

## Phosphorus availability in the Paraná floodplain lakes (Argentina): Influence of pH and phosphate buffering by fluvial sediments

R. Carignan

Département de sciences biologiques, Université de Montréal, C.P. 6128, Montréal, Quebec, Canada H3C 3J7

P. Vaithiyathan

Wetland Center, Duke University, 17127 Prado Boulevard, Loxahatchee, Florida 33470

### Abstract

The phosphate-buffering properties and P chemistry of suspended particulate matter (SPM) collected in three geologically contrasting rivers (Bermejo, Paraguay, and Upper Paraná) are compared in order to explain the abundance of dissolved  $\text{PO}_4\text{-P}$  in the Paraná floodplain lakes. The rivers show distinctive P-buffering capacities related to the chemical composition of their SPM. At natural pH, the linear adsorption coefficient of  $\text{PO}_4\text{-P}$  ( $K_d$ ) ranges from 0.25 liter  $\text{g}^{-1}$  for the Paraguay River to 1.38 liter  $\text{g}^{-1}$  for the Upper Paraná River. Equilibrium  $\text{PO}_4\text{-P}$  ranges from 0.17  $\mu\text{mol liter}^{-1}$  for the Upper Paraná River to 2.92  $\mu\text{mol liter}^{-1}$  for the Bermejo River. Short-term (60 h) desorbable  $\text{PO}_4\text{-P}$  ranges from 0.23  $\mu\text{mol g}^{-1}$  for the Paraguay to 0.77  $\mu\text{mol g}^{-1}$  for the Upper Paraná. These values increase substantially with a small decrease in pH representative of conditions experienced by riverine SPM when it enters the floodplain environment. For the carbonate-bearing SPM of the Bermejo and Paraguay Rivers, a pH decrease of 1–1.5 units causes a 10-fold increase in equilibrium  $\text{PO}_4\text{-P}$  and a 5- to 10-fold increase in desorbable  $\text{PO}_4\text{-P}$ , and it is associated with the release of Ca. In the Upper Paraná, a similar decrease in pH has opposite effects that are consistent with a stronger complexation of  $\text{PO}_4\text{-P}$  by hydrous iron oxides at low pH. Compared to the parent riverine SPM, floodplain lake sediments are depleted in Ca-bound P and enriched in Fe-bound P. Although Ca-bound P is often considered biologically unavailable, our observations suggest that in the Paraná floodplain lakes, most of the available P originates from the acid dissolution of Ca-bound P. Loading of fluvial sediments to the lakes and the acidic dissolution of Ca-bound P appear sufficient to explain the permanent excess of dissolved  $\text{PO}_4\text{-P}$  in these waters.

Phosphate exchange reactions taking place between the liquid and solid phases influence the concentration of dissolved phosphate in waters having a high SPM concentration (e.g., Mayer and Gloss 1980). These reactions may involve adsorption, desorption, precipitation, and dissolution, and they are often collectively referred to as phosphate “buffering” (Froelich 1988). They are influenced by pH, dissolved phosphate concentration (hereafter expressed as  $\text{PO}_4\text{-P}$ ), competing anions, and solid-phase composition. Phosphate buffering can play an important role in the P economy of aquatic systems. Algal uptake of  $\text{PO}_4\text{-P}$  can be balanced by P desorption from bottom and suspended sediments, thus enabling the sustained productivity of streams (Ellis and Stanford 1988) and floodplain lakes (Engle and Sarnelle 1990). Phosphate released from fluvial SPM is an important source of P to estuaries (e.g., Chase and Sayles 1980; Fox et al. 1986).

In most freshwaters, dissolved phosphate concentrations are usually undetectable or low ( $<0.1 \mu\text{mol liter}^{-1}$ ) and limit biological productivity. This generality does not always apply to floodplain lakes, however, where rivers can supply large amounts of P during floods. In the floodplain lakes of

the Amazon and the Orinoco,  $\text{PO}_4\text{-P}$  typically ranges from 0.1 to 1  $\mu\text{mol liter}^{-1}$ , although it may sometimes become depleted during low water phases (Setaro and Melack 1984; Hamilton and Lewis 1987; Forsberg et al. 1988). At our study site in the Paraná floodplain,  $\text{PO}_4\text{-P}$  is noticeably higher (0.5–4  $\mu\text{mol liter}^{-1}$ ) than in the Amazon and the Orinoco at any phase of the flood cycle, even in the presence of very high biological demand by floating macrophytes and algae (Carignan and Neiff 1992; Carignan and Planas 1994). In the present report, we compare the  $\text{PO}_4\text{-P}$ -buffering characteristics of the SPM in three contrasting rivers of the Paraná system (Bermejo, Paraguay, and Upper Paraná) to those of floodplain lake sediments. We propose a geochemical mechanism linking the high  $\text{PO}_4\text{-P}$  of the Paraná floodplain lakes to the properties of the parent riverine sediments.

### Study area

The Bermejo, Paraguay, and Paraná Rivers belong to the second largest hydrographic system of South America. The Bermejo merges with the Paraguay 100 km before the confluence of the Paraguay and Upper Paraná near Corrientes, Argentina (Fig. 1). The mean annual discharges of the Bermejo, Paraguay, and Upper Paraná Rivers are 600, 4,200, and 13,700  $\text{m}^3 \text{s}^{-1}$ , respectively. These rivers have contrasting subbasin geologies. The Bermejo drains Andean sedimentary rocks rich in carbonates, whereas the Paraguay drains the Pantanal, a 100,000- $\text{km}^2$  wetland located on the Brazilian Shield. The Upper Paraná drains part of the Bra-

### Acknowledgments

This study was supported by an operating grant from the Natural Sciences and Engineering Research Council of Canada to R.C. and by a PDF fellowship grant from the Institut National de la Recherche Scientifique (Université du Québec) to P.V. We thank Sylvie St-Pierre for laboratory assistance and Juan-José Neiff and the staff of the Centro de Ecología Aplicada del Litoral for field support.



Fig. 1. Study area showing the fluvial and floodplain sampling locations. (A) Lake San Nicolás North, (B) Lake Puente South, (C) Lake Guaycurú, (D) Bermejo River, (E) Upper Paraná River, and (F) Paraguay River. The floodplain insert is based on a SPOT image taken in April 1990.

zilian Shield and Jurassic–Cretaceous basalts and sandstones covered by lateritic soils and aeolian deposits rich in iron and aluminum oxides. These different basin lithologies are reflected in the major ion composition and SPM concentrations of each river (Table 1).

The high suspended load of the Bermejo (3 to  $>10$  g liter<sup>-1</sup>), originating from erosion of the Andes, strongly influences that of the Paraguay, which increases from 100 to 600 mg liter<sup>-1</sup> after their confluence (Drago 1990). About 60% of the annual suspended load carried by the Paraná ( $10^{11}$  kg yr<sup>-1</sup>; Depetris and Cascante 1985; Drago and Amsler 1988) below its confluence with the Paraguay originates from the Bermejo. Clay-sized particles (mostly chlorite and kaolinite) represent about 75% of the SPM in the Upper Paraná and about 30% (mostly illite and montmorillonite) in the Paraguay and Bermejo Rivers (Depetris and Griffin 1968; Bonetto and Orfeo 1984). Carbonates are not detectable in the SPM x-ray diffraction patterns of any of the three rivers, which implies that their importance does not exceed 1–2%.

