., Sposito, G., 1993. Organic matter role in illitic soil colloids flocculation: II surface charge. Soil Sci. Soc. Am. J. 57, 1246–1253.

Holdren Jr., G.C., Armstrong, D.E., 1980. Factors affecting phosphorus release from intact lake sediment cores. Environ. Sci. Technol. 14, 79–87.

Jin, X., Wang, S., Pang, Y., Wu, F.C., 2006. Phosphorus fractions and the effect of pH on the phosphorus release of the sediments from different trophic areas in Taihu lake, China. Environ. Poll. 139, 288–295.

Kim, L.-H., Choi, E., Stenstrom, M.K., 2003. Sediment characteristics, phosphorus types and phosphorus release rates between river and lake sediments. Chemosphere 50, 53–61.

Koski-Vähälä, J., Hartikainen, H., Tallberg, P., 2001. Phosphorus mobilization from various sediment pools in response to increased pH and silicate concentration. J. Environ. Qual. 30, 546–552.

Lasaga, A.C., 1997. Kinetic Theory in the Earth Sciences. Princeton Series in Geochemistry. Princeton University Press, Princeton, NJ, (811pp).

Lijklema, L., 1980. Interaction of orthophosphate with iron (III) and aluminum hydroxides. Environ. Sci. Technol. 14, 537–540.

Lookman, R., Freese, D., Merckx, R., Vlassak, K., van Riemsdijk, W.H., 1995. Long-term kinetics of phosphate release from soil. Environ. Sci. Technol. 29, 1569–1575.

Murphy, J., Riley, J.P., 1962. A modified single solution method for determination of phosphate in natural waters. Anal. Chim. Acta 27, 31–36.

Selig, U., 2003. Particle size-related phosphate binding and P-release at the sediment-water interface in a shallow German lake. Hydrobiologia 492, 107–118.

Sposito, G., 2004. The Surface Chemistry of Natural Particles. Oxford University Press, New York, (242pp).

Sparks, D., 2003. Environmental Soil Chemistry, second ed. Academic Press, Amsterdam, (352pp).

Strauss, R., Brümmer, G.W., Barrow, N.J., 1997. Effects of crystallinity of goethite: II. Rates of sorption and desorption of phosphate. Eur. J. Soil Sci., 101–114.

Stumm, W., 1992. Chemistry of the Solid–Water Interface. Wiley, New York, (428pp).

Tipping, E., Cooke, D., 1982. The effect of adsorbed humic substances on the surface charge of goethite in fresh water. Geochim. Cosmochim. Acta 46, 75–80.

Torn, L.H., de Keizer, A., Koopal, L.K., Blokzijl, W., Lyklema, J., 1998. Polymer adsorption on a patchwise heterogeneous surface. Progr. Colloid Polym. Sci. 109, 153–160.

Wang, F., Chen, J., Chen, J., Forsling, W., 1997. Surface properties of natural aquatic sedimens. Water Res. 31, 1796–1800.