In this report, we use the term “lake” for any permanent (decades) waterbody, large or small, located on the floodplain and the term “pond” for temporary waterbodies (Wel-

Table 1. Mean chemical composition of the Bermejo, Paraguay, Upper Paraná (above the Paraná–Paraguay confluence) and Lower Paraná (below the confluence) Rivers and synthetic river water used in the PO<sub>4</sub>-P exchange experiments. From Bonetto and Lancellotti 1981; Pedrozo and Bonetto 1987; Drago and Amsler 1988; and Carignan unpubl. data.

	Bermejo	Paraguay	U. Paraná	L. Paraná	Synthetic
pH	7.8–8.8	7.7	7.5	7.6	7.6
HCO <sub>3</sub> <sup>-</sup> (mmol liter <sup>-1</sup> )	2.64	0.90	0.45	0.60	0.60
Cl <sup>-</sup> (mmol liter <sup>-1</sup> )	—	0.68	0.09	0.26	0.26
SO <sub>4</sub> <sup>2-</sup> (mmol liter <sup>-1</sup> )	—	0.16	0.20	0.06	0.06
Ca (mmol liter <sup>-1</sup> )	1.08	0.33	0.11	0.17	0.17
Mg (mmol liter <sup>-1</sup> )	—	0.20	0.27	0.14	0.13
Na (mmol liter <sup>-1</sup> )	—	0.84	0.11	0.34	0.34
K (mmol liter <sup>-1</sup> )	—	0.08	0.03	0.04	0.04
PO <sub>4</sub> (μmol liter <sup>-1</sup> )	1.97	0.40	0.32	—	0.0–5.0
SPM (mg liter <sup>-1</sup> )	6,500	575	90	250	0

comme 1985). Near our study site, the lakes and ponds of the fringing floodplain are generally small (100–500 m wide, 500–3,000 m long), shallow (1–4 m), and often turbid (Secchi depth = 25–100 cm). Direct hydrologic contact with the river occurs irregularly, only every 3–10 yr, during exceptionally high floods (Carignan and Neiff 1992). Lakes smaller than about 15 ha often sustain extensive floating meadows of water hyacinth (*Eichhornia crassipes*), whereas larger lakes (>15 ha) tend to remain macrophyte free. Dissolved inorganic nitrogen concentrations are generally low or below detection limit ( $<0.05$ – $5$  μmol liter<sup>-1</sup>), and PO<sub>4</sub>-P is unusually high for freshwaters (0.5–4 μmol liter<sup>-1</sup>). During hydrologic isolation, lake-water pH varies from 6.0 to 6.6 and is considerably lower than that of the Upper Paraná (7.5) and Paraguay (7.4–7.7) Rivers, due to CO<sub>2</sub> production by decaying organic matter. The lakes have a 10–30-cm-thick layer of organic (3–10% C) sediments that sustain relatively high internal nutrient fluxes to the water column (on the order of 1.2 mmol m<sup>-2</sup> d<sup>-1</sup> of NH<sub>4</sub>-N and 0.4 mmol m<sup>-2</sup> d<sup>-1</sup> of PO<sub>4</sub>-P) with a remarkably low N:P ratio compared to Redfield proportions. At our study site, located on the west margin of the Paraná, 30 km downstream from its confluence with the Paraguay River, both waters are normally well separated, and complete mixing occurs only some 200–300 km downstream. Alluvial SPM deposited in the lakes and surrounding forests during floods thus originates essentially from the Paraguay River.

## Methods

Surface-water samples (50–200 liters) were collected in the middle of the three rivers (Fig. 1) in December 1991 during low waters, in the Upper Paraná during a high water phase in July 1992, and in April 1993 in the Paraguay. The SPM was concentrated by decantation (3–7 d) in 50-liter polyethylene containers and stored for 10–60 d at 4°C in 1 liter of river water to which a few drops of chloroform were added. In December 1991, cores were taken in three floodplain lakes with a piston corer. The cores were sliced at 2-cm intervals, and the sections were dried at 60°C. Additional

surficial sediments (upper 2 cm) were collected with an Eckman dredge in August 1992, 3 weeks after the end of a major flood event. These samples were kept frozen until used for PO<sub>4</sub>-P adsorption-desorption experiments. Upon thawing, the lake sediments were bubbled with air for 48 h to oxidize any FeS and Fe<sup>2+</sup> before the start of the experiments.

**Phosphate adsorption and desorption experiments**—Unless specified, all adsorption and desorption experiments were carried out at 22 ± 2°C at a constant solid/solution ratio of 1 g liter<sup>-1</sup> in synthetic river water of composition similar to that of the Lower Paraná (1:3 mixture of Paraguay and Upper Paraná, Table 1). The suspensions were equilibrated for 60 h in polyethylene tubes on a wrist-action shaker. Initial PO<sub>4</sub>-P varied from 0 to 5 μmol liter<sup>-1</sup> and spanned the range of concentrations observed in the rivers and floodplain lakes. Experiments were performed at both natural pH of the rivers and under slightly acidic conditions to investigate the fate of SPM-bound P deposited in the lakes during floods. Initial pH was adjusted to give a final pH varying between 6.5 and the natural river pH (7.4–8.3), thus providing a range representative of conditions observed in the rivers and lakes. At the end of the experiments, the suspensions were centrifuged at 10,000 rpm for 15 min, and an aliquot of the supernatant was sampled for measurement of pH, PO<sub>4</sub>-P, and Ca. Results are reported on a dry-weight (105°C) basis. All laboratory ware was cleaned with a P-free detergent, soaked in 10% HCl overnight or longer, and rinsed with P-free demineralized water. Phosphate was measured by an automated molybdenum-blue method (APHA 1985). Calcium was measured by atomic absorption.

Phosphate sorption on solids is often described using Langmuir or Freundlich isotherms. These isotherms are linear for low to moderate equilibrium PO<sub>4</sub>-P (e.g., Krom and Berner 1980; Carman and Wulff 1989) and can be expressed as (Froelich 1988)

$$P_s = K_d EPC \quad (1)$$

where P<sub>s</sub> (micromoles per gram) is the PO<sub>4</sub>-P adsorbed onto particles, K<sub>d</sub> (liters per gram) is the linear adsorption coefficient, and EPC (micromoles per liter) is the equilibrium PO<sub>4</sub>-P concentration in the solution. When conducting experiments where dissolved phosphate is either removed or added to the suspension, Eq. 1 can also be expressed as

$$P_s = K_d EPC = P_{si} + \Delta P_s \quad (2)$$

where P<sub>si</sub> (micromoles per gram) is the initial quantity of exchangeable PO<sub>4</sub>-P held by sediments before the experiment, and ΔP<sub>s</sub> (micromoles per gram) is the amount of P adsorbed or desorbed during the experiment. ΔP<sub>s</sub> is obtained by the difference between initial and final equilibrium PO<sub>4</sub>-P. The adsorption coefficient K<sub>d</sub> and P<sub>si</sub> are found by linear regression of ΔP<sub>s</sub> against EPC (see Fig. 3). The slope of the line yields K<sub>d</sub>, and the intercept provides the value of P<sub>si</sub>. The value of EPC at ΔP<sub>s</sub> = 0 (no adsorption or desorption) is called EPC<sub>0</sub>, the zero equilibrium PO<sub>4</sub>-P concentration. EPC<sub>0</sub> values should be close to natural dissolved PO<sub>4</sub>-P measured in the rivers and lakes when realistic solid:solution ratios are used. Under the assumption of linear adsorption of PO<sub>4</sub>, P<sub>si</sub> can also be viewed as the amount of PO<sub>4</sub>-P re-

leased by the sediment at infinite dilution within the time scale (60 h) of the experiment. P<sub>si</sub> is therefore an estimate of the particulate P fraction that is most available in the short term (60 h) for biological uptake.

**P and Fe fractions**—We used the sequential extraction procedure of Olsen and Sommers (1982) to separate the particulate inorganic P of 0.5-g sediment samples into the following operational fractions: (1) nonoccluded P (P<sub>noc</sub>): Presumably associated with iron and aluminum hydroxide surfaces. Extracted sequentially with 25 ml of 0.1 N NaOH + 1 M NaCl (17 h at room temperature), 20 ml of 1 M NaCl, and 20 ml of citrate-bicarbonate (0.3 M Na<sub>3</sub>C<sub>6</sub>H<sub>5</sub>O<sub>7</sub>·H<sub>2</sub>O and 1 M NaHCO<sub>3</sub>, 15 min at 85°C); (2) occluded P (P<sub>oc</sub>): Presumably present in the crystal structure of iron oxides. Extracted with 25 ml of citrate-bicarbonate (0.3 M Na<sub>3</sub>C<sub>6</sub>H<sub>5</sub>O<sub>7</sub>·H<sub>2</sub>O and 1 M NaHCO<sub>3</sub>) and 0.5 g of Na<sub>2</sub>S<sub>2</sub>O<sub>4</sub>·2H<sub>2</sub>O (dithionite) 15 min at 85°C; (3) calcium-bound P (P<sub>ca</sub>): Extracted with 25 ml of 1 N HCl for 1 h at room temperature; (4) inorganic P: Estimated as the sum of the above three fractions; and (5) organic P: Estimated as the difference between total P and inorganic P.

The PO<sub>4</sub>-P content of the first three fractions was measured as in the adsorption-desorption experiments, after dilution of the extracts. Iron extracted in fractions 1 (Fe<sub>NaOH</sub>) and 2 (Fe<sub>CDB</sub>) was measured by atomic absorption. Total concentrations were measured after the complete sequential digestion in Teflon beakers of 0.5-g sediment samples with 15 ml of concentrated HNO<sub>3</sub> (120°C), 4 ml of concentrated HClO<sub>4</sub> (refluxed at 200°C), and 10 ml of HF (80°C). The residual salts were evaporated to dryness and redissolved in 5% HCl before P, Fe, Al, and Ca measurements by inductively coupled plasma spectrometry (Jarrell Atomscan 25).

**SPM weathering under acidic conditions**—This experiment was performed to measure the effect of a decrease in pH on EPC, Ca, and the above-defined operational particulate P fractions and to observe the rate at which these reactions occurred. Two liters of a fresh suspension (10 g liter<sup>-1</sup> of Paraguay SPM collected in April 1993) were slowly titrated with 0.1 N HCl from its natural pH of 7.66 to 6.25 in 24 h and maintained at pH 6.25 ± 0.04 for the following 30 d using a programmable titrator. Forty-milliliter samples were periodically taken and centrifuged 20 min at 10,000 rpm. The supernatant was analyzed for PO<sub>4</sub>-P and dissolved Ca. The solids were freeze dried for measurements of P<sub>noc</sub>, P<sub>oc</sub>, and P<sub>ca</sub>.

**Carbonates**—The concentration of carbonates in riverine SPM was measured as CO<sub>2</sub> liberated after acidification of duplicate 250-mg SPM samples with 1 ml of 0.5 N HCl in sealed tubes (Vacutainers). The evolved CO<sub>2</sub> was measured by gas chromatography using a Porapak Q column and thermal conductivity detection, and the results are expressed as % CaCO<sub>3</sub>. Reagent grade CaCO<sub>3</sub> was used for standards.

## Results

Preliminary experiments carried out in phosphate-free synthetic river water showed that PO<sub>4</sub>-P was rapidly released

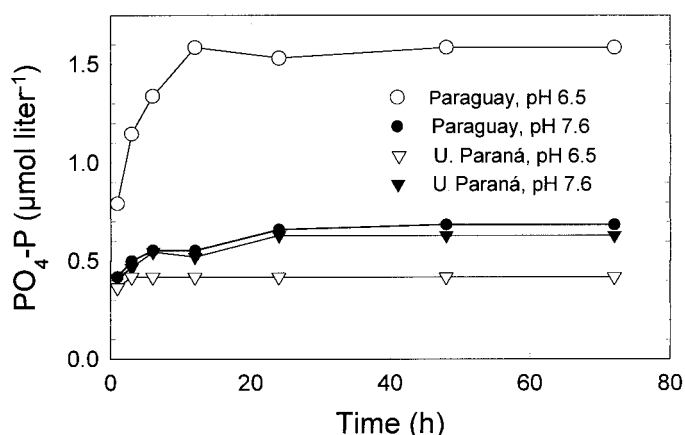


Fig. 2. Phosphate desorption vs. time from SPM collected in the Upper Paraná (triangles) and Paraguay (circles) Rivers, resuspended in phosphate-free synthetic river water at pH 7.6 (filled symbols) and pH 6.5 (open symbols).

from SPM during the first hour and reached a constant value after about 48 h (Figs. 2, 6). On the basis of these results, we ran all subsequent experiments for 60 h. The plots (Fig. 3) of  $\text{PO}_4\text{-P}$  adsorbed or desorbed ( $\Delta P_s$ ) vs. final equilibrium  $\text{PO}_4\text{-P}$  (EPC) show that  $\text{PO}_4\text{-P}$  sorption by the sediments can be represented by simple linear isotherms at low concentrations, as found by others (e.g., Krom and Berner 1980; Carman and Wulff 1989). At natural pH,  $r^2$  values of linear regressions of  $\Delta P_s$  vs. EPC exceeded 0.95 in most cases.

The three rivers exhibit contrasting  $\text{EPC}_0$ ,  $K_d$ , and  $P_{\text{Si}}$  values at natural pH (Table 2; Fig. 3). The zero equilibrium  $\text{PO}_4\text{-P}$  values obtained in the laboratory under natural pH ( $\text{EPC}_0 = 1.94, 0.63\text{--}2.92$ , and  $0.17\text{--}0.69 \mu\text{mol liter}^{-1}$  for the Bermejo, Paraguay, and Upper Paraná Rivers, respectively) are similar to the natural  $\text{PO}_4\text{-P}$  concentrations reported for the three rivers (Table 1). Of the three rivers,  $K_d$  is highest in the Upper Paraná (Table 2).  $K_d$  values are not affected by a decrease in pH, as shown by the nearly parallel slopes of Fig. 3, except for the April 1993 Paraguay SPM sample,

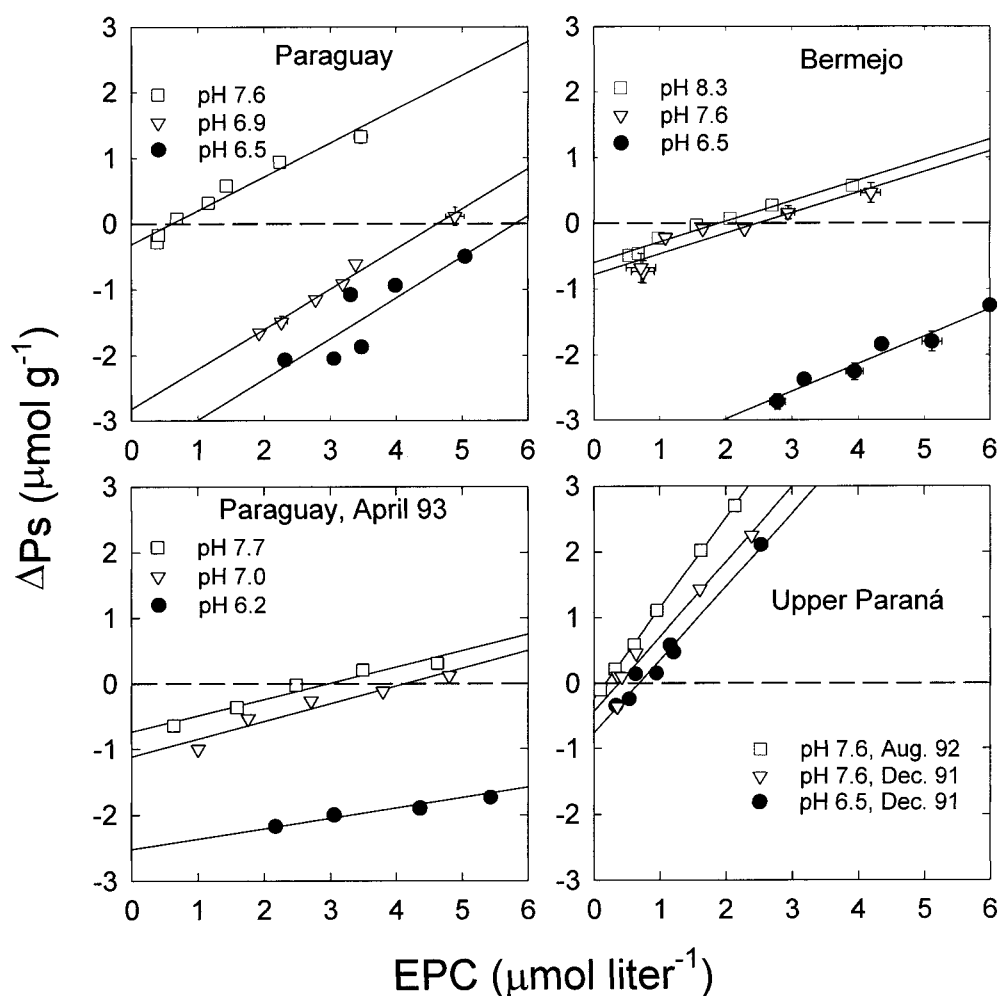


Fig. 3. Buffer diagram showing  $\text{PO}_4\text{-P}$  uptake and release by SPM of the Bermejo, Paraguay, and Upper Paraná Rivers. The y-axis ( $\Delta P_s$ ) represents the mean ( $n = 3$ ) amount of  $\text{PO}_4\text{-P}$  adsorbed (+) or desorbed (-) during the experiment, and the x-axis is the mean final equilibrium dissolved phosphate concentration (EPC). The lines are linear least-squares fits to the model  $\Delta P_s = K_d \text{EPC} - P_{\text{Si}}$  (see Eq. 2). Error bars, when larger than symbols, represent  $\pm 1$  SE of triplicate experiments.

Table 2. Influence of pH on P-buffering characteristics of the SPM sediments of the Bermejo, Paraguay, and Upper Paraná Rivers in December 1991 and August 1992 (Upper Paraná only).  $K_d$  = linear adsorption coefficient;  $EPC_0$  = equilibrium dissolved phosphate concentration;  $P_{Si}$  = exchangeable phosphate concentration on the solid phase of 1 g liter<sup>-1</sup> suspensions in synthetic river water. Asterisks indicate experiments conducted at natural pH values.

River	Date	pH	$K_d$ (liter g <sup>-1</sup> )	$EPC_0$ ( $\mu\text{mol liter}^{-1}$ )	$P_{Si}$ ( $\mu\text{mol g}^{-1}$ )
Bermejo	Dec 91	8.3*	0.31 ± 0.02	1.94 ± 0.08	0.60 ± 0.05
Bermejo	Dec 91	7.6	0.32 ± 0.06	2.53 ± 0.22	0.81 ± 0.14
Bermejo	Dec 91	6.5	0.42 ± 0.05	9.12 ± 0.55	3.83 ± 0.21
Paraguay	Dec 91	7.6*	0.51 ± 0.05	0.63 ± 0.12	0.32 ± 0.09
Paraguay	Dec 91	6.9	0.54 ± 0.05	4.89 ± 0.19	2.64 ± 0.17
Paraguay	Dec 91	6.5	0.62 ± 0.18	5.84 ± 0.54	3.62 ± 0.66
Paraguay	Apr 93	7.7*	0.25 ± 0.03	2.92 ± 0.19	0.73 ± 0.10
Paraguay	Apr 93	7.0	0.27 ± 0.05	4.15 ± 0.30	1.12 ± 0.14
Paraguay	Apr 93	6.2	0.15 ± 0.02	16.7 ± 1.5	2.50 ± 0.09
U. Paraná	Dec 91	7.6*	1.11 ± 0.07	0.69 ± 0.05	0.77 ± 0.09
U. Paraná	Dec 91	6.5	1.14 ± 0.11	0.38 ± 0.09	0.43 ± 0.13
U. Paraná	Aug 92	7.6*	1.38 ± 0.01	0.17 ± 0.01	0.23 ± 0.02

where  $K_d$  was significantly lower at pH 6.2 than at pHs 7.0 and 7.7. A decrease in pH causes a pronounced increase in  $EPC_0$  and  $P_{Si}$  for the Bermejo and Paraguay SPM (Fig. 3; Table 2), but it has an opposite effect in the Upper Paraná. In other words, lowering the pH by 0.7 to 1.8 units causes an important release of  $\text{PO}_4\text{-P}$  by SPM from the Bermejo and Paraguay Rivers, followed by a redistribution of the released P as dissolved and adsorbed  $\text{PO}_4\text{-P}$ .

In another experiment, where river SPM was equilibrated in synthetic  $\text{PO}_4\text{-free}$  water of varying pH, lowering the pH increased the release of  $\text{PO}_4\text{-P}$  by the SPM of the Bermejo and Paraguay Rivers, whereas  $\text{PO}_4\text{-P}$  release decreased with decreasing pH for the Upper Paraná (Fig. 4). Between pH 7 and 6, the SPM of the Bermejo and Paraguay released about 1.3  $\mu\text{mol g}^{-1}$  of dissolved  $\text{PO}_4\text{-P}$  per unit pH. When pH was lowered from its natural value to 6.5, the Bermejo SPM lost 2.3  $\mu\text{mol g}^{-1}$  of  $\text{PO}_4\text{-P}$  and 44  $\mu\text{mol g}^{-1}$  of Ca (P:Ca =

0.05, Fig. 5), whereas the Paraguay SPM lost 1.9  $\mu\text{mol g}^{-1}$  of  $\text{PO}_4\text{-P}$  and 13.2  $\mu\text{mol g}^{-1}$  of Ca (P:Ca = 0.14). These ratios are much lower than those expected from the dissolution of pure mineral phases containing both P and Ca such as apatites (P:Ca = 0.6).

During the 30-d-long exposure of SPM from the Paraguay to low pH (6.2), dissolved  $\text{PO}_4\text{-P}$  reached a new equilibrium concentration within 48 h (Fig. 6), as previously found. Dissolved Ca increased rapidly during the first few days and kept increasing more slowly thereafter. In the solid-phase P fractions,  $P_{\text{noc}}$  increased during the first 2–5 d at the expense of  $P_{\text{Ca}}$  and  $P_{\text{oc}}$ , which decreased by 1.1 and 0.9  $\mu\text{mol g}^{-1}$ , respectively. P fractionation remained essentially constant during the last 20 d.

The  $\text{PO}_4\text{-P}$ -buffering characteristics of the floodplain lake sediments differed completely from those of the fluvial SPM. Nearly constant  $EPC_0$  values were obtained in the adsorption/desorption experiments regardless of the initial  $\text{PO}_4\text{-P}$  added (0–5  $\mu\text{mol liter}^{-1}$ ) to the synthetic river water (Fig. 7). These floodplain sediments thus exhibited a large and nearly perfect buffer capacity within the range of initial  $\text{PO}_4\text{-P}$  used in this study.  $EPC_0$  values ranged between 0.4 and 1  $\mu\text{mol liter}^{-1}$  and are within the range of  $\text{PO}_4\text{-P}$  concentrations observed in the lakes under oxic conditions (Carignan and Neiff 1992; Carignan and Planas 1994).

Sequential extractions and total element concentrations show important differences between the SPM of each river and between fluvial SPM and floodplain sediments (Table 3). Calcium-bound P ( $P_{\text{Ca}}$ ) is the major P form in SPM collected in the Paraguay and Bermejo Rivers (80 and 65%, respectively), whereas P adsorbed onto hydrous iron oxides ( $P_{\text{noc}}$ ) and P associated with crystalline iron oxides ( $P_{\text{oc}}$ ) are the most important forms in the Upper Paraná ( $P_{\text{noc}} + P_{\text{oc}} = 90\%$ ). These results are consistent with those reported by Pedrozo et al. (1986) and Pedrozo and Bonetto (1987). In contrast, most of the P in the floodplain sediments is present as  $P_{\text{noc}}$ . Floodplain sediments have relatively low amounts of  $P_{\text{oc}}$  compared to Upper Paraná and low  $P_{\text{Ca}}$  content compared to the Bermejo and Paraguay, even though most floodplain sediments originate from the Paraguay River in this region.

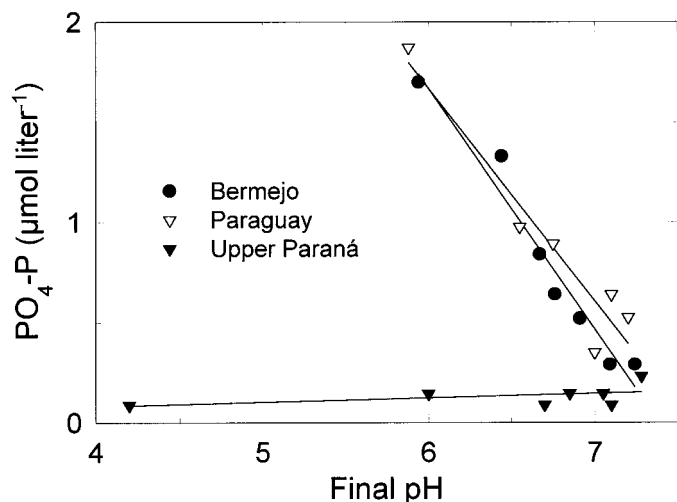


Fig. 4. Effect of pH on  $\text{PO}_4\text{-P}$  release from the SPM of the Bermejo, Paraguay, and Upper Paraná Rivers, resuspended (1 g liter<sup>-1</sup>) in phosphate-free synthetic river water. Note the contrasting effect of decreasing pH on  $\text{PO}_4\text{-P}$  release in the three rivers.

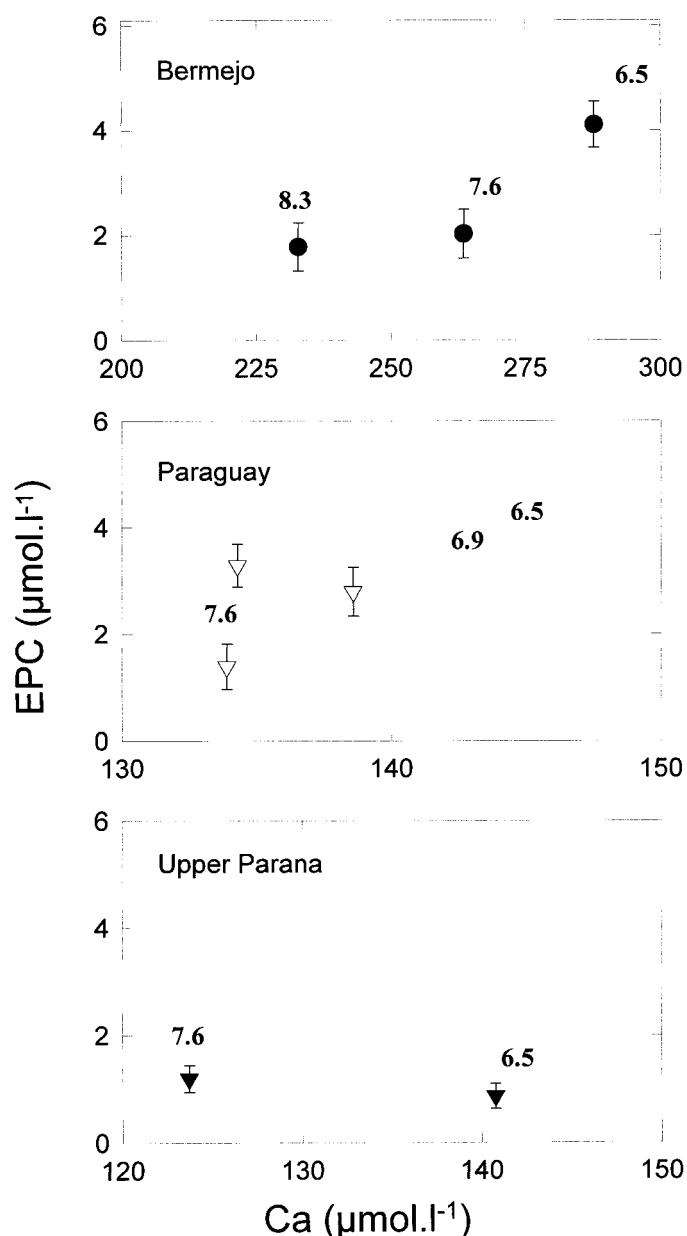


Fig.5. Phosphate (EPC) vs. Ca released by the SPM ( $1 \text{ g liter}^{-1}$ ) of the Bermejo (circles), Paraguay (squares), and Upper Paraná (triangles) Rivers at different final pH values shown in parentheses. Points are means  $\pm$  1 SE of seven to nine replicates.

Note that the three lake sediments have a relatively high sand content that dilutes P and Fe fractions associated with fine particulate matter. For example, the relatively low absolute concentrations of some P and Fe forms observed in L. Puente sediments are due to its high (83.2%) sand content compared to other lakes.

## Discussion

Laboratory experiments show that a rapid and substantial  $\text{PO}_4\text{-P}$  exchange between fluvial SPM and the aqueous phase occurs when  $\text{PO}_4\text{-P}$  is increased or decreased relative to nat-

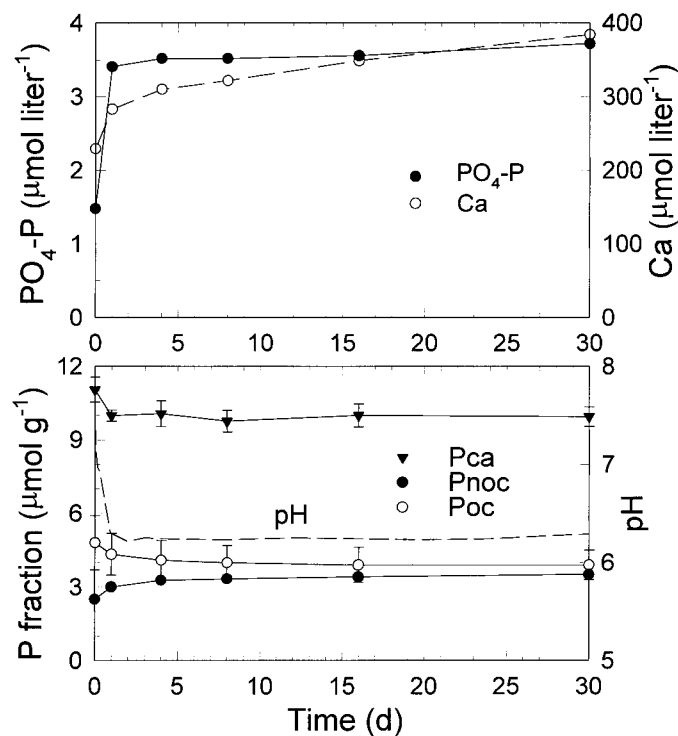


Fig. 6. Long-term evolution of dissolved  $\text{PO}_4\text{-P}$ , dissolved Ca, and solid-phase P fractions of SPM ( $10 \text{ g liter}^{-1}$ ) collected (April 1993) in the Paraguay River and maintained at pH 6.2. See Methods for P fraction definitions.

ural  $\text{EPC}_0$ , as observed by others (e.g., Froelich 1988). The  $K_d$  values observed for  $\text{PO}_4\text{-P}$  in the three rivers ( $0.25\text{--}1.38 \text{ liters g}^{-1}$ ) are comparable to those reported for Colorado River sediments ( $0.8 \text{ liter g}^{-1}$ ; Mayer and Gloss 1980) and to the lake and stream sediments of the Mississippi River floodplain ( $0.4 \text{ liter g}^{-1}$ ; Wauchope and McDowell 1984). The linear absorption coefficients and average SPM concentrations can be used to estimate the relative importance of dissolved and adsorbed  $\text{PO}_4\text{-P}$  transported P by each river. In the Bermejo, for example, with a mean SPM concentration of  $6.5 \text{ g liter}^{-1}$ , a  $K_d$  value of  $0.31 \text{ liter g}^{-1}$  at pH = 8.3, and an  $\text{EPC}_0$  of  $2 \mu\text{mol liter}^{-1}$  (Tables 1, 2), the adsorbed  $\text{PO}_4\text{-P}$  held by the SPM (micromoles per gram) is  $K_d \text{ EPC}_0 = 0.62 \mu\text{mol g}^{-1}$ , and the  $\text{PO}_4\text{-P}$  concentration held onto the SPM amounts to  $4 \mu\text{mol liter}^{-1}$ . Thus, 67% of the rapidly available  $\text{PO}_4\text{-P}$  transported by the Bermejo in December 1991 was associated with the particulate phase. Similar calculations for the Paraguay and Upper Paraná indicate that  $\text{PO}_4\text{-P}$  loosely held by the SPM represents about 23 and 10%, respectively, of the available P transported by these rivers. These estimates are, of course, approximate since SPM concentrations and properties, as well as  $\text{PO}_4\text{-P}$  vary with river discharge. They nevertheless indicate that most of the available P is likely to be transported mainly as particulate P in the Bermejo River and mainly as dissolved  $\text{PO}_4\text{-P}$  in the two other rivers.

Among the three rivers,  $K_d$  is the highest for the Upper Paraná. The high  $K_d$  value for this river is most likely related to the relatively high hydrous iron oxide ( $\text{Fe}_{\text{NaOH}}$ ) content of

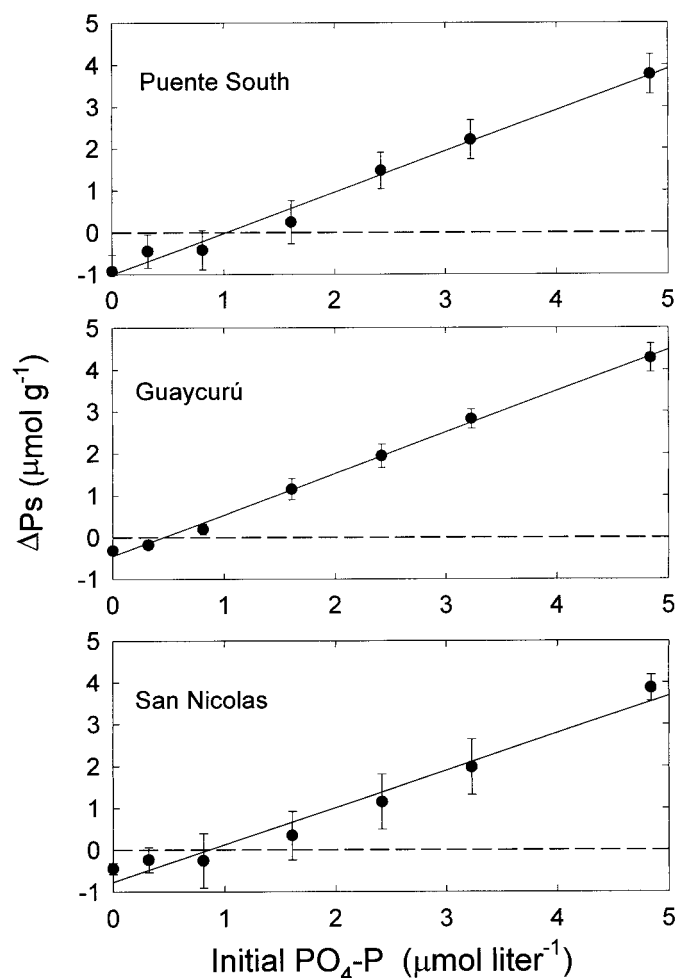


Fig. 7. Cross-over plots for phosphorus uptake and release by the surficial sediments ( $1 \text{ g liter}^{-1}$ ) of Paraná floodplain lakes. Data are plotted as  $\Delta P_s$  vs. initial phosphate concentration and compared to the slope expected for a perfectly buffered system ( $\Delta P_s/\text{initial PO}_4\text{-P} = 1$ , solid lines).

its SPM ( $20\text{--}100 \mu\text{mol g}^{-1}$ ) compared to that of the two other rivers ( $12\text{--}19 \mu\text{mol g}^{-1}$ , Table 3). That  $K_d$  increases with a decrease in pH (Table 2) in the Upper Paraná, as predicted by surface complexation theory (Dzombak and Morel 1990), provides further indication that iron oxides play an important role in  $\text{PO}_4\text{-P}$  adsorption in this river. The high  $\text{PO}_4\text{-P}$ -buffering capacity of the floodplain sediments (Fig. 7) is most likely related to their high  $\text{Fe}_{\text{NaOH}}$  content ( $46\text{--}135 \mu\text{mol g}^{-1}$ ) compared to fluvial SPM.

At our study site, most of the SPM entering the floodplain originated from the Bermejo River but was delivered to the floodplain via the Paraguay River during irregular flood events (Fig. 1). Upon mixing of the Bermejo and Paraguay waters, the SPM originating from the Bermejo appears to lose most but not all of its carbonates, which decrease from  $140$  to  $6 \mu\text{mol g}^{-1}$ . Loss of carbonates does not result in major modifications of P fractions, which remain dominated by Ca-bound P (Table 3). However, upon entering the floodplain waterbodies, the SPM is exposed to at least two additional changes in chemical conditions: (1) a decrease in pH of  $1\text{--}1.5$  units due to  $\text{CO}_2$  production from decaying floating macrophytes and terrestrial vegetation debris trapped in the lakes during floods, and (2) the frequent occurrence of anoxic conditions. Our laboratory and field observations show that these changes result in two major modifications of the chemical properties and P retention capacity of the SPM.

First, the decrease in pH causes an important release of  $\text{PO}_4\text{-P}$  and Ca by the SPM (Table 2; Figs. 2–6). This phenomenon could be due to the dissolution of microcrystalline apatite minerals or P-bearing carbonates (Kuo and Lotse 1972; House 1990). Our data indicate that  $\text{PO}_4\text{-P}$  release by SPM of the Paraguay River occurs through apatite dissolution. Indeed, the amount of  $\text{PO}_4\text{-P}$  remobilized by the Paraguay SPM following a pH reduction from  $7.6$  to  $6.5$  can be calculated (Table 2) as

$$\begin{aligned} \Delta \text{PO}_4\text{-P} &= [\text{EPC}_0 (\text{pH } 6.5) - \text{EPC}_0 (\text{pH } 7.6)] \\ &+ [\text{P}_{\text{Si}} (\text{pH } 6.5) - \text{P}_{\text{Si}} (\text{pH } 7.6)] \\ &= 8.5 \mu\text{mol g}^{-1}. \end{aligned} \quad (3)$$

Table 3. Chemical characteristics of the SPM of the Bermejo, Paraguay, and Upper Paraná Rivers and of the surficial bottom sediments of the floodplain lakes.  $\text{P}_{\text{noc}}$  = nonoccluded  $\text{PO}_4\text{-P}$ ;  $\text{P}_{\text{oc}}$  = occluded  $\text{PO}_4\text{-P}$ ;  $\text{P}_{\text{Ca}}$  =  $\text{PO}_4\text{-P}$  bound to calcium;  $\text{Fe}_{\text{NaOH}}$  = nonoccluded (hydrated) iron oxides;  $\text{Fe}_{\text{CDB}}$  = occluded (crystalline) iron oxides;  $\Sigma$  = total. Values in parentheses are corrected for dilution by sand.

	$\text{P}_{\text{noc}}$	$\text{P}_{\text{oc}}$	$\text{P}_{\text{Ca}}$	$\text{P}_i$	$\text{P}_{\text{org}}$	$\Sigma\text{P}$ ( $\mu\text{mol g}^{-1}$ )	$\text{Fe}_{\text{NaOH}}$	$\text{Fe}_{\text{CDB}}$	$\Sigma\text{Fe}$	$\Sigma\text{Al}$	$\Sigma\text{Ca}$	Sand (%)
Rivers												
Bermejo Dec 1991	1.2	3.2	16.9	21.3	4.4	25.6	12.5	178	731	3,490	253	0
Paraguay Dec 1991	3.3	3.4	12.4	19.1	4.5	23.6	18.6	158	710	3,330	116	0
Paraguay Mar 1993	2.5	2.5	11.8	16.8	—	—	—	—	—	—	—	0
U. Paraná Dec 1991	16.6	11.1	3.8	31.6	8.7	40.3	21.7	503	1,580	3,760	97	0
U. Paraná Mar 1993	19.5	11.6	1.8	33.0	1.3	34.3	98.0	1,050	2,830	2,830	76	0
Lakes												
Puente	10.9 (64.9)	2.0 (11.9)	1.4 (.3)	14.4 (85.7)	1.1 (6.5)	15.4 (91.6)	45.5 (270)	74 (441)	234	731	34	83.2
Guaycurú	23.2 (42.6)	3.5 (6.4)	2.5 (4.6)	28.5 (52.3)	8.4 (15.4)	36.9 (67.7)	107 (196)	101 (185)	651	3,130	12	45.4
San Nicolás	29.5 (66.4)	3.5 (7.9)	4.9 (11.0)	38.0 (85.6)	9.7 (21.8)	47.7 (107)	135 (304)	131 (295)	732	2,900	78	55.6

This pH reduction also causes the release of  $13.2 \mu\text{mol g}^{-1}$  of Ca (Fig. 5). Thus, the molar  $\text{PO}_4:\text{Ca}$  ratio of 0.64 is very close to the theoretical ratio of 0.6 expected for pure apatite. Furthermore, the low  $\text{CaCO}_3$  content ( $5.5\text{--}6.8 \mu\text{mol g}^{-1}$ ) of the Paraguay SPM suggests that the dissolution of P-bearing carbonates plays a minor role. In the Bermejo River,  $\text{PO}_4\text{-P}$  remobilization (Eq. 3) and Ca dissolution (Fig. 5) between pH 8.3 and 6.5 amount to  $10.4$  and  $44 \mu\text{mol g}^{-1}$ , respectively, with a  $\text{PO}_4:\text{Ca}$  ratio of 0.24. SPM from the Bermejo had a much higher  $\text{CaCO}_3$  concentration ( $140 \mu\text{mol g}^{-1}$ ) than that of the Paraguay, which suggests that  $\text{PO}_4\text{-P}$  release may occur through both apatite and carbonate dissolution in this river.

Phosphate release at low pH has particularly important implications regarding the biological availability of P associated with fluvial SPM in the floodplain environment. Indeed, the Ca-bound P fraction ( $P_{\text{Ca}}$ ) of SPM or bottom sediments is generally regarded as unavailable, whereas the P fraction bound to hydrous iron oxides ( $P_{\text{noc}}$ ) is considered the most available form (e.g., Williams et al. 1980; Ellis and Stanford 1988; Engle and Sarnelle 1990). At high pH,  $P_{\text{Ca}}$  may be present as  $\text{PO}_4$  strongly sorbed onto calcite or as apatite and may indeed not be available. Our results show, however, that a small decrease in pH entirely changes this situation. From Eq. 3, the SPM of the Bermejo and Paraguay Rivers can release  $8\text{--}10 \mu\text{mol g}^{-1}$  of  $\text{PO}_4\text{-P}$ , which is redistributed as dissolved and loosely adsorbed  $\text{PO}_4\text{-P}$ . This quantity is much larger than the measured  $P_{\text{noc}}$  of the Paraguay and Bermejo Rivers' SPM ( $3.3$  and  $1.2 \mu\text{mol g}^{-1}$ , respectively, Table 3). Thus, in a context of decreasing pH, the most important available P fraction in the SPM of these two rivers may not be the  $P_{\text{noc}}$  but the  $P_{\text{Ca}}$ . Our laboratory results are consistent with the observed differences in P fractions between fluvial SPM and the surficial sediments of the floodplain lakes. Indeed, while the  $P_{\text{Ca}}$  ( $12.4 \mu\text{mol g}^{-1}$ ) is the dominant (65%) inorganic P fraction in the Paraguay SPM, the  $P_{\text{Ca}}$  content of the fine-grained (sand-corrected) floodplain sediments decreases to  $8.9 \pm 2.2 \mu\text{mol g}^{-1}$  and represents only 12% of the inorganic P (Table 3). These results suggest that some of the  $P_{\text{Ca}}$  originally present in the SPM is dissolved and redistributed as available Fe-bound P, as confirmed by the long-term acidification experiment (Fig. 6) of SPM collected in the Paraguay. This  $P_{\text{Ca}}$  dissolution mechanism would explain why the  $0.3 \text{PO}_4\text{-P}:\text{NH}_4\text{-N}$  flux ratio from these sediments (Carignan and Neiff 1992) is much higher than the 0.06 Redfield ratio expected from the decay of fresh organic matter. This mechanism is expected to be common in other productive floodplain lakes since the SPM load of the Paraguay ( $0.6 \text{ g liter}^{-1}$ ) is typical of many large rivers draining semiarid watersheds and since carbonate rocks represent an important proportion of the superficial continental crust.

A second potentially important chemical modification of fluvial SPM once it has entered the floodplain involves the possible transformation of crystalline iron oxides ( $\text{Fe}_{\text{CDB}}$ ) into hydrous iron oxides ( $\text{Fe}_{\text{NaOH}}$ ). This reaction should be favored by anoxic conditions that occur in the entire water column during floods (Carignan and Neiff 1992), under floating meadows, in bottom waters during diurnal stratification, and in the organic sediments. Table 3 shows that

$\text{Fe}_{\text{CDB}}$  is about 10 times more important than  $\text{Fe}_{\text{NaOH}}$  in the SPM of the Bermejo and Paraguay Rivers. In contrast, both fractions are about equal in the surficial floodplain sediments. Thus,  $\text{Fe}_{\text{NaOH}}$  appears to be produced at the expense of  $\text{Fe}_{\text{CDB}}$  in the floodplain. The biological importance of this transformation stems from the fact that P bound to crystalline Fe ( $P_{\text{oc}}$ ) is not expected to be available in a permanently oxic environment, whereas P bound to hydrous iron oxides ( $P_{\text{noc}}$ ) has repeatedly been found to be available (Williams et al. 1980; Ellis and Stanford 1988; Engle and Sarnelle 1990). The transformation of  $\text{Fe}_{\text{CDB}}$  into  $\text{Fe}_{\text{NaOH}}$  presumably taking place in the floodplain environment is also reflected in the different proportions of inorganic P fractions in fluvial SPM and surficial sediments (Table 3). In the Paraguay SPM,  $P_{\text{noc}}$  and  $P_{\text{oc}}$  share about equal proportions, whereas  $P_{\text{noc}}$  is by far the dominant inorganic P fraction in the floodplain sediments.

It is difficult to estimate the quantitative importance of fluvial P loading to the lakes at our study site. Unfortunately, SPM and P budgets cannot be easily calculated due to the occurrence of sheet flow on the floodplain every 2–5 yr, when the lakes become totally unconfined. Nevertheless, the possible importance of P loading from the rivers can be roughly estimated by combining P fractionation data with some plausible assumptions regarding the effect of floods on sediment exchange between the river and the lakes.

Cores taken in 1991 in the three lakes (Fig. 1) and previous cores taken in 1989 and 1990 reveal that the unconsolidated sediment thickness rarely exceeds 30 cm. Therefore, permanent (long-term) sediment accumulation does not occur in the lakes. Rather, the average effect of floods seems to be limited to replacing some of the older sediments with new riverine SPM mixed with sand and fresh autochthonous and allochthonous organic detritus. The thickness of the sediment layer replaced during the floods most probably depends on flood intensity and duration, which are highly variable in the Paraná. In one of the lakes, organic C and N profiles taken before and after an unusually large flood in 1990 suggest that about 15 cm of old sediment had been replaced by new sediments (Carignan and Neiff 1992).  $^{210}\text{Pb}$  and  $^{137}\text{Cs}$  data from 18 cores collected in three lakes (Carignan unpubl. data) also suggest that during large floods, 10–20 cm of old sediments are replaced by new sediments. The average dry solids content of the upper 15-cm layer is about  $0.3 \text{ g cm}^{-3}$ , or  $4\text{--}5 \text{ g cm}^{-2}$ . Assuming a 50% content of inert material (sand) and a 15% organic matter content, about  $1.6 \text{ g cm}^{-2}$  ( $16 \text{ kg m}^{-2}$ ) of new fine-grained SPM could have been deposited during the 1990 flood. If we take the sum of  $P_{\text{noc}}$  and  $P_{\text{Ca}}$  ( $15.7 \mu\text{mol g}^{-1}$ ) shown in Table 3 for the Paraguay SPM as an estimate of available P, then  $247 \text{ mmol m}^{-2}$  of available P could have been deposited in the lake. If we take, instead, the  $8.5 \mu\text{mol g}^{-1}$  found for P release from  $P_{\text{Ca}}$  dissolution (Eq. 3) as a measure of the available P carried by new SPM, then  $134 \text{ mmol m}^{-2}$  of available P could have been deposited. Carignan and Neiff (1992) estimated the N requirement of *Eichhornia* floating meadows to about  $1 \text{ mol m}^{-2} \text{ yr}^{-1}$  during the 6-month growth period. The P requirement of such meadows translates into  $60 \text{ mmol m}^{-2} \text{ yr}^{-1}$  if a molar P:N Redfield ratio of 0.06 is used. Annual biological demand thus appears to be much smaller than the

amount of available P potentially supplied by the river by occasional large flood events. Therefore, SPM supply by the river and the observed  $P_{ca}$  dissolution mechanism appear to account for the permanent excess of dissolved  $PO_4$ -P in these waters.

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Received: 15 September 1998

Accepted: 15 December 1998

Amended: 17 May 1